Analytical Methods

Aroclor PCBs

8082

METHOD 8082

POLYCHLORINATED BIPHENYLS (PCBs) BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8082 is used to determine the concentrations of polychlorinated biphenyls (PCBs) as Aroclors or as individual PCB congeners in extracts from solid and aqueous matrices. Open-tubular, capillary columns are employed with electron capture detectors (ECD) or electrolytic conductivity detectors (ELCD). When compared to packed columns, these fused-silica, open-tubular columns offer improved resolution, better selectivity, increased sensitivity, and faster analysis. The target compounds listed below may be determined by either a single- or dual-column analysis system. The PCB congeners listed below have been tested by this method, and the method may be appropriate for additional congeners.

Compound	CAS Registry No.	IUPAC #
Aroclor 1016	12674-11-2	-
Aroclor 1221	11104-28-2	-
Aroclor 1232	11141-16-5	-
Aroclor 1242	53469-21-9	-
Aroclor 1248	12672-29-6	-
Aroclor 1254	11097-69-1	-
Aroclor 1260	11096-82-5	-
2-Chlorobiphenyl	2051-60-7	1
2,3-Dichlorobiphenyl	16605-91-7	5
2,2',5-Trichlorobiphenyl	37680-65-2	18
2,4',5-Trichlorobiphenyl	16606-02-3	31
2,2',3,5'-Tetrachlorobiphenyl	41464-39-5	44
2,2',5,5'-Tetrachlorobiphenyl	35693-99-3	52
2,3',4,4'-Tetrachlorobiphenyl	32598-10-0	66
2,2',3,4,5'-Pentachlorobiphenyl	38380-02-8	87
2,2',4,5,5'-Pentachlorobiphenyl	37680-73-2	101
2,3,3',4',6-Pentachlorobiphenyl	38380-03-9	110
2,2',3,4,4',5'-Hexachlorobiphenyl	35065-28-2	138
2,2',3,4,5,5'-Hexachlorobiphenyl	52712-04-6	141
2,2',3,5,5',6-Hexachlorobiphenyl	52663-63-5	151
2,2',4,4',5,5'-Hexachlorobiphenyl	35065-27-1	153
2,2',3,3',4,4',5-Heptachlorobiphenyl	35065-30-6	170
2,2',3,4,4',5,5'-Heptachlorobiphenyl	35065-29-3	180
2,2',3,4,4',5',6-Heptachlorobiphenyl	52663-69-1	183
2,2',3,4',5,5',6-Heptachlorobiphenyl	52663-68-0	187
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	40186-72-9	206

1.2 Aroclors are multi-component mixtures. When samples contain more than one Aroclor, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. The same is true of Aroclors that have been subjected to environmental degradation ("weathering") or degradation by treatment technologies. Such weathered multi-component mixtures may have significant differences in peak patterns than those of Aroclor standards.

1.3 Quantitation of PCBs as Aroclors is appropriate for many regulatory compliance determinations, but is particularly difficult when the Aroclors have been weathered by long exposure in the environment. Therefore, this method provides procedures for the determination of selected individual PCB congeners. The 19 PCB congeners listed above have been tested by this method.

1.4 The PCB congener approach potentially affords greater quantitative accuracy when PCBs are known to be present. As a result, this method may be used to determine Aroclors, some PCB congeners, or "total PCBs," depending on regulatory requirements and project needs. The congener method is of particular value in determining weathered Aroclors. However, analysts should use caution when using the congener method when regulatory requirements are based on Aroclor concentrations.

1.5 Compound identification based on single-column analysis should be confirmed on a second column, or should be supported by at least one other qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm the measurements made with the primary column. GC/MS Method 8270 is also recommended as a confirmation technique when sensitivity permits (Sec. 8.0).

1.6 This method also describes a dual-column option. The option allows a hardware configuration of two analytical columns joined to a single injection port. The option allows one injection to be used for dual-column analysis. Analysts are cautioned that the dual-column option may not be appropriate when the instrument is subject to mechanical stress, many samples are to be run in a short period, or when highly contaminated samples are analyzed.

1.7 The analyst must select columns, detectors and calibration procedures most appropriate for the specific analytes of interest in a study. Matrix-specific performance data must be established and the stability of the analytical system and instrument calibration must be established for each analytical matrix (e.g., hexane solutions from sample extractions, diluted oil samples, etc.). Example chromatograms and GC conditions are provided as guidance.

1.8 The MDLs for Aroclors vary in the range of 0.054 to 0.90 µg/L in water and 57 to 70 µg/kg in soils. Estimated quantitation limits may be determined using the data in Table 1.

1.9 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatographs (GC) and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample (approximately 1 L for liquids, 2 g to 30 g for solids) is extracted using the appropriate matrix-specific sample extraction technique.

2.2 Aqueous samples are extracted at neutral pH with methylene chloride using Method 3510 (separatory funnel), Method 3520 (continuous liquid-liquid extractor), or other appropriate technique.

2.3 Solid samples are extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using Method 3540 (Soxhlet), Method 3541 (automated Soxhlet), or other appropriate technique.

2.4 Extracts for PCB analysis may be subjected to a sulfuric acid/potassium permanganate cleanup (Method 3665) designed specifically for these analytes. This cleanup technique will remove (destroy) many single component organochlorine or organophosphorus pesticides. Therefore, Method 8082 is not applicable to the analysis of those compounds. Instead, use Method 8081.

2.5 After cleanup, the extract is analyzed by injecting a 2-µL aliquot into a gas chromatograph with a narrow- or wide-bore fused silica capillary column and electron capture detector (GC/ECD).

2.6 The chromatographic data may be used to determine the seven Aroclors in Sec. 1.1, individual PCB congeners, or total PCBs.

3.0 INTERFERENCES

3.1 Refer to Methods 3500 (Sec. 3.0, in particular), 3600, and 8000 for a discussion of interferences.

3.2 Interferences co-extracted from the samples will vary considerably from matrix to matrix. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation. Sources of interference in this method can be grouped into three broad categories.

3.2.1 Contaminated solvents, reagents, or sample processing hardware.

3.2.2 Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.

3.2.3 Compounds extracted from the sample matrix to which the detector will respond.

3.3 Interferences by phthalate esters introduced during sample preparation can pose a major problem in PCB determinations.

3.3.1 Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations. Interferences from phthalate esters can best be minimized by avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination.

3.3.2 Exhaustive cleanup of solvents, reagents and glassware may be required to eliminate background phthalate ester contamination.

3.3.3 These materials can be removed through the use of Method 3665 (sulfuric acid/permanganate cleanup).

3.4 Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Glassware must be scrupulously cleaned.

Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water, and rinses with tap water and organic-free

reagent water. Drain the glassware, and dry it in an oven at 130°C for several hours, or rinse with methanol and drain. Store dry glassware in a clean environment.

NOTE: Oven-drying of glassware used for PCB analysis can increase contamination because PCBs are readily volatilized in the oven and spread to other glassware. Therefore, exercise caution, and do not dry glassware from samples containing high concentrations of PCBs with glassware that may be used for trace analyses.

3.5 Elemental sulfur (S_8) is readily extracted from soil samples and may cause chromatographic interferences in the determination of PCBs. Sulfur can be removed through the use of Method 3660.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph - An analytical system complete with gas chromatograph suitable for on-column and split-splitless injection and all required accessories including syringes, analytical columns, gases, electron capture detectors (ECD), and recorder/integrator or data system.

4.2 GC columns

This method describes procedures for both single-column and dual-column analyses. The single-column approach involves one analysis to determine that a compound is present, followed by a second analysis to confirm the identity of the compound (Sec. 8.4 describes how GC/MS confirmation techniques may be employed). The single-column approach may employ either narrow-bore (≤ 0.32 mm ID) columns or wide-bore (0.53 mm ID) columns. The dual-column approach involves a single injection that is split between two columns that are mounted in a single gas chromatograph. The dual-column approach employs only wide-bore (0.53 mm ID) columns. A third alternative is to employ dual columns mounted in a single GC, but with each column connected to a separate injector and a separate detector.

The columns listed in this section were the columns used to develop the method performance data. Listing these columns in this method is not intended to exclude the use of other columns that may be developed. Laboratories may use other capillary columns provided that they document method performance (e.g., chromatographic resolution, analyte breakdown, and MDLs) that equals or exceeds the performance specified in this method.

4.2.1 Narrow-bore columns for single-column analysis (use both columns to confirm compound identifications unless another confirmation technique such as GC/MS is employed). Narrow bore columns should be installed in split/splitless (Grob-type) injectors.

4.2.1.1 30 m x 0.25 or 0.32 mm ID fused silica capillary column chemically bonded with SE-54 (DB-5 or equivalent), 1 µm film thickness.

4.2.1.2 30 m x 0.25 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, or equivalent), 2.5 µm coating thickness, 1 µm film thickness.

4.2.2 Wide-bore columns for single-column analysis (use two of the three columns listed to confirm compound identifications unless another confirmation technique such as GC/MS is employed). Wide-bore columns should be installed in 1/4 inch injectors, with deactivated liners designed specifically for use with these columns.

4.2.2.1 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, RTx-35, or equivalent), 0.5 µm or 0.83 µm film thickness.

4.2.2.2 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 14% cyanopropylmethylpolysiloxane (DB-1701, or equivalent), 1.0 µm film thickness.

4.2.2.3 30 m x 0.53 mm ID fused silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 1.5 µm film thickness.

4.2.3 Wide-bore columns for dual-column analysis (choose one of the two pairs of columns listed below).

4.2.3.1 Column pair 1

30 m x 0.53 mm ID fused silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 1.5 µm film thickness.

30 m x 0.53 mm ID fused silica capillary column chemically bonded with 14% cyanopropylmethylpolysiloxane (DB-1701, or equivalent), 1.0 µm film thickness.

Column pair 1 is mounted in a press-fit Y-shaped glass 3-way union splitter (J&W Scientific, Catalog No. 705-0733) or a Y-shaped fused-silica connector (Restek, Catalog No. 20405), or equivalent.

4.2.3.2 Column pair 2

30 m x 0.53 mm ID fused silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 0.83 µm film thickness.

30 m x 0.53 mm ID fused silica capillary column chemically bonded with 14% cyanopropylmethylpolysiloxane (DB-1701, or equivalent), 1.0 µm film thickness.

Column pair 2 is mounted in an 8 in. deactivated glass injection tee (Supelco, Catalog No. 2-3665M), or equivalent.

4.3 Column rinsing kit - Bonded-phase column rinse kit (J&W Scientific, Catalog No. 430-3000), or equivalent.

4.4 Volumetric flasks - 10-mL and 25-mL, for preparation of standards.

5.0 REAGENTS

5.1 Reagent grade or pesticide grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

NOTE: Store the standard solutions (stock, composite, calibration, internal, and surrogate standards) at 4°C in polytetrafluoroethylene (PTFE)-sealed containers

in the dark. When a lot of standards is prepared, it is recommended that aliquots of that lot be stored in individual small vials. All stock standard solutions must be replaced after one year or sooner if routine QC (Sec. 8.0) indicates a problem. All other standard solutions must be replaced after six months or sooner if routine QC (Sec. 8.0) indicates a problem.

5.2 Sample extracts prepared by Methods 3510, 3520, 3540, 3541, 3545, or 3550 need to undergo a solvent exchange step prior to analysis. The following solvents are necessary for dilution of sample extracts. All solvent lots should be pesticide quality or equivalent and should be determined to be phthalate-free.

5.2.1 n-Hexane, C_6H_{14}

5.2.2 Isooctane, $(CH_3)_3CCH_2CH(CH_3)_2$

5.3 The following solvents may be necessary for the preparation of standards. All solvent lots must be pesticide quality or equivalent and should be determined to be phthalate-free.

5.3.1 Acetone, $(CH_3)_2CO$

5.3.2 Toluene, $C_6H_5CH_3$

5.4 Organic-free reagent water - All references to water in this method refer to organic-free reagent water as defined in Chapter One.

5.5 Stock standard solutions (1000 mg/L) - May be prepared from pure standard materials or can be purchased as certified solutions.

5.5.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure compound. Dissolve the compound in isooctane or hexane and dilute to volume in a 10-mL volumetric flask. If compound purity is 96 percent or greater, the weight may be used without correction to calculate the concentration of the stock standard solution.

5.5.2 Commercially-prepared stock standard solutions may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.6 Calibration standards for Aroclors

5.6.1 A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other five Aroclor mixtures. As a result, a multi-point initial calibration employing a mixture of Aroclors 1016 and 1260 at five concentrations should be sufficient to demonstrate the linearity of the detector response without the necessity of performing initial calibrations for each of the seven Aroclors. In addition, such a mixture can be used as a standard to demonstrate that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample. Prepare a minimum of five calibration standards containing equal concentrations of both Aroclor 1016 and Aroclor 1260 by dilution of the stock standard with isooctane or hexane. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector.

5.6.2 Single standards of each of the other five Aroclors are required to aid the analyst in pattern recognition. Assuming that the Aroclor 1016/1260 standards described in Sec. 5.6.1 have been used to demonstrate the linearity of the detector, these single standards of the remaining five Aroclors are also used to determine the calibration factor for each Aroclor. Prepare a standard for each of the other Aroclors. The concentrations should correspond to the mid-point of the linear range of the detector.

5.7 Calibration standards for PCB congeners

5.7.1 If results are to be determined for individual PCB congeners, then standards for the pure congeners must be prepared. The table in Sec. 1.1 lists 19 PCB congeners that have been tested by this method along with the IUPAC numbers designating these congeners. This procedure may be appropriate for other congeners as well.

5.7.2 Stock standards may be prepared in a fashion similar to that described for the Aroclor standards, or may be purchased as commercially-prepared solutions. Stock standards should be used to prepare a minimum of five concentrations by dilution of the stock standard with isooctane or hexane. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector.

5.8 Internal standard

5.8.1 When PCB congeners are to be determined, the use of an internal standard is highly recommended. Decachlorobiphenyl may be used as an internal standard, added to each sample extract prior to analysis, and included in each of the initial calibration standards.

5.8.2 When PCBs are to be determined as Aroclors, an internal standard is not used, and decachlorobiphenyl is employed as a surrogate (see Sec. 5.8).

5.9 Surrogate standards

5.9.1 When PCBs are to be determined as Aroclors, decachlorobiphenyl is used as a surrogate, and is added to each sample prior to extraction. Prepare a solution of decachlorobiphenyl at a concentration of 5 mg/L in acetone.

5.9.2 When PCB congeners are to be determined, decachlorobiphenyl is recommended for use as an internal standard, and therefore, cannot also be used as a surrogate. Therefore, tetrachloro-meta-xylene may be used as a surrogate for PCB congener analysis. Prepare a solution of tetrachloro-meta-xylene at a concentration of 5 mg/L in acetone.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Four, Organic Analytes for sample collection and preservation instructions.

6.2 Extracts must be stored under refrigeration in the dark and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Sample extraction

7.1.1 Refer to Chapter Two and Method 3500 for guidance in choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral pH with methylene chloride using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520) or other appropriate procedure. Solid samples are extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using one of the Soxhlet extraction (Method 3540 or 3541) procedures, ultrasonic extraction (Method 3550), or other appropriate procedure.

NOTE: Use of hexane-acetone generally reduces the amount of interferences that are extracted and improves signal-to-noise.

7.1.2 Reference materials, field-contaminated samples, or spiked samples should be used to verify the applicability of the selected extraction technique to each new sample type. Such samples should contain or be spiked with the compounds of interest in order to determine the percent recovery and the limit of detection for that sample type (see Chapter One). When other materials are not available and spiked samples are used, they should be spiked with the analytes of interest, either specific Aroclors or PCB congeners. When the presence of specific Aroclors is not anticipated, the Aroclor 1016/1260 mixture may be an appropriate choice for spiking. See Methods 3500 and 8000 for guidance on demonstration of initial method proficiency as well as guidance on matrix spikes for routine sample analysis.

7.2 Extract cleanup

Refer to Methods 3660 and 3665 for information on extract cleanup.

7.3 GC conditions

This method allows the analyst to choose between a single-column or a dual-column configuration in the injector port. Either wide- or narrow-bore columns may be used. See Sec. 7.7 for information on techniques for making positive identifications of multi-component analytes.

7.3.1 Single-column analysis

This capillary GC/ECD method allows the analyst the option of using 0.25-0.32 mm ID capillary columns (narrow-bore) or 0.53 mm ID capillary columns (wide-bore). The use of narrow-bore (0.25-0.32 mm ID) columns is recommended when the analyst requires greater chromatographic resolution. Use of narrow-bore columns is suitable for relatively clean samples or for extracts that have been prepared with one or more of the clean-up options referenced in the method. Wide-bore columns (0.53 mm ID) are suitable for more complex environmental and waste matrices.

7.3.2 Dual-column analysis

The dual-column/dual-detector approach involves the use of two 30 m x 0.53 mm ID fused-silica open-tubular columns of different polarities, thus different selectivities towards the target compounds. The columns are connected to an injection tee and ECD detectors.

7.3.3 GC temperature programs and flow rates

7.3.3.1 Table 2 lists GC operating conditions for the analysis of PCBs as Aroclors for single-column analysis, using either narrow-bore or wide-bore capillary columns. Table 3 lists GC operating conditions for the dual-column analysis. Use the conditions in these tables as guidance and establish the GC temperature program and flow rate necessary to separate the analytes of interest.

7.3.3.2 When determining PCBs as congeners, difficulties may be encountered with coelution of congener 153 and other sample components. When determining PCBs as Aroclors, chromatographic conditions should be adjusted to give adequate separation of the characteristic peaks in each Aroclor (see Sec. 7.4.6).

7.3.3.3 Tables 4 and 5 summarize the retention times of up to 73 Aroclor peaks determined during dual-column analysis using the operating conditions listed in Table 2. These retention times are provided as guidance as to what may be achieved using the GC columns, temperature programs, and flow rates described in this method. Note that the peak numbers used in these tables are *not* the IUPAC congener numbers, but represent the elution order of the peaks on these GC columns.

7.3.3.4 Once established, the same operating conditions must be used for the analysis of samples and standards.

7.4 Calibration

7.4.1 Prepare calibration standards as described in Sec. 5.0. Refer to Method 8000 (Sec. 7.0) for proper calibration techniques for both initial calibration and calibration verification. When PCBs are to be determined as congeners, the use of internal standard calibration is highly recommended. Therefore, the calibration standards must contain the internal standard (see Sec. 5.7) at the same concentration as the sample extracts. When PCBs are to be determined as Aroclors, external standard calibration should be used.

NOTE: Because of the sensitivity of the electron capture detector, the injection port and column should always be cleaned prior to performing the initial calibration.

7.4.2 When PCBs are to be quantitatively determined as congeners, an initial five-point calibration must be performed that includes standards for all the target analytes (congeners).

7.4.3 When PCBs are to be quantitatively determined as Aroclors, the initial calibration consists of two parts, described below.

7.4.3.1 As noted in Sec. 5.6.1, a standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other five Aroclor mixtures. Thus, such a standard may be used to demonstrate the linearity of the detector and that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample. Therefore, an initial five-point calibration is performed using the mixture of Aroclors 1016 and 1260 described in Sec. 5.6.1.

7.4.3.2 Standards of the other five Aroclors are necessary for pattern recognition. These standards are also used to determine a single-point calibration factor for each Aroclor, assuming that the Aroclor 1016/1260 mixture in Sec. 7.3.4.1 has been used to describe the detector response. The standards for these five Aroclors should be analyzed before the analysis of any samples, and may be analyzed before or after the analysis of the five 1016/1260 standards in Sec. 7.3.4.1.

7.4.3.3 In situations where only a few Aroclors are of interest for a specific project, the analyst may employ a five-point initial calibration of each of the Aroclors of interest (e.g., five standards of Aroclor 1232 if this Aroclor is of concern) and not use the 1016/1260 mixture described in Sec. 7.4.3.1 or the pattern recognition standards described in 7.4.3.2.

7.4.4 Establish the GC operating conditions appropriate for the configuration (single-column or dual column, Sec. 7.3). Optimize the instrumental conditions for resolution of the target compounds and sensitivity. A final temperature of 240-270°C may be required to elute decachlorobiphenyl. Use of injector pressure programming will improve the chromatography of late eluting peaks.

NOTE: Once established, the same operating conditions must be used for both calibrations and sample analyses.

7.4.5 A 2-µL injection of each calibration standard is recommended. Other injection volumes may be employed, provided that the analyst can demonstrate adequate sensitivity for the compounds of interest.

7.4.6 Record the peak area (or height) for each congener or each characteristic Aroclor peak to be used for quantitation.

7.4.6.1 A minimum of 3 peaks must be chosen for each Aroclor, and preferably 5 peaks. The peaks must be characteristic of the Aroclor in question. Choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. For each Aroclor, the set of 3 to 5 peaks should include at least one peak that is unique to that Aroclor. Use at least five peaks for the Aroclor 1016/1260 mixture, none of which should be found in both of these Aroclors.

7.4.6.2 Late-eluting Aroclor peaks are generally the most stable in the environment. Table 6 lists diagnostic peaks in each Aroclor, along with their retention times on two GC columns suitable for single-column analysis. Table 7 lists 13 specific PCB congeners found in Aroclor mixtures. Table 8 lists PCB congeners with corresponding retention times on a DB-5 wide-bore GC column. Use these tables as guidance in choosing the appropriate peaks.

7.4.7 When determining PCB congeners by the internal standard procedure, calculate the response factor (RF) for each congener in the calibration standards relative to the internal standard, decachlorobiphenyl, using the equation that follows.

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Peak area (or height) of the analyte or surrogate.
A_{is} = Peak area (or height) of the internal standard.
C_s = Concentration of the analyte or surrogate, in µg/L.
C_{is} = Concentration of the internal standard, in µg/L.

7.4.8 When determining PCBs as Aroclors by the external standard technique, calculate the calibration factor (CF) for each characteristic Aroclor peak in each of the initial calibration standards (from either Sec. 7.4.3.1 or 7.4.3.2) using the equation below.

$$CF = \frac{\text{Peak Area (or Height) in the Standard}}{\text{Total Mass of the Standard Injected (in nanograms)}}$$

Five sets of calibration factors will be generated for the Aroclor 1016/1260 mixture, each set consisting of the calibration factors for each of the five (or more) peaks chosen for this mixture. The single standard for each of the other Aroclors (see Sec. 7.4.3.1) will generate at least three calibration factors, one for each selected peak.

7.4.9 The response factors or calibration factors from the initial calibration are used to evaluate the linearity of the initial calibration. This involves the calculation of the mean response or calibration factor, the standard deviation, and the relative standard deviation (RSD) for each congener or Aroclor peak. See Method 8000 for the specifics of the evaluation of the linearity of the calibration and guidance on performing non-linear calibrations. When the Aroclor 1016/1260 mixture is used to demonstrate the detector response, the calibration model (see Method 8000) chosen for this mixture must be applied to the other five Aroclors for which only single standards are analyzed. If multi-point calibration is performed for individual Aroclors (see Sec. 7.4.3.3), use the calibration factors from those standards to evaluate linearity.

7.5 Retention time windows

Retention time windows are crucial to the identification of target compounds. Absolute retention times are used for the identification of PCBs as Aroclors. When PCBs are determined as congeners by an internal standard technique, absolute retention times may be used in conjunction with relative retention times (relative to the internal standard). Retention time windows are established to compensate for minor shifts in absolute retention times as a result of sample loadings and normal chromatographic variability. The width of the retention time window should be carefully established to minimize the occurrence of both false positive and false negative results. Tight retention time windows may result in false negatives and/or may cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified. Overly wide retention time windows may result in false positive results that cannot be confirmed upon further analysis. Analysts should consult Method 8000 for the details of establishing retention time windows.

7.6 Gas chromatographic analysis of sample extracts

7.6.1 The same GC operating conditions used for the initial calibration must be employed for samples analyses.

7.6.2 Verify calibration each 12-hour shift by injecting calibration verification standards prior to conducting any sample analyses. A calibration standard must also be injected at intervals of not less than once every twenty samples (after every 10 samples is recommended to minimize the number of samples requiring re-injection when QC limits are exceeded) and at the end of the analysis sequence. For Aroclor analyses, the calibration verification standard should be a mixture of Aroclor 1016 and Aroclor 1260. The calibration verification process

does not *require* analysis of the other Aroclor standards used for pattern recognition, but the analyst may wish to include a standard for one of these Aroclors after the 1016/1260 mixture used for calibration verification throughout the analytical sequence.

7.6.2.1 The calibration factor for each analyte calculated from the calibration verification standard (CF_v) must not exceed a difference of more than ± 15 percent when compared to the mean calibration factor from the initial calibration curve.

$$\% \text{ Difference} = \frac{\overline{CF} - CF_v}{\overline{CF}} \times 100$$

7.6.2.2 When internal standard calibration is used for PCB congeners, the response factor calculated from the calibration verification standard (RF_v) must not exceed a ± 15 percent difference when compared to the mean response factor from the initial calibration

$$\% \text{ Difference} = \frac{\overline{RF} - RF_v}{\overline{RF}} \times 100$$

7.6.2.3 If this criterion is exceeded for any calibration factor or response factor, inspect the gas chromatographic system to determine the cause and perform whatever maintenance is necessary before verifying calibration and proceeding with sample analysis.

7.6.2.4 If routine maintenance does not return the instrument performance to meet the QC requirements (Sec. 8.2) based on the last initial calibration, then a new initial calibration must be performed.

7.6.3 Inject a 2-µL aliquot of the concentrated sample extract. Record the volume injected to the nearest 0.05 µL and the resulting peak size in area (or peak height) units.

7.6.4 Qualitative identifications of target analytes are made by examination of the sample chromatograms, as described in Sec. 7.7.

7.6.5 Quantitative results are determined for each identified analyte (Aroclors or congeners), using the procedures described in Secs. 7.8 and 7.9 for either the internal or the external calibration procedure (Method 8000). If the responses in the sample chromatogram exceed the calibration range of the system, dilute the extract and reanalyze. Peak height measurements are recommended over peak area when overlapping peaks cause errors in area integration.

7.6.6 Each sample analysis must be bracketed with an acceptable initial calibration, calibration verification standard(s) (each 12-hour shift), or calibration standards interspersed within the samples. When a calibration verification standard fails to meet the QC criteria, all samples that were injected after the last standard that last met the QC criteria must be re-injected.

Multi-level standards (mixtures or multi-component analytes) are highly recommended to ensure that detector response remains stable for all analytes over the calibration range.

7.6.7 Sample injections may continue for as long as the calibration verification standards and standards interspersed with the samples meet instrument QC requirements. It is *recommended* that standards be analyzed after every 10 samples (*required* after every 20 samples and at the end of a set) to minimize the number of samples that must be re-injected when the standards fail the QC limits. The sequence ends when the set of samples has been injected or when qualitative or quantitative QC criteria are exceeded.

7.6.8 If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The analyst should consult with the source of the sample to determine whether further concentration of the sample is warranted.

7.6.9 Use the calibration standards analyzed during the sequence to evaluate retention time stability. If any of the standards fall outside their daily retention time windows, the system is out of control. Determine the cause of the problem and correct it.

7.6.10 If compound identification or quantitation is precluded due to interference (e.g., broad, rounded peaks or ill-defined baselines are present) cleanup of the extract or replacement of the capillary column or detector is warranted. Rerun the sample on another instrument to determine if the problem results from analytical hardware or the sample matrix. Refer to Method 3600 for the procedures to be followed in sample cleanup.

7.7 Qualitative identification

The identification of PCBs as either Aroclors or congeners using this method with an electron capture detector is based on agreement between the retention times of peaks in the sample chromatogram with the retention time windows established through the analysis of standards of the target analytes. See Method 8000 for information on the establishment of retention time windows.

Tentative identification of an analyte occurs when a peak from a sample extract falls within the established retention time window for a specific target analyte. Each tentative identification must be confirmed: using a second GC column of dissimilar stationary phase (as in the dual-column analysis), based on a clearly identifiable Aroclor pattern, or using another technique such as GC/MS (see Sec. 7.10).

7.7.1 When simultaneous analyses are performed from a single injection (the dual-column GC configuration described in Sec. 7.3), it is not practical to designate one column as the analytical (primary) column and the other as the confirmation column. Since the calibration standards are analyzed on both columns, the results for both columns must meet the calibration acceptance criteria. If the retention times of the peaks on both columns fall within the retention time windows on the respective columns, then the target analyte identification has been confirmed.

7.7.2 The results of a single column/single injection analysis may be confirmed on a second, dissimilar, GC column. In order to be used for confirmation, retention time windows must have been established for the second GC column. In addition, the analyst must demonstrate the sensitivity of the second column analysis. This demonstration must include the analysis of a standard of the target analyte at a concentration at least as low as the concentration estimated from the primary analysis. That standard may be either the individual congeners, individual Aroclor or the Aroclor 1016/1260 mixture.

7.7.3 When samples are analyzed from a source known to contain specific Aroclors, the results from a single-column analysis may be confirmed on the basis of a clearly recognizable Aroclor pattern. This approach should not be attempted for samples from unknown or unfamiliar sources or for samples that appear to contain mixtures of Aroclors. In order to employ this approach, the analyst must document:

- The peaks that were evaluated when comparing the sample chromatogram and the Aroclor standard.
- The absence of major peaks representing any other Aroclor.
- The source-specific information indicating that Aroclors are anticipated in the sample (e.g., historical data, generator knowledge, etc.).

This information should either be provided to the data user or maintained by the laboratory.

7.7.4 See Sec. 7.10 for information on GC/MS confirmation.

7.8 Quantitation of PCBs as congeners

7.8.1 The quantitation of PCB congeners is accomplished by the comparison of the sample chromatogram to those of the PCB congener standards, using the internal standard technique (see Method 8000). Calculate the concentration of each congener.

7.8.2 Depending on project requirements, the PCB congener results may be reported as congeners, or may be summed and reported as total PCBs. The analyst should use caution when using the congener method for quantitation when regulatory requirements are based on Aroclor concentrations. See Sec. 9.3.

7.9 Quantitation of PCBs as Aroclors

The quantitation of PCB residues as Aroclors is accomplished by comparison of the sample chromatogram to that of the most similar Aroclor standard. A choice must be made as to which Aroclor is most similar to that of the residue and whether that standard is truly representative of the PCBs in the sample.

7.9.1 Use the individual Aroclor standards (not the 1016/1260 mixtures) to determine the pattern of peaks on Aroclors 1221, 1232, 1242, 1248, and 1254. The patterns for Aroclors 1016 and 1260 will be evident in the mixed calibration standards.

7.9.2 Once the Aroclor pattern has been identified, compare the responses of 3 to 5 major peaks in the single-point calibration standard for that Aroclor with the peaks observed in the sample extract. The amount of Aroclor is calculated using the individual calibration factor for each of the 3 to 5 characteristic peaks chosen in Sec. 7.4.6.1. and the calibration model (linear or non-linear) established from the multi-point calibration of the 1016/1260 mixture. A concentration is determined using each of the characteristic peaks and then those 3 to 5 concentrations are averaged to determine the concentration of that Aroclor.

7.9.3 Weathering of PCBs in the environment and changes resulting from waste treatment processes may alter the PCBs to the point that the pattern of a specific Aroclor is no longer recognizable. Samples containing more than one Aroclor present similar problems. If the purpose of the analysis is not regulatory compliance monitoring on the basis of Aroclor

concentrations, then it may be more appropriate to perform the analyses using the PCB congener approach described in this method. If results in terms of Aroclors are required, then the quantitation as Aroclors may be performed by measuring the total area of the PCB pattern and quantitating on the basis of the Aroclor standard that is most similar to the sample. Any peaks that are not identifiable as PCBs on the basis of retention times should be subtracted from the total area. When quantitation is performed in this manner, the problems should be fully described for the data user and the specific procedures employed by the analyst should be thoroughly documented.

7.10 GC/MS confirmation may be used in conjunction with either single-or dual-column analysis if the concentration is sufficient for detection by GC/MS.

7.10.1 Full-scan quadrupole GC/MS will normally require a higher concentration of the analyte of interest than full-scan ion trap or selected ion monitoring techniques. The concentrations will be instrument-dependent, but values for full-scan quadrupole GC/MS may be as high as 10 ng/µL in the final extract, while ion trap or SIM may only require a concentration of 1 ng/µL.

7.10.2 The GC/MS must be calibrated for the specific target analytes. When using SIM techniques, the ions and retention times should be characteristic of the Aroclors to be confirmed.

7.10.3 GC/MS confirmation should be accomplished by analyzing the same extract used for GC/ECD analysis and the extract of the associated blank.

7.10.4 The base/neutral/acid extract and the associated blank may be used for GC/MS confirmation if the surrogates and internal standards do not interfere. However, if the compounds are *not* detected in the base/neutral/acid extract, then GC/MS analysis of the pesticide extract should be performed.

7.10.5 A QC reference sample containing the compound must also be analyzed by GC/MS. The concentration of the QC reference sample must demonstrate that those PCBs identified by GC/ECD can be confirmed by GC/MS.

7.11 Chromatographic System Maintenance as Corrective Action

When system performance does not meet the established QC requirements, corrective action is required, and may include one or more of the following.

7.11.1 Splitter connections

For dual columns which are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector, clean and deactivate the splitter port insert or replace with a cleaned and deactivated splitter. Break off the first few inches (up to one foot) of the injection port side of the column. Remove the columns and solvent backflush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the columns.

7.11.2 Metal injector body

Turn off the oven and remove the analytical columns when the oven has cooled. Remove the glass injection port insert (instruments with on-column injection). Lower the

injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

7.11.2.1 Place a beaker beneath the injector port inside the oven. Using a wash bottle, rinse the entire inside of the injector port with acetone and then rinse it with toluene, catching the rinsate in the beaker.

7.11.2.2 Consult the manufacturer's instructions regarding deactivating the injector port body. Glass injection port liners may require deactivation with a silanizing solution containing dimethyldichlorosilane.

7.11.3 Column rinsing

The column should be rinsed with several column volumes of an appropriate solvent. Both polar and nonpolar solvents are recommended. Depending on the nature of the sample residues expected, the first rinse might be water, followed by methanol and acetone. Methylene chloride is a good final rinse and in some cases may be the only solvent required. The column should then be filled with methylene chloride and allowed to stand flooded overnight to allow materials within the stationary phase to migrate into the solvent. The column is then flushed with fresh methylene chloride, drained, and dried at room temperature with a stream of ultrapure nitrogen.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation techniques can be found in Method 3500. If an extract cleanup procedure was performed, refer to Method 3600 for the appropriate quality control procedures. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000, Sec. 7.0 and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0 for information on how to accomplish this demonstration.

8.3.1 The QC Reference Sample concentrate (Method 3500) should contain PCBs as Aroclors at 10-50 mg/L for water samples, or PCBs as congeners at the same concentrations. A 1-mL volume of this concentrate spiked into 1 L of organic-free reagent water will result in a sample concentration of 10-50 µg/L. If Aroclors are not expected in samples from a particular source, then prepare the QC reference samples with a mixture of Aroclors 1016 and 1260. However, when specific Aroclors are known to be present or expected in samples, the specific Aroclors should be used for the QC reference sample.

8.3.1.1 The frequency of analysis of the QC reference sample analysis is equivalent to a minimum of 1 per 20 samples or 1 per batch if less than 20 samples.

8.3.1.2 If the recovery of any compound found in the QC reference sample is less than 80 percent or greater than 120 percent of the certified value, the laboratory performance is judged to be out of control, and the problem must be corrected. A new set of calibration standards should be prepared and analyzed.

8.3.2 Include a calibration standard after each group of 20 samples (it is *recommended* that a calibration standard be included after every 10 samples to minimize the number of repeat injections) in the analysis sequence as a calibration check. The response factors for the calibration should be within 15 percent of the initial calibration. When this continuing calibration is out of this acceptance window, the laboratory should stop analyses and take corrective action.

8.3.3 Whenever quantitation is accomplished using an internal standard, internal standards must be evaluated for acceptance. The measured area of the internal standard must be no more than 50 percent different from the average area calculated during calibration. When the internal standard peak area is outside the limit, all samples that fall outside the QC criteria must be reanalyzed.

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

8.4.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair, spiked with the Aroclor 1016/1260 mixture. However, when specific Aroclors are known to be present or expected in samples, the specific Aroclors should be used for spiking. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample.

8.4.2 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.4.3 See Method 8000, Sec. 8.0 for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0 for information on evaluating surrogate data and developing and updating surrogate limits.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 The MDL is defined in Chapter One. The MDLs for Aroclors vary in the range of 0.054 to 0.90 µg/L in water and 57 to 70 µg/kg in soils, with the higher MDLs for the more heavily chlorinated Aroclors. Estimated quantitation limits may be determined using the data in Table 1.

9.2 Estimated quantitation limits for PCBs as congeners vary by congener, in the range of 5 - 25 ng/L in water and 160 - 800 ng/kg in soils, with the higher values for the more heavily chlorinated congeners.

9.3 The accuracy and precision obtainable with this method depend on the sample matrix, sample preparation technique, optional cleanup techniques, and calibration procedures used. Table 9 provides single laboratory recovery data for Aroclors spiked into clay and soil and extracted with automated Soxhlet. Table 10 provides multiple laboratory data on the precision and accuracy for Aroclors spiked into soil and extracted by automated Soxhlet.

9.4 During method performance studies, the concentrations determined as Aroclors were larger than those obtained using the congener method. In certain soils, interference prevented the measurement of congener 66. Recoveries of congeners from soils spiked with Aroclor 1254 and Aroclor 1260 were between 80% and 90%. Recoveries of congeners from environmental reference materials ranged from 51 - 66% of the certified Aroclor values.

10.0 REFERENCES

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TABLE 1

FACTORS FOR DETERMINATION OF ESTIMATED QUANTITATION LIMITS[a] (EQLs) FOR VARIOUS MATRICES

Matrix	Factor
Ground water	10
Low-concentration soil by sonication with GPC cleanup	670
High-concentration soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a]EQL = [MDL for water (see Sec. 1.8)] times [Factor in this table]

For nonaqueous samples, the factor is on a wet-weight basis. Sample EQLs are highly matrix-dependent. EQLs determined using these factors are provided as guidance and may not always be achievable.

TABLE 2

GC OPERATING CONDITIONS FOR PCBs AS AROCLORS
SINGLE COLUMN ANALYSIS

Narrow-bore columns

Narrow-bore Column 1 - 30 m x 0.25 or 0.32 mm ID fused silica capillary column chemically bonded with SE-54 (DB-5 or equivalent), 1 µm film thickness.

Carrier gas (He)	16 psi
Injector temperature	225°C
Detector temperature	300°C
Initial temperature	100°C, hold 2 minutes
Temperature program	100°C to 160°C at 15°C/min, followed by 160°C to 270°C at 5°C/min
Final temperature	270°C

Narrow-bore Column 2 - 30 m x 0.25 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, or equivalent) 25 µm coating thickness, 1 µm film thickness

Carrier gas (N_2)	20 psi
Injector temperature	225°C
Detector temperature	300°C
Initial temperature	160°C, hold 2 minutes
Temperature program	160°C to 290°C at 5°C/min
Final temperature	290°C, hold 1 min

Wide-bore columns

Wide-bore Column 1 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, RTx-35, or equivalent), 0.5 µm or 0.83 µm film thickness.

Wide-bore Column 2 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 14% cyanopropylmethylpolysiloxane (DB-1701, or equivalent), 1.0 µm film thickness.

Carrier gas (He)	5-7 mL/minute
Makeup gas (argon/methane [P-5 or P-10] or N_2)	30 mL/min
Injector temperature	250°C
Detector temperature	290°C
Initial temperature	150°C, hold 0.5 minute
Temperature program	150°C to 270°C at 5°C/min
Final temperature	270°C, hold 10 min

(continued)

TABLE 2 (cont.)

GC OPERATING CONDITIONS FOR PCBs AS AROCLORS
SINGLE COLUMN ANALYSIS

Wide-bore Columns (continued)

Wide-bore Column 3 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 1.5 µm film thickness.

Carrier gas (He)	6 mL/minute
Makeup gas (argon/methane [P-5 or P-10] or N_2)	30 mL/min
Injector temperature	205°C
Detector temperature	290°C
Initial temperature	140°C, hold 2 min
Temperature program	140°C to 240°C at 10°C/min, hold 5 minutes at 240°C, 240°C to 265°C at 5°C/min
Final temperature	265°C, hold 18 min

TABLE 3

GC OPERATING CONDITIONS FOR PCBs AS AROCLORS
FOR THE DUAL COLUMN METHOD OF ANALYSIS
HIGH TEMPERATURE, THICK FILM

Column 1 -	DB-1701 or equivalent, 30 m x 0.53 mm ID, 1.0 µm film thickness.
Column 2 -	DB-5 or equivalent, 30 m x 0.53 mm ID, 1.5 µm film thickness.
Carrier gas (He) flow rate	6 mL/min
Makeup gas (N_2) flow rate	20 mL/min
Temperature program	0.5 min hold 150°C to 190°C, at 12°C/min, 2 min hold 190°C to 275°C, at 4°C/min, 10 min hold
Injector temperature	250°C
Detector temperature	320°C
Injection volume	2 µL
Solvent	Hexane
Type of injector	Flash vaporization
Detector type Dual ECD	
Range	10
Attenuation 64 (DB-1701)/64 (DB-5)	
Type of splitter	J&W Scientific press-fit Y-shaped inlet splitter

TABLE 4

SUMMARY OF RETENTION TIMES OF AROCLORS
ON THE DB-5 COLUMN[a], DUAL COLUMN ANALYSIS

Peak No.[b]	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
1		5.85	5.85				
2		7.63	7.64	7.57			
3	8.41	8.43	8.43	8.37			
4	8.77	8.77	8.78	8.73			
5	8.98	8.99	9.00	8.94	8.95		
6	9.71			9.66			
7	10.49	10.50	10.50	10.44	10.45		
8	10.58	10.59	10.59	10.53			
9	10.90		10.91	10.86	10.85		
10	11.23	11.24	11.24	11.18	11.18		
11	11.88		11.90	11.84	11.85		
12	11.99		12.00	11.95			
13	12.27	12.29	12.29	12.24	12.24		
14	12.66	12.68	12.69	12.64	12.64		
15	12.98	12.99	13.00	12.95	12.95		
16	13.18		13.19	13.14	13.15		
17	13.61		13.63	13.58	13.58	13.59	13.59
18	13.80		13.82	13.77	13.77	13.78	
19	13.96		13.97	13.93	13.93	13.90	
20	14.48		14.50	14.46	14.45	14.46	
21	14.63		14.64	14.60	14.60		
22	14.99		15.02	14.98	14.97	14.98	
23	15.35		15.36	15.32	15.31	15.32	
24	16.01			15.96			
25			16.14	16.08	16.08	16.10	
26	16.27		16.29	16.26	16.24	16.25	16.26
27						16.53	
28			17.04		16.99	16.96	16.97
29			17.22	17.19	17.19	17.19	17.21
30			17.46	17.43	17.43	17.44	
31					17.69	17.69	
32				17.92	17.91	17.91	
33				18.16	18.14	18.14	
34			18.41	18.37	18.36	18.36	18.37
35			18.58	18.56	18.55	18.55	
36							18.68

(continued)

[a] GC operating conditions are given in Table 3. All retention times in minutes.
[b] The peaks listed in this table are sequentially numbered in elution order for illustrative purposes only and are not isomer numbers.

TABLE 4 (cont.)

SUMMARY OF RETENTION TIMES OF AROCLORS
ON THE DB-5 COLUMN[a], DUAL COLUMN ANALYSIS

Peak No.[b]	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
37			18.83	18.80	18.78	18.78	18.79
38			19.33	19.30	19.29	19.29	19.29
39						19.48	19.48
40						19.81	19.80
41			20.03	19.97	19.92	19.92	
42						20.28	20.28
43					20.46	20.45	
44						20.57	20.57
45				20.85	20.83	20.83	20.83
46			21.18	21.14	21.12	20.98	
47					21.36	21.38	21.38
48						21.78	21.78
49				22.08	22.05	22.04	22.03
50						22.38	22.37
51						22.74	22.73
52						22.96	22.95
53						23.23	23.23
54							23.42
55						23.75	23.73
56						23.99	23.97
57							24.16
58						24.27	
59							24.45
60						24.61	24.62
61						24.93	24.91
62							25.44
63						26.22	26.19
64							26.52
65							26.75
66							27.41
67							28.07
68							28.35
69							29.00

[a] GC operating conditions are given in Table 3. All retention times in minutes.
[b] The peaks listed in this table are sequentially numbered in elution order for illustrative purposes only and are not isomer numbers.

TABLE 5

SUMMARY OF RETENTION TIMES OF AROCLORS
ON THE DB-1701 COLUMN[a], DUAL COLUMN ANALYSIS

Peak No.[b]	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
1		4.45	4.45				
2		5.38					
3		5.78					
4		5.86	5.86				
5	6.33	6.34	6.34	6.28			
6	6.78	6.78	6.79	6.72			
7	6.96	6.96	6.96	6.90	6.91		
8	7.64			7.59			
9	8.23	8.23	8.23	8.15	8.16		
10	8.62	8.63	8.63	8.57			
11	8.88		8.89	8.83	8.83		
12	9.05	9.06	9.06	8.99	8.99		
13	9.46		9.47	9.40	9.41		
14	9.77	9.79	9.78	9.71	9.71		
15	10.27	10.29	10.29	10.21	10.21		
16	10.64	10.65	10.66	10.59	10.59		
17				10.96	10.95	10.95	
18	11.01		11.02	11.02	11.03		
19	11.09		11.10				
20	11.98		11.99	11.94	11.93	11.93	
21	12.39		12.39	12.33	12.33	12.33	
22			12.77	12.71	12.69		
23	12.92			12.94	12.93		
24	12.99		13.00	13.09	13.09	13.10	
25	13.14		13.16				
26						13.24	
27	13.49		13.49	13.44	13.44		
28	13.58		13.61	13.54	13.54	13.51	13.52
29				13.67		13.68	
30			14.08	14.03	14.03	14.03	14.02
31			14.30	14.26	14.24	14.24	14.25
32					14.39	14.36	
33			14.49	14.46	14.46		
34						14.56	14.56
35					15.10	15.10	
36			15.38	15.33	15.32	15.32	

(continued)

[a]GC operating conditions are given in Table 3. All retention times in minutes.
[b]The peaks listed in this table are sequentially numbered in elution order for illustrative purposes only and are not isomer numbers.

TABLE 5 (cont.)

SUMMARY OF RETENTION TIMES OF AROCLORS
ON THE DB-1701 COLUMN[a], DUAL COLUMN ANALYSIS

Peak No.[b]	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
37			15.65	15.62	15.62	15.61	16.61
38			15.78	15.74	15.74	15.74	15.79
39			16.13	16.10	16.10	16.08	
40							16.19
41						16.34	16.34
42						16.44	16.45
43						16.55	
44			16.77	16.73	16.74	16.77	16.77
45			17.13	17.09	17.07	17.07	17.08
46						17.29	17.31
47				17.46	17.44	17.43	17.43
48				17.69	17.69	17.68	17.68
49					18.19	18.17	18.18
50				18.48	18.49	18.42	18.40
51						18.59	
52						18.86	18.86
53				19.13	19.13	19.10	19.09
54						19.42	19.43
55						19.55	19.59
56						20.20	20.21
57						20.34	
58							20.43
59					20.57	20.55	
60						20.62	20.66
61						20.88	20.87
62							21.03
63						21.53	21.53
64						21.83	21.81
65						23.31	23.27
66							23.85
67							24.11
68							24.46
69							24.59
70							24.87
71							25.85
72							27.05
73							27.72

[a] GC operating conditions are given in Table 3. All retention times in minutes.
[b] The peaks listed in this table are sequentially numbered in elution order for illustrative purposes only and are not isomer numbers.

TABLE 6

PEAKS DIAGNOSTIC OF PCBs OBSERVED ON 0.53 mm ID COLUMN
DURING SINGLE COLUMN ANALYSIS

Peak No.[a]	RT on DB-608[b]	RT on DB-1701[b]	Aroclor[c]
I	4.90	4.66	1221
II	7.15	6.96	1221, 1232, 1248
III	7.89	7.65	1061, 1221, 1232, 1242,
IV	9.38	9.00	1016, 1232, 1242, 1248,
V	10.69	10.54	1016, 1232, 1242,
VI	14.24	14.12	1248, 1254
VII	14.81	14.77	1254
VIII	16.71	16.38	1254
IX	19.27	18.95	1254, 1260
X	21.22	21.23	1260
XI	22.89	22.46	1260

[a] Peaks are sequentially numbered in elution order and are not isomer numbers

[b] Temperature program: T_i = 150°C, hold 30 seconds; 5°C/minute to 275°C.

[c] Underline indicates largest peak in the pattern for that Aroclor

TABLE 7

SPECIFIC PCB CONGENERS IN AROCLORS

Congener	IUPAC number	Aroclor 1016	1221	1232	1242	1248	1254	1260
Biphenyl	--		X					
2-CB	1	X	X	X	X			
23-DCB	5	X	X	X	X	X		
34-DCB	12	X		X	X	X		
244'-TCB	28*	X		X	X	X	X	
22'35'-TCB	44			X	X	X	X	X
23'44'-TCB	66*					X	X	X
233'4'6-PCB	110						X	
23'44'5-PCB	118*						X	X
22'44'55'-HCB	153							X
22'344'5'-HCB	138							X
22'344'55'-HpCB	180							X
22'33'44'5-HpCB	170							X

*Apparent co-elution of

28 with 31 (2,4',5-trichlorobiphenyl)
66 with 95 (2,2',3,5',6-pentachlorobiphenyl)
118 with 149 (2,2',3,4',5',6-hexachlorobiphenyl)

TABLE 8

RETENTION TIMES OF PCB CONGENERS
ON THE DB-5 WIDE-BORE COLUMN

IUPAC #	Retention Time (min)	
1	6.52	
5	10.07	
18	11.62	
31	13.43	
52	14.75	
44	15.51	
66	17.20	
101	18.08	
87	19.11	
110	19.45	
151	19.87	
153	21.30	
138	21.79	
141	22.34	
187	22.89	
183	23.09	
180	24.87	
170	25.93	
206	30.70	
209	32.63	(internal standard)

TABLE 9

SINGLE LABORATORY RECOVERY DATA FOR EXTRACTION OF PCBs FROM CLAY AND SOIL BY METHOD 3541[a] (AUTOMATED SOXHLET)

Matrix	Aroclor	Spike Level (ppm)	Trial	Percent Recovery[b]
Clay	1254	5	1	87.0
			2	92.7
			3	93.8
			4	98.6
			5	79.4
			6	28.3
Clay	1254	50	1	65.3
			2	72.6
			3	97.2
			4	79.6
			5	49.8
			6	59.1
Clay	1260	5	1	87.3
			2	74.6
			3	60.8
			4	93.8
			5	96.9
			6	113.1
Clay	1260	50	1	73.5
			2	70.1
			3	92.4
			4	88.9
			5	90.2
			6	67.3

(continued)

[a] The operating conditions for the automated Soxhlet

Immersion time: 60 min
Reflux time: 60 min

[b] Multiple results from two different extractors.

Data from Reference 9.

TABLE 9 (cont.)

SINGLE LABORATORY RECOVERY DATA FOR EXTRACTION OF PCBs FROM CLAY AND SOIL BY METHOD 3541[a] (AUTOMATED SOXHLET)

Matrix	Aroclor	Spike Level (ppm)	Trial	Percent Recovery[b]
Soil	1254	5	1	69.7
			2	89.1
			3	91.8
			4	83.2
			5	62.5
Soil	1254	50	1	84.0
			2	77.5
			3	91.8
			4	66.5
			5	82.3
			6	61.6
Soil	1260	5	1	83.9
			2	82.8
			3	81.6
			4	96.2
			5	93.7
			6	93.8
			7	97.5
Soil	1260	50	1	76.9
			2	69.4
			3	92.6
			4	81.6
			5	83.1
			6	76.0

[a] The operating conditions for the automated Soxhlet

Immersion time: 60 min
Reflux time: 60 min

[b] Multiple results from two different extractors.

Data from Reference 9.

TABLE 10

MULTIPLE LABORATORY PRECISION AND ACCURACY DATA
FOR THE EXTRACTION OF PCBs FROM SPIKED SOIL
BY METHOD 3541 (AUTOMATED SOXHLET)

		Percent Recovery						
		Aroclor 1254			Aroclor 1260			
		Spike Conc. (µg/kg)			Spike Conc. (µg/kg)			
		5	50	500	5	50	500	All Levels
Laboratory 1	N	3	3		3	3		12
	Mean	101.2	74.0		83.9	78.5		84.4
	S. D.	34.9	41.8		7.4	7.4		26.0
Laboratory 2	N		6	6		6	6	24
	Mean		56.5	66.9		70.1	74.5	67.0
	S. D.		7.0	15.4		14.5	10.3	13.3
Laboratory 3	N	3	3		3	3		12
	Mean	72.8	63.3		70.6	57.2		66.0
	S. D.	10.8	8.3		2.5	5.6		9.1
Laboratory 4	N	6	6		6	6		24
	Mean	112.6	144.3		100.3	84.8		110.5
	S. D.	18.2	30.4		13.3	3.8		28.5
Laboratory 5	N		3	3		3	3	12
	Mean		97.1	80.1		79.5	77.0	83.5
	S. D.		8.7	5.1		3.1	9.4	10.3
Laboratory 6	N	2	3		3	4		12
	Mean	140.9	127.7		138.7	105.9		125.4
	S. D.	4.3	15.5		15.5	7.9		18.4
Laboratory 7	N	3	3		3	3		12
	Mean	100.1	123.4		82.1	94.1		99.9
	S. D.	17.9	14.6		7.9	5.2		19.0
Laboratory 8	N	3	3		3	3		12
	Mean	65.0	38.3		92.8	51.9		62.0
	S. D.	16.0	21.9		36.5	12.8		29.1
All Laboratories	N	20	30	9	21	31	9	120
	Mean	98.8	92.5	71.3	95.5	78.6	75.3	87.6
	S. D.	28.7	42.9	14.1	25.3	18.0	9.5	29.7

Data from Reference 7.

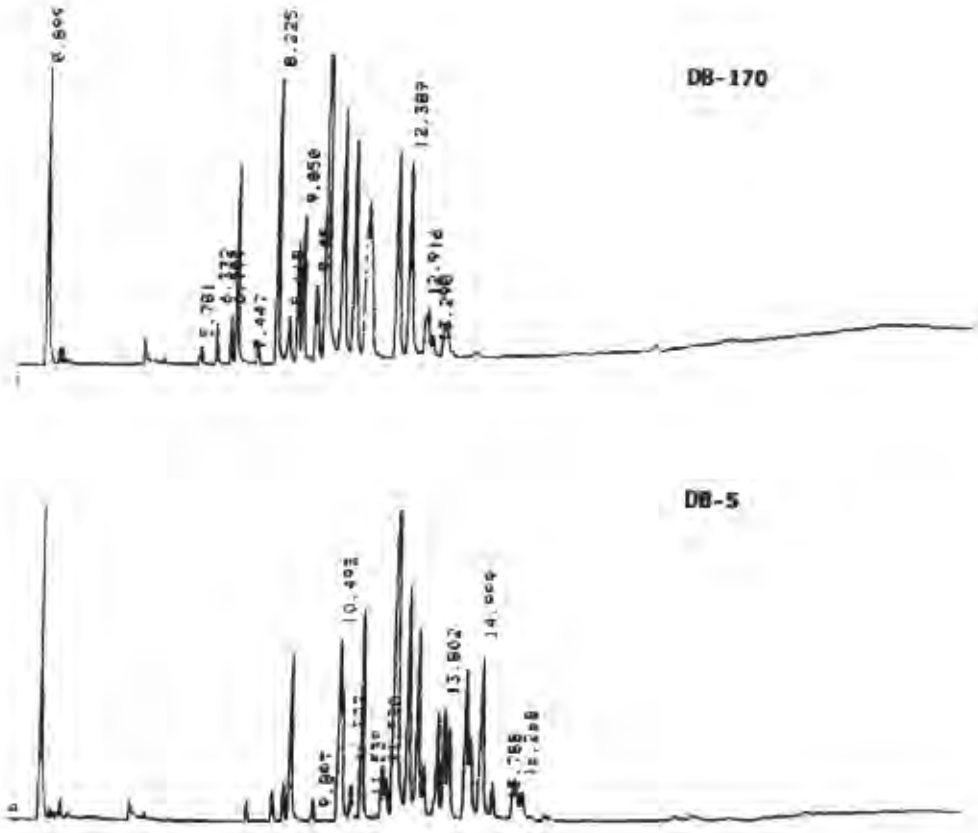


FIGURE 1. GC/ECD chromatogram of Aroclor 1016 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

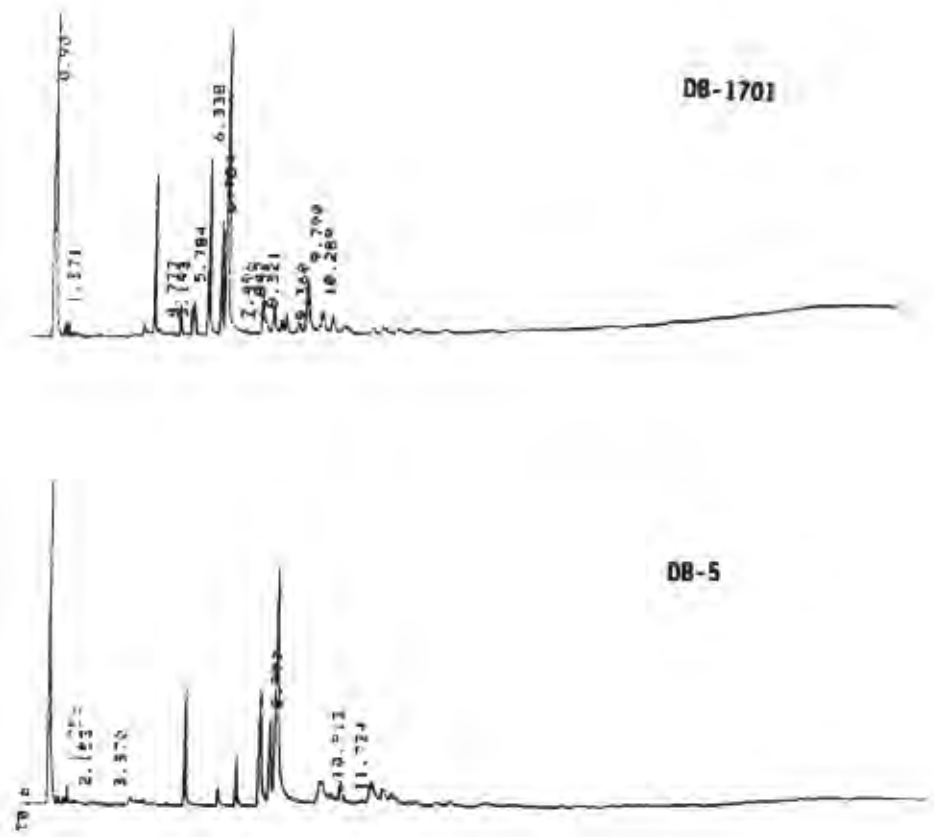


FIGURE 2. GC/ECD chromatogram of Aroclor 1221 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

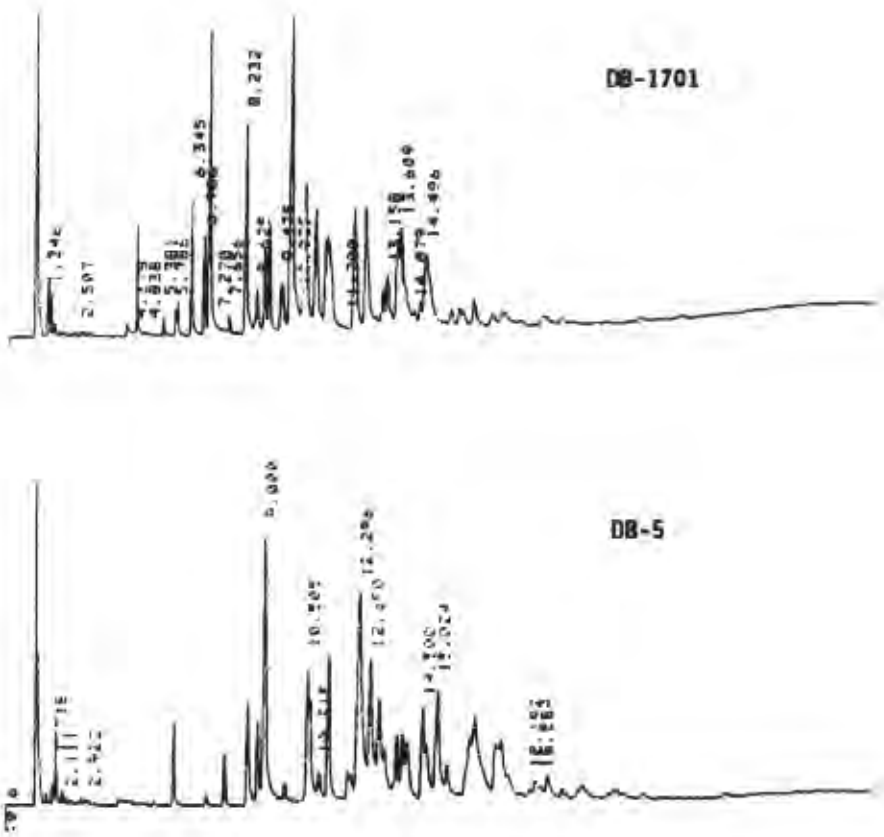


FIGURE 3. GC/ECD chromatogram of Aroclor 1232 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

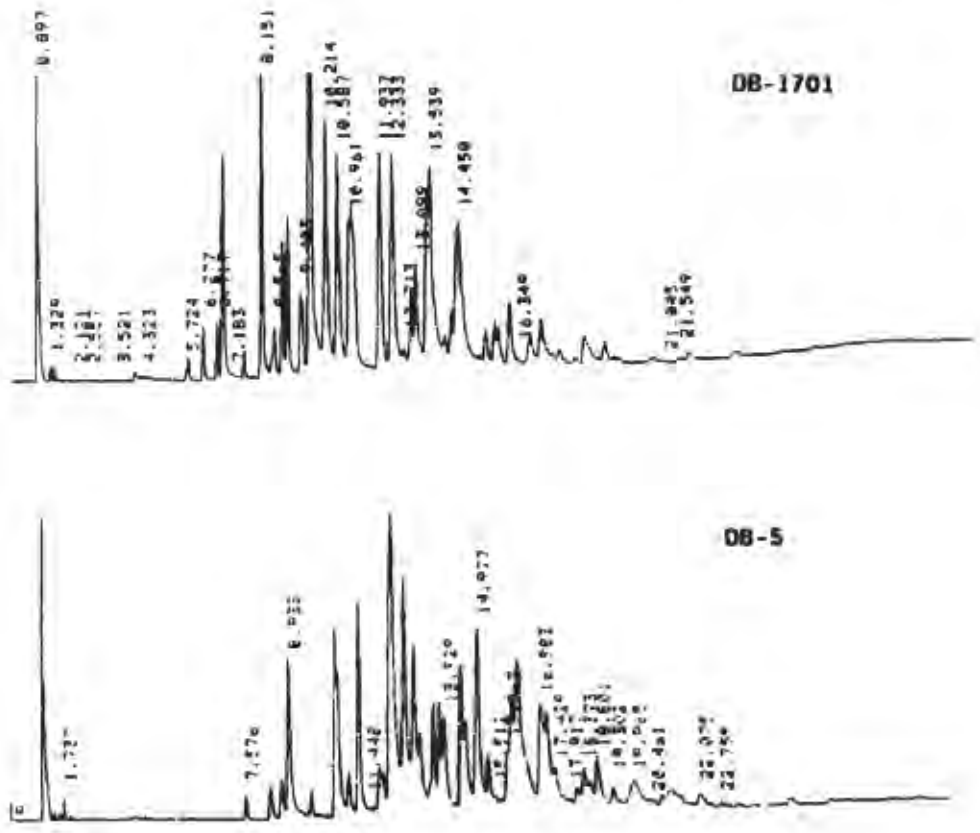


FIGURE 4. GC/ECD chromatogram of Aroclor 1242 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

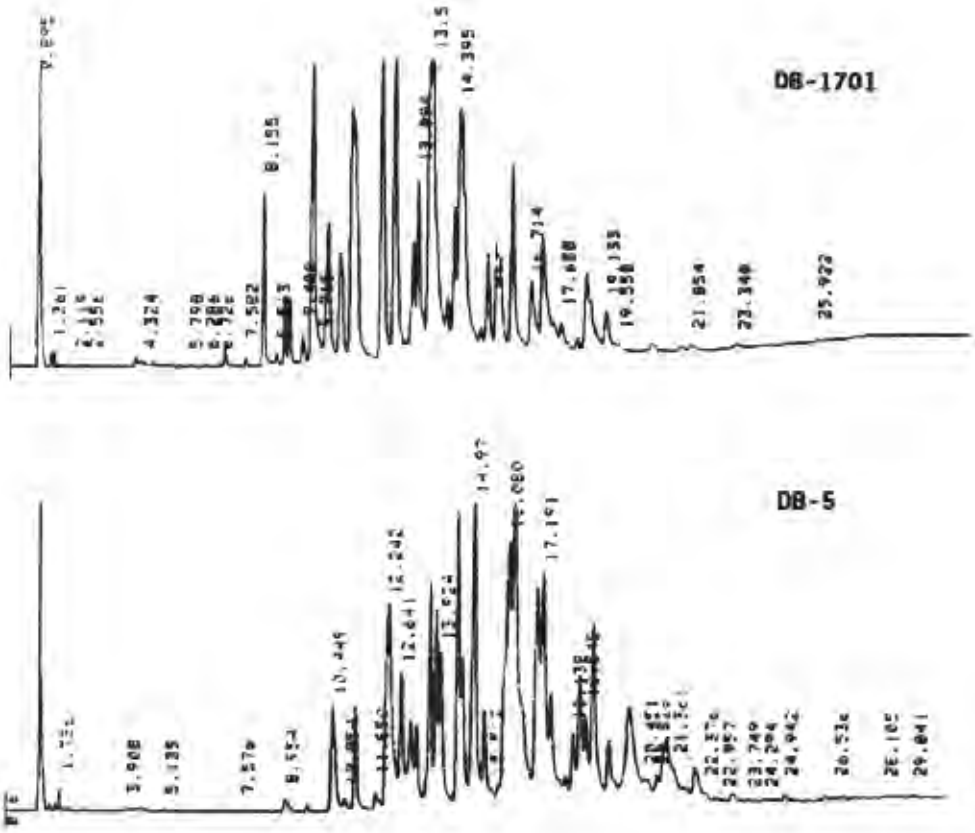


FIGURE 5. GC/ECD chromatogram of Aroclor 1248 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

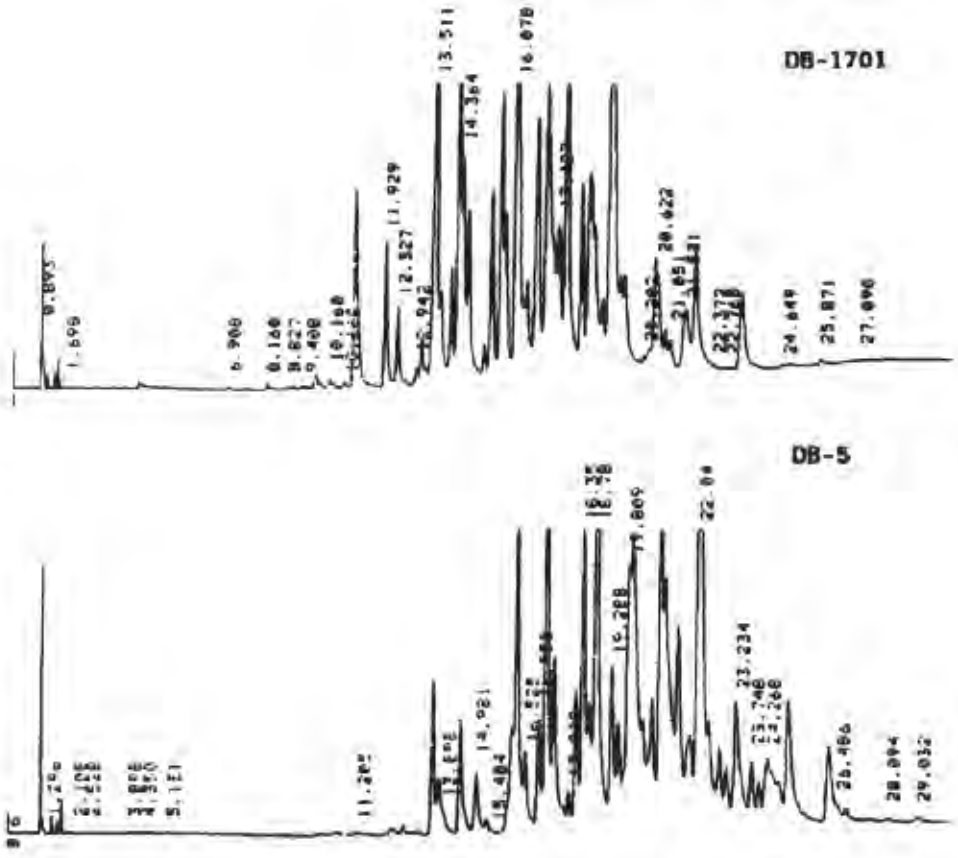


FIGURE 6. GC/ECD chromatogram of Aroclor 1254 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

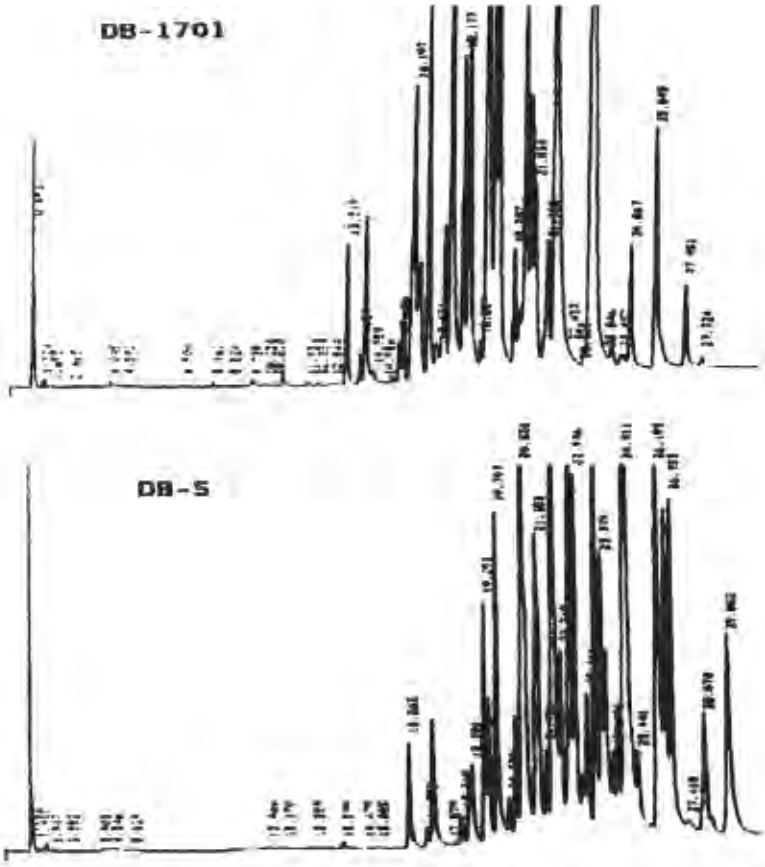
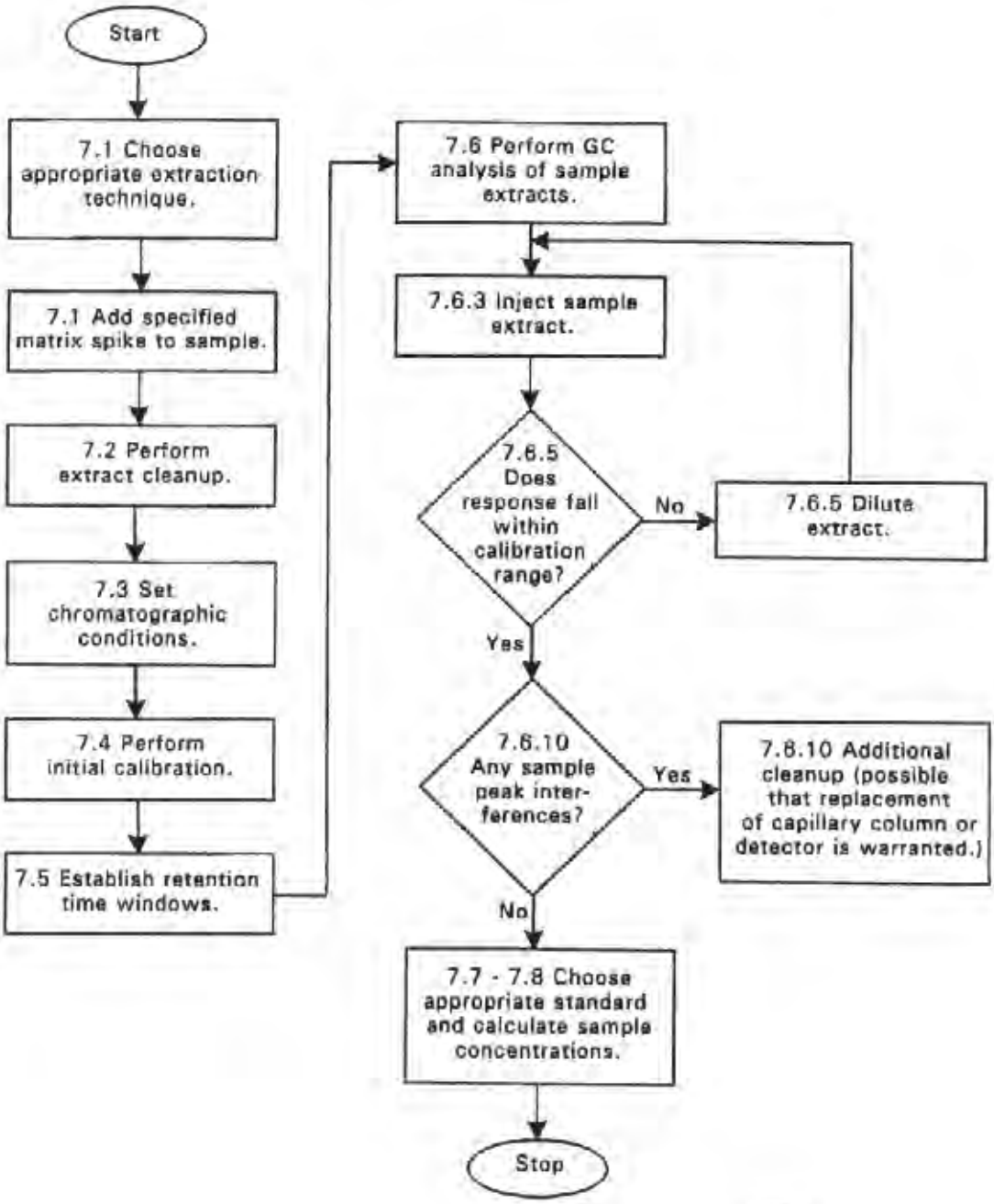


FIGURE 7. GC/ECD chromatogram of Aroclor 1260 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.


Start
7.1 Choose appropriate extraction technique.
7.1 Add specified matrix spike to sample.
7.2 Perform extract cleanup.
7.3 Set chromatographic conditions.
7.4 Perform initial calibration.
7.5 Establish retention time windows.
7.6 Perform GC analysis of sample extracts.
7.6.3 Inject sample extract.
7.6.5 Does response fall within calibration range?
No
7.6.5 Dilute extract.
Yes
7.8.10 Any sample peak interferences?
Yes
7.8.10 Additional cleanup (possible that replacement of capillary column or detector is warranted.)
No
7.7 - 7.8 Choose appropriate standard and calculate sample concentrations.
Stop

Analytical Methods

Chlorinated Herbicides

8151A

METHOD 8151A

CHLORINATED HERBICIDES BY GC USING METHYLATION OR PENTAFLUOROBENZYLATION DERIVATIZATION

1.0 SCOPE AND APPLICATION

1.1 Method 8151 is a capillary gas chromatographic (GC) method for determining certain chlorinated acid herbicides and related compounds in aqueous, soil and waste matrices. Specifically, Method 8151 may be used to determine the following compounds:

Compound	CAS No.[a]
2,4-D	94-75-7
2,4-DB	94-82-6
2,4,5-TP (Silvex)	93-72-1
2,4,5-T	93-76-5
Dalapon	75-99-0
Dicamba	1918-00-9
Dichloroprop	120-36-5
Dinoseb	88-85-7
MCPA	94-74-6
MCPP	93-65-2
4-Nitrophenol	100-02-1
Pentachlorophenol	87-86-5

[a] Chemical Abstract Service Registry Number

1.2 Because these compounds are produced and used in various forms (i.e., acid, salt, ester, etc.), Method 8151 describes a hydrolysis step that can be used to convert herbicide esters into the acid form prior to analysis. Herbicide esters generally have a half-life of less than one week in soil.

1.3 When Method 8151 is used to analyze unfamiliar samples, compound identifications should be supported by at least one additional qualitative technique. Sec. 8.4 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

1.4 The estimated detection limits for each of the compounds in aqueous and soil matrices are listed in Table 1. The detection limits for a specific waste sample may differ from those listed, depending upon the nature of the interferences and the sample matrix.

1.5 The following compounds may also be determined using this method:

Compound	CAS No.[a]
Acifluorfen	50594-66-6
Bentazon	25057-89-0
Chloramben	133-90-4
DCPA diacid[b]	2136-79-0
3,5-Dichlorobenzoic acid	51-36-5
5-Hydroxydicamba	7600-50-2
Picloram	1918-02-1

[a] Chemical Abstract Service Registry Number
[b] DCPA monoacid and diacid metabolites included in method scope; DCPA diacid metabolite used for validation studies. DCPA is a dimethyl ester.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.7 Only experienced analysts should be allowed to work with diazomethane due to the potential hazards associated with its use (explosive, carcinogenic).

2.0 SUMMARY OF METHOD

2.1 Method 8151 provides extraction, derivatization, and gas chromatographic conditions for the analysis of chlorinated acid herbicides in water, soil, and waste samples. An option for the hydrolysis of esters is also described.

2.2 Water samples are extracted with diethyl ether and then esterified with either diazomethane or pentafluorobenzyl bromide. The derivatives are determined by gas chromatography with an electron capture detector (GC/ECD). The results are reported as acid equivalents.

2.3 Soil and waste samples are extracted and esterified with either diazomethane or pentafluorobenzyl bromide. The derivatives are determined by gas chromatography with an electron capture detector (GC/ECD). The results are reported as acid equivalents.

2.4 If herbicide esters are to be determined using this method, hydrolysis conditions for the esters in water and soil extracts are described.

2.5 The sensitivity of Method 8151 depends on the level of interferences in addition to instrumental limitations. Table 1 lists the GC/ECD and GC/MS detection limits that can be obtained in aqueous and soil matrices in the absence of interferences. Detection limits for a typical waste sample should be higher.

3.0 INTERFERENCES

3.1 Refer to Method 8000.

3.2 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts or elevated baselines in gas chromatograms. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis, by analyzing reagent blanks.

3.2.1 Glassware must be scrupulously cleaned. Clean each piece of glassware as soon as possible after use by rinsing it with the last solvent used in it. This should be followed by detergent washing with hot water and rinses with tap water, then with organic-free reagent water. Glassware should be solvent-rinsed with acetone and pesticide-quality hexane. After rinsing and drying, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store glassware inverted or capped with aluminum foil. Immediately prior to use, glassware should be rinsed with the next solvent to be used.

3.2.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from waste to waste, depending upon the nature and diversity of the waste being sampled.

3.4 Organic acids, especially chlorinated acids, cause the most direct interference with the determination by methylation. Phenols, including chlorophenols, may also interfere with this procedure. The determination using pentafluorobenzylation is more sensitive, and more prone to interferences from the presence of organic acids or phenols than by methylation.

3.5 Alkaline hydrolysis and subsequent extraction of the basic solution removes many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis. However, hydrolysis may result in the loss of dinoseb and the formation of aldol condensation products if any residual acetone remains from the extraction of solids.

3.6 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware must be acid-rinsed and then rinsed to constant pH with organic-free reagent water. Sodium sulfate must be acidified.

3.7 Sample extracts should be dry prior to methylation or else poor recoveries will be obtained.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph - Analytical system complete with gas chromatograph suitable for Grob-type injection using capillary columns, and all required accessories including detector, capillary analytical columns, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.2 GC columns

The analyst may chose either narrow-bore or wide-bore GC columns. Narrow-bore column 1a is useful for GC/MS confirmation of these analytes. When using an electron capture detector, analyses two columns are necessary to provide confirmation of identifications.

Although not specifically evaluated under the chromatographic conditions described in this procedure, the analyst may opt to configure the GC for simultaneous dual-column operation using commercially-available Y-adapters to connect both columns to a single injector port and employing a separate electron capture detector for each column.

4.2.1 Narrow-bore columns

4.1.2.1 Primary column 1 - 30 m x 0.25 mm, 5% phenyl/95% methyl silicone (DB-5, J&W Scientific, or equivalent), 0.25 µm film thickness.

4.1.2.2 Primary column 1a (GC/MS) - 30 m x 0.32 mm, 5% phenyl/95% methyl silicone, (DB-5, J&W Scientific, or equivalent), 1 µm film thickness.

4.1.2.3 Column 2 - 30 m x 0.25 mm, 35% phenyl methylpolysiloxane (DB-608, J&W Scientific or equivalent), a 0.25 µm film thickness.

4.1.2.4 Confirmation column - 30 m x 0.25 mm, 14% cyanopropyl phenyl silicone, (DB-1701, J&W Scientific, or equivalent), 0.25 µm film thickness.

4.2.2 Wide-bore columns

4.2.2.1 Primary Column - 30 m x 0.53 mm DB-608 (J&W Scientific or equivalent) with 0.83 µm film thickness.

4.2.2.2 Confirmation Column - 30 m x 0.53 mm, 14% cyanopropyl phenyl silicone, (DB-1701, J&W Scientific, or equivalent), 1.0 µm film thickness.

4.3 Electron capture detector (ECD).

4.4 Kuderna-Danish (K-D) apparatus.

4.4.1 Concentrator tube - 10-mL graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.

4.4.2 Evaporation flask - 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.4.3 Snyder column - Three-ball macro (Kontes K-503000-0121 or equivalent).

4.4.4 Snyder column - Two-ball micro (Kontes K-569001-0219 or equivalent).

4.4.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

NOTE: The following glassware is recommended for the purpose of solvent recovery during the concentration procedures requiring the use of Kuderna-Danish evaporative concentrators. Incorporation of this apparatus may be required

by State or local municipality regulations that govern air emissions of volatile organics. EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program. Solvent recovery is a means to conform with waste minimization and pollution prevention initiatives.

4.4.6 Solvent vapor recovery system (Kontes K-545000-1006 or K-547300-0000, Ace Glass 6614-30, or equivalent).

4.5 Diazomethane generator - Refer to Sec. 7.5 to determine which method of diazomethane generation should be used for a particular generation.

4.5.1 Diazald kit - Recommended for the generation of diazomethane (Aldrich Chemical Co., Catalog No. 210,025-0, or equivalent).

4.5.2 As an alternative, assemble from two 20 mm x 150 mm test tubes, two Neoprene rubber stoppers, and a source of nitrogen. Use Neoprene rubber stoppers with holes drilled in them to accommodate glass delivery tubes. The exit tube must be drawn to a point to bubble diazomethane through the sample extract. The generator assembly is shown in Figure 1. The procedure for use of this type of generator is given in Sec. 7.5.

4.6 Beaker - 400-mL, thick-walled.

4.7 Funnel - 75 mm diameter.

4.8 Separatory funnel - 500-mL, with polytetrafluoroethylene (PTFE) stopcock.

4.9 Centrifuge bottle - 500-mL, Pyrex® 1260 or equivalent.

4.10 Erlenmeyer flasks - 250-mL and 500-mL, with a ground-glass joint at the neck.

4.11 Pipet - Pasteur, glass, disposable (140 mm x 5 mm ID).

4.12 Vials - 10-mL, glass, with PTFE-lined screw-caps.

4.13 Volumetric flasks, Class A - 10-mL to 1000-mL.

4.14 Filter paper - 15 cm diameter (Whatman No. 1 or equivalent).

4.15 Glass wool - Pyrex®, acid washed.

4.16 Boiling chips - Solvent-extracted with methylene chloride, approximately 10/40 mesh (silicon carbide or equivalent).

4.17 Water bath - Heated, with concentric ring cover, capable of temperature control (± 2°C). The bath should be used in a hood.

4.18 Balance - Analytical, capable of accurately weighing to 0.0001 g.

4.19 Centrifuge.

4.20 Ultrasonic extraction system - A horn-type device equipped with a titanium tip, or a device that will give equivalent performance, should be used. The disrupter must have a minimum power wattage of 300 watts, with pulsing capability. A device designed to reduce the cavitation sound is recommended. Follow the manufacturer's instructions for preparing the disrupter for extraction of samples. Use a 3/4" horn for most samples.

4.21 Sonabox - Recommended with above disrupters for decreasing cavitation sound (Heat Systems - Ultrasonics, Inc., Model 432B or equivalent).

4.22 pH paper - wide range

4.23 Silica gel cleanup column (Bond Elut™ - Analytichem, Harbor City, CA or equivalent).

4.24 Microsyringe - 10-µL.

4.25 Wrist shaker - Burrell Model 75 or equivalent.

4.26 Drying column - 400 mm x 20 mm ID Pyrex® chromatographic column with Pyrex® glass wool at bottom and a PTFE stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex® glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free water, as defined in Chapter One.

5.3 Sodium hydroxide solution (0.1 N), NaOH - Dissolve 4 g of NaOH in organic-free reagent water and dilute to 1.0 L.

5.4 Potassium hydroxide solution (37% aqueous solution (w/v)), KOH - Dissolve 37 g of potassium hydroxide pellets in organic-free reagent water and dilute to 100 mL.

5.5 Phosphate buffer (0.1 M), pH = 2.5 - Dissolve 12 g sodium phosphate (NaH_2PO_4) in organic-free reagent water and dilute to 1.0 L. Add phosphoric acid to adjust the pH to 2.5.

5.6 N-methyl-N-nitroso-p-toluenesulfonamide (Diazald) - High purity (Aldrich Chemical Co., or equivalent).

5.7 Silicic acid, H_2SiO_5 - 100-mesh powder, store at 130°C.

5.8 Potassium carbonate, K_2CO_3.

5.9 2,3,4,5,6-Pentafluorobenzyl bromide (PFBBr), $C_6F_5CH_2Br$ - Pesticide quality or equivalent.

5.10 Sodium sulfate (granular, acidified, anhydrous), Na_2SO_4 - Purify by heating at 400 C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate. Acidify by slurrying 100 g sodium sulfate with enough diethyl ether to just cover the solid; then add 0.1 mL of concentrated sulfuric acid and mix thoroughly. Remove the ether under vacuum. Mix 1 g of the resulting solid with 5 mL of organic-free reagent water and measure the pH of the mixture. It must be below a pH of 4. Store the remaining solid at 130 C.

5.11 Solvents - All solvents should be pesticide quality or equivalent.

5.11.1 Methylene chloride, CH_2Cl_2.

5.11.2 Acetone, CH_3COCH_3.

5.11.3 Methanol, CH_3OH.

5.11.4 Toluene, $C_6H_5CH_3$.

5.11.5 Diethyl Ether, $C_2H_5OC_2H_5$. Must be free of peroxides as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the test strips.

NOTE: Diethyl ether used for this procedure should be stabilized with BHT, not with ethanol, as when ethanol-stabilized ether is used, the methylation reaction may not proceed efficiently, leading to low recoveries of target analytes.

5.11.6 Isooctane, $(CH_3)_3CH_2CH(CH_3)_2$.

5.11.7 Hexane, C_6H_{14}.

5.11.8 Carbitol (diethylene glycol monoethyl ether), $C_2H_5OCH_2CH_2OCH_2CH_2O$ - optional, for producing alcohol-free diazomethane.

5.12 Stock standard solutions (1000 mg/L) - May be prepared from pure standard materials or purchased as certified solutions.

5.12.1 Prepare stock standard solutions by accurately weighing about 0.010 g of pure acid. Dissolve the material in pesticide quality acetone and dilute to volume in a 10-mL volumetric flask. Stocks prepared from pure methyl esters are dissolved in 10% acetone/isooctane (v/v). Larger volumes may be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard.

5.12.2 Transfer the stock standard solutions to vials with PTFE-lined screw-caps. Store at 4 C, protected from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially immediately prior to preparing calibration standards from them.

5.12.3 Stock standard solutions of the derivatized acids must be replaced after 1 year, or sooner, if comparison with check standards indicates a problem. Stock standard solutions of the free acids degrade more quickly and should be replaced after two months, or sooner if comparison with check standards indicates a problem.

5.13 Internal Standard Spiking Solution (If internal standard calibration is used) - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences.

5.13.1 The compound 4,4'-dibromooctafluorobiphenyl (DBOB) has been shown to be an effective internal standard, but other compounds, such as 1,4-dichlorobenzene, may be used if there is a DBOB interference.

5.13.2 Prepare an internal standard spiking solution by accurately weighing approximately 0.0025 g of pure DBOB. Dissolve the DBOB in acetone and dilute to volume in a 10 mL volumetric flask. Transfer the internal standard spiking solution to a vial with a PTFE-lined screw-cap, and store at room temperature. Addition of 10 µL of the internal standard spiking solution to 10 mL of sample extract results in a final internal standard concentration of 0.25 µg/L. The solution should be replaced if there is a change in internal standard response greater than 20 percent of the original response recorded.

5.14 Calibration standards - Prepare a minimum of five different concentrations for each parameter of interest, through dilution of the stock standards with diethyl ether or hexane. One of the standards should be at a concentration near, but above, the method detection limit. The remaining standards should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.14.1 Derivatize each calibration standard prepared from free acids in a 10-mL K-D concentrator tube, according to the procedures beginning at Sec. 7.5.

5.14.2 Add a known, constant, amount of one or more internal standards to each derivatized calibration standard, and dilute to volume with the solvent indicated in the derivative option used.

5.15 Surrogate standards - The analyst should monitor the performance of the extraction, cleanup (when used), and determinative step, and the effectiveness of the method in dealing with each sample matrix, by spiking each sample, standard, and blank with one or two herbicide surrogates (e.g., herbicides that are not expected to be present in the sample) recommended to encompass the range of the temperature program used in this method. Deuterated analogs of analytes should not be used as surrogates in gas chromatographic analysis due to coelution problems.

5.15.1 The recommended surrogate is 2,4-Dichlorophenylacetic acid (DCAA).

5.15.2 Prepare a surrogate spiking solution by accurately weighing approximately 0.001 g of pure DCAA. Dissolve the DCAA in acetone, and dilute to volume in a 10-mL volumetric flask. Transfer the surrogate spiking solution to a vial with a PTFE-lined screw-cap, and store at room temperature. Addition of 50 µL of the surrogate spiking solution to 1 L of sample, prior to extraction, results in a final concentration in the extract of 0.5 mg/L.

5.16 pH Adjustment Solutions

5.16.1 Sodium hydroxide, NaOH, 6 N.

5.16.2 Sulfuric acid, H_2SO_4, 12 N.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1. One-Liter samples should be collected.

6.2 Extracts must be stored under refrigeration (4 C) and protected from light.

7.0 PROCEDURE

7.1 Extraction and hydrolysis of high concentration waste samples

7.1.1 Follow Method 3580, Waste Dilution, with the following exceptions:

7.1.1.1 Use diethyl ether as the dilution solvent.

7.1.1.2 Use acidified anhydrous sodium sulfate and acidified glass wool.

7.1.1.3 Spike the sample with surrogate(s) according to Sec. 5.15.

7.1.2 If the sample is to be analyzed for both herbicide esters and acids, then the sample extract must be hydrolyzed. In this case, transfer 1.0 mL (a smaller volume or a dilution may be required if herbicide concentrations are large) to a 250-mL Erlenmeyer flask with a ground-glass joint at the neck. Proceed to Sec. 7.2.3. If the analysis is for acid herbicides only, proceed to Sec. 7.5 for derivatization by diazomethane (if PFB derivatization is selected, reduce the volume of diethyl ether to 0.1 -0.5 mL as per Sec. 7.2 and then dilute to 4 mL with acetone).

7.2 Extraction and hydrolysis of soil, sediment, and other solid samples

Two extraction procedures are applicable to solid samples: ultrasonic extraction and shaker extraction. The same hydrolysis procedures (Sec. 7.2.3) apply to both types of extracts.

7.2.1 Ultrasonic extraction

7.2.1.1 Add 30 g (dry weight) of the well-mixed solid sample to a 400-mL thick-wall beaker. Adjust the pH to 2 with concentrated hydrochloric acid or acidify solids in the beaker with 85 mL of 0.1 M phosphate buffer (pH = 2.5) and thoroughly mix the contents with a glass stirring rod. Spike the sample with surrogate(s) (Sec. 5.15).

7.2.1.2 The ultrasonic extraction of solids must be optimized for each type of sample. In order for the ultrasonic extractor to efficiently extract solid samples, the sample must be free flowing when the solvent is added. Acidified anhydrous sodium sulfate should be added to clay type soils (normally 1:1), or any other solid that is not a free flowing sandy mixture, until a free flowing mixture is obtained.

7.2.1.3 Add 100 mL of methylene chloride/acetone (1:1 v/v) to the beaker. Perform ultrasonic extraction for 3 minutes, with output control knob set at 10 (full power) and with mode switch on Pulse (pulsing energy rather than continuous energy) and percent-duty cycle knob set at 50% (energy on 50% of time and off 50% of time). Allow the solids to settle. Transfer the organic layer into a 500-mL centrifuge bottle.

7.2.1.4 Ultrasonically extract the sample twice more using 100 mL of methylene chloride and the same ultrasonic conditions.

7.2.1.5 Combine the three organic extracts from the sample in the centrifuge bottle and centrifuge 10 minutes to settle the fine particles. Filter the combined extract through filter paper (Whatman #1, or equivalent) containing 7-10 g of acidified sodium sulfate into a 500-mL 24/40 Erlenmeyer flask. Add 10 g of acidified anhydrous sodium sulfate. Periodically, vigorously shake the extract and drying agent and allow the drying agent to remain in contact with the extract for a minimum of 2 hours. See NOTE in Sec. 7.3.6 that emphasizes the need for a dry extract prior to esterification.

7.2.1.6 Quantitatively transfer the contents of the flask to a 500-mL K-D flask with a 10-mL concentrator tube attached. Add boiling chips and attach the macro Snyder column. Evaporate the extract on the water bath to a volume of approximately 5 mL. Remove the flasks from the water bath and allow them to cool.

7.2.1.7 If hydrolysis or additional cleanup is not required and the sample is dry, proceed to Sec. 7.4.4. Otherwise, proceed to Sec. 7.2.3 for hydrolysis or Sec. 7.2.4 for cleanup.

7.2.2 Shaker extraction

7.2.2.1 Add 50 g (dry weight) of the well mixed, moist solid sample to a 500-mL wide-mouth Erlenmeyer flask. Adjust the pH to 2 with concentrated HCl and monitor the pH for 15 minutes with occasional stirring. If necessary, add additional HCl until the pH remains at 2. Spike the sample with surrogate(s) (Sec. 5.15).

7.2.2.2 Add 20 mL of acetone to the flask and mix the contents with the wrist shaker for 20 minutes. Add 80 mL diethyl ether to the same flask and shake again for 20 minutes. Decant the extract and measure the volume of solvent recovered.

7.2.2.3 Extract the sample twice more using 20 mL of acetone followed by 80 mL of diethyl ether. After addition of each solvent, the mixture should be shaken with the wrist shaker for 10 minutes and the acetone-ether extract decanted.

7.2.2.4 After the third extraction, the volume of extract recovered should be at least 75% of the volume of added solvent. If this is not the case, additional extractions may be necessary. Combine the extracts in a 2-L separatory funnel containing 250 mL of reagent water. If an emulsion forms, slowly add 5 g of acidified sodium sulfate (anhydrous) until the solvent-water mixture separates. A quantity of acidified sodium sulfate equal to the weight of the sample may be added, if necessary.

7.2.2.5 Check the pH of the extract. If it is not at or below pH 2, add more concentrated HCl until stabilized at the desired pH. Gently mix the contents of the separatory funnel for 1 minute and allow the layers to separate. Collect the aqueous phase in a clean beaker and the extract phase (top layer) in a 500-mL ground glass-

stoppered Erlenmeyer flask. Place the aqueous phase back into the separatory funnel and re-extract using 25 mL of diethyl ether. Allow the layers to separate and discard the aqueous layer. Combine the ether extracts in a 500-mL K-D flask.

7.2.2.6 If hydrolysis or additional cleanup is not required and the sample is dry, proceed to Sec. 7.4.4. Otherwise , proceed to Sec. 7.2.3 for hydrolysis or Sec. 7.2.4 for extract cleanup.

7.2.3 Hydrolysis of soil, sediment, or other solid sample extracts

Use this step only if herbicide esters in addition to herbicide acids are to be determined.

7.2.3.1 Add 5 mL of 37% aqueous potassium hydroxide and 30 mL of water to the extract. Add additional boiling chips to the K-D flask. Reflux the mixture on a water bath at 60 - 65°C until the hydrolysis step is completed (usually 1 - 2 hours). Remove the flasks from the water bath and cool to room temperature.

CAUTION: The presence of residual acetone will result in the formation of aldol condensation products which will cause GC interference.

7.2.3.2 Transfer the hydrolyzed aqueous solution to a 500-mL separatory funnel and extract the solution three times with 100-mL portions of methylene chloride. Discard the methylene chloride phase. At this point, the basic (aqueous) solution contains the herbicide salts.

7.2.3.3 Adjust the pH of the solution to <2 with cold (4°C) sulfuric acid (1:3) and extract once with 40 mL of diethyl ether and twice with 20-mL portions of ether. Combine the extracts and pour them through a pre-rinsed drying column containing 7 to 10 cm of acidified anhydrous sodium sulfate. Collect the dried extracts in a 500-mL Erlenmeyer flask (with a 24/40 joint) containing 10 g of acidified anhydrous sodium sulfate. Periodically, vigorously shake the extract and drying agent and allow the drying agent to remain in contact with the extract for a minimum of 2 hours. See NOTE in Sec. 7.3.6 that emphasizes the need for a dry extract prior to esterification. Quantitatively transfer the contents of the flask to a 500-mL Kuderna-Danish flask with a 10-mL concentrator tube attached when the extract is known to be dry.

7.2.3.4 Proceed to Sec. 7.4 for extract concentration. If additional cleanup is required, proceed to Sec. 7.2.4.

7.2.4 Cleanup of non-hydrolyzed herbicides

Use this step if additional cleanup of the non-hydrolyzed herbicides is required.

7.2.4.1 Partition the herbicides by extracting the methylene chloride from 7.2.1.7 (or diethyl ether from 7.2.3.4) three times with 15-mL portions of aqueous base prepared by carefully mixing 30 mL of reagent water into 15 mL of 37% aqueous potassium hydroxide. Discard the methylene chloride or ether phase. At this point the basic (aqueous) solution contains the herbicide salts.

7.2.4.2 Adjust the pH of the solution to <2 with cold (4°C) sulfuric acid (1:3) and extract once with 40 mL of diethyl ether and twice with 20-mL portions of ether. Combine the extracts and pour them through a pre-rinsed drying column containing 7-10 cm of

acidified anhydrous sodium sulfate. Collect the dried extracts in a 500-mL Erlenmeyer flask (with a 24/40 joint) containing 10 g of acidified anhydrous sodium sulfate. Periodically, vigorously shake the extract and drying agent and allow the drying agent to remain in contact with the extract for a minimum of 2 hours. See NOTE in Sec. 7.3.6 that emphasizes the need for a dry extract prior to esterification. Quantitatively transfer the contents of the flask to a 500-mL Kuderna-Danish flask with a 10-mL concentrator tube attached when the extract is known to be dry.

7.2.4.3 Proceed to Sec. 7.4 for extract concentration.

7.3 Preparation of aqueous samples

7.3.1 Using a graduated cylinder, transfer a 1-L sample aliquot to a 2-L separatory funnel. Spike the sample with surrogate compound(s) according to Sec. 5.15.

7.3.2 Add 250 g of NaCl to the sample, seal, and shake to dissolve the salt.

7.3.3 Use this step only if herbicide esters, in addition to herbicide acids, are to be determined

7.3.3.1 Add 17 mL of 6 N NaOH to the sample, seal, and shake. Check the pH of the sample with pH paper. If the sample does not have a pH greater than or equal to 12, adjust the pH by adding more 6 N NaOH. Let the sample sit at room temperature until the hydrolysis step is completed (usually 1 - 2 hours), shaking the separatory funnel and contents periodically.

7.3.3.2 Add 60 mL of methylene chloride to the sample bottle and rinse both the bottle and the graduated cylinder. Transfer the methylene chloride to the separatory funnel and extract the sample by vigorously shaking the funnel for 2 minutes, with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between the layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Discard the methylene chloride phase.

7.3.3.3 Add a second 60-mL volume of methylene chloride to the separatory funnel and repeat the extraction procedure a second time, discarding the methylene chloride layer. Perform a third extraction in the same manner.

7.3.4 Add 17 mL of cold (4 C) 12 N sulfuric acid to the sample (or hydrolyzed sample), seal, and shake to mix. Check the pH of the sample with pH paper. If the sample does not have a pH less than or equal to 2, adjust the pH by adding more acid.

7.3.5 Add 120 mL diethyl ether to the sample, seal, and extract the sample by vigorously shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum techniques to complete the phase separation depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Remove the aqueous phase to a 2-L Erlenmeyer flask and collect the ether phase in a 500-mL Erlenmeyer

flask containing approximately 10 g of acidified anhydrous sodium sulfate. Periodically, vigorously shake the extract and drying agent.

7.3.6 Return the aqueous phase to the separatory funnel, add 60 mL of diethyl ether to the sample, and repeat the extraction procedure a second time, combining the extracts in the 500-mL Erlenmeyer flask. Perform a third extraction with 60 mL diethyl ether in the same manner. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hours.

NOTE: The drying step is very critical to ensuring complete esterification. Any moisture remaining in the ether will result in low herbicide recoveries. The amount of sodium sulfate is adequate if some free flowing crystals are visible when swirling the flask. If all of the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate and again test by swirling. The 2 hour drying time is a minimum, however, the extracts may be held in contact with the sodium sulfate overnight.

7.3.7 Pour the dried extract through a funnel plugged with acid washed glass wool, and collect the extract in the K-D concentrator. Use a glass rod to crush any caked sodium sulfate during the transfer. Rinse the Erlenmeyer flask and funnel with 20 to 30 mL of diethyl ether to complete the quantitative transfer. Proceed to Sec. 7.4 for extract concentration.

7.4 Extract concentration

7.4.1 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of diethyl ether to the top of the column. Attach the solvent vapor recovery glassware (condenser and collection device) (Sec. 4.4.6) to the Snyder column of the K-D apparatus following manufacturer's instructions. Place the K-D apparatus on a hot water bath (15 - 20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10 - 20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.4.2 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1 - 2 mL of diethyl ether. The extract may be further concentrated by using either the micro Snyder column technique (Sec. 7.4.3) or nitrogen blowdown technique (Sec. 7.4.4).

7.4.3 Micro Snyder column technique

7.4.3.1 Add another one or two clean boiling chips to the concentrator tube and attach a two-ball micro Snyder column. Prewet the column by adding about 0.5 mL of diethyl ether to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column, rinse the flask and its lower

joints with about 0.2 mL of diethyl ether and add to the concentrator tube. Proceed to Sec. 7.4.5.

7.4.4 Nitrogen blowdown

7.4.4.1 Place the concentrator tube in a warm water bath (approximately 35 C) and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: Do not use plasticized tubing between the carbon trap and the sample.

7.4.4.2 The internal wall of the tube must be rinsed down several times with diethyl ether during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry. Proceed to Sec. 7.4.5.

7.4.5 Dilute the extract with 1 mL of isooctane and 0.5 mL of methanol. Dilute to a final volume of 4 mL with diethyl ether. The sample is now ready for methylation with diazomethane. If PFB derivation is being performed, dilute to 4 mL with acetone.

7.5 Esterification - For diazomethane derivatization proceed with Sec. 7.5.1. For PFB derivatization proceed with Sec. 7.5.2.

7.5.1 Diazomethane derivatization - Two methods may be used for the generation of diazomethane: the bubbler method (see Figure 1), Sec. 7.5.1.1, and the Diazald kit method, Sec. 7.5.1.2.

CAUTION: Diazomethane is a carcinogen and can explode under certain conditions.

The bubbler method is suggested when small batches of samples (10 - 15) require esterification. The bubbler method works well with samples that have low concentrations of herbicides (e.g., aqueous samples) and is safer to use than the Diazald kit procedure. The Diazald kit method is good for large quantities of samples needing esterification. The Diazald kit method is more effective than the bubbler method for soils or samples that may contain high concentrations of herbicides (e.g., samples such as soils that may result in yellow extracts following hydrolysis may be difficult to handle by the bubbler method).

The diazomethane derivatization procedures described below will react efficiently with all of the chlorinated herbicides described in this method and should be used only by experienced analysts, due to the potential hazards associated with its use.

The following precautions should be taken:

- Use a safety screen.
- Use mechanical pipetting aides.
- Do not heat above 90 C - EXPLOSION may result.
- Avoid grinding surfaces, ground-glass joints, sleeve bearings, and glass stirrers - EXPLOSION may result.

Store away from alkali metals - EXPLOSION may result.
Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips.

7.5.1.1 Bubbler method - Assemble the diazomethane bubbler (see Figure 1).

7.5.1.1.1 Add 5 mL of diethyl ether to the first test tube. Add 1 mL of diethyl ether, 1 mL of carbitol, 1.5 mL of 37% KOH, and 0.1 - 0.2 g of Diazald to the second test tube. Immediately place the exit tube into the concentrator tube containing the sample extract. Apply nitrogen flow (10 mL/min) to bubble diazomethane through the extract for 10 minutes or until the yellow color of diazomethane persists. The amount of Diazald used is sufficient for esterification of approximately three sample extracts. An additional 0.1 - 0.2 g of Diazald may be added (after the initial Diazald is consumed) to extend the generation of the diazomethane. There is sufficient KOH present in the original solution to perform a maximum of approximately 20 minutes of total esterification.

7.5.1.1.2 Remove the concentrator tube and seal it with a Neoprene or PTFE stopper. Store at room temperature in a hood for 20 minutes.

7.5.1.1.3 Destroy any unreacted diazomethane by adding 0.1 - 0.2 g of silicic acid to the concentrator tube. Allow to stand until the evolution of nitrogen gas has stopped. Adjust the sample volume to 10.0 mL with hexane. Stopper the concentrator tube or transfer 1 mL of sample to a GC vial, and store refrigerated if further processing will not be performed immediately. Analyze by gas chromatography.

7.5.1.1.4 Extracts should be stored at 4 C away from light. Preservation study results indicate that most analytes are stable for 28 days; however, it is recommended that the methylated extracts be analyzed immediately to minimize the trans-esterification and other potential reactions that may occur.

7.5.1.2 Diazald kit method - Instructions for preparing diazomethane are provided with the generator kit.

7.5.1.2.1 Add 2 mL of diazomethane solution and let the sample stand for 10 minutes with occasional swirling. The yellow color of diazomethane should be evident and should persist for this period.

7.5.1.2.2 Rinse the inside wall of the ampule with 700 µL of diethyl ether. Reduce the sample volume to approximately 2 mL to remove excess diazomethane by allowing the solvent to evaporate spontaneously at room temperature. Alternatively, 10 mg of silicic acid can be added to destroy the excess diazomethane.

7.5.1.2.3 Dilute the sample to 10.0 mL with hexane. Analyze by gas chromatography. It is recommended that the methylated extracts be analyzed immediately to minimize the trans-esterification and other potential reactions that may occur.

7.5.2 PFB derivatization

7.5.2.1 Add 30 µL of 10% K_2CO_3 and 200 µL of 3% PFBBr in acetone. Close the tube with a glass stopper and mix on a vortex mixer. Heat the tube at 60 C for 3 hours.

7.5.2.2 Evaporate the solution to 0.5 mL with a gentle stream of nitrogen. Add 2 mL of hexane and repeat evaporation just to dryness at ambient temperature.

7.5.2.3 Redissolve the residue in 2 mL of toluene:hexane (1:6) for column cleanup.

7.5.2.4 Top a silica column (Bond Elut™ or equivalent) with 0.5 cm of anhydrous sodium sulfate. Prewet the column with 5 mL hexane and let the solvent drain to the top of the adsorbent. Quantitatively transfer the reaction residue to the column with several rinsings of the toluene:hexane solution (total 2 - 3 mL).

7.5.2.5 Elute the column with sufficient toluene:hexane to collect 8 mL of eluent. Discard this fraction, which contains excess reagent.

7.5.2.6 Elute the column with toluene:hexane (9:1) to collect 8 mL of eluent containing PFB derivatives in a 10-mL volumetric flask. Dilute to 10 mL with hexane. Analyze by GC/ECD.

7.6 Gas chromatographic conditions (recommended)

7.6.1 Narrow-bore columns

Temperature program:	60 C to 300 C, at 4 C/min
Helium carrier flow:	30 cm/sec
Injection volume:	2 µL, splitless, 45 sec delay
Injector temperature:	250 C
Detector temperature:	320 C

7.6.2 Wide-bore columns

Temperature program:	0.5 minute at 150 C, 150 C to 270 C, at 5 C/min
Helium carrier flow:	7 mL/min
Injection volume:	1 µL
Injector temperature:	250 C
Detector temperature:	320 C

7.7 Calibration

The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures. Use Table 1 for guidance on selecting the lowest point on the calibration curve.

7.8 Gas chromatographic analysis of samples

7.8.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 µL of internal standard to the sample prior to injection.

7.8.2 Follow Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

7.8.3 An example of a chromatogram for a methylated chlorophenoxy herbicide is shown in Figure 2. Tables 2 and 3 present retention times for the target analytes after esterification, using the diazomethane derivatization procedure and the PFBBr derivatization procedure, respectively.

7.8.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.8.5 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes.

7.8.6 If calibration standards have been analyzed in the same manner as the samples (e.g., have undergone hydrolysis and esterification), then the calculation of concentration given in Method 8000 should be used. However, if calibration is performed using standards made from methyl ester compounds (compounds not esterified by application of this method), then the calculation of concentration must include a correction for the molecular weight of the methyl ester versus the acid herbicide.

7.8.7 If peak detection and identification are prevented due to interferences, further cleanup is required. Before using any cleanup procedure, the analyst must process a series of standards through the procedure to validate elution patterns and the absence of interferences from reagents.

7.9 GC/MS confirmation

7.9.1 GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. Refer to Method 8270 for the appropriate GC/MS operating conditions and analysis procedures.

7.9.2 When available, chemical ionization mass spectra may be employed to aid the qualitative identification process.

7.9.3 Should these MS procedures fail to provide satisfactory results, additional steps may be taken before reanalysis. These steps may include the use of alternate GC columns or additional cleanup.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation and/or sample introduction techniques can be found in Method 3500. Each laboratory should maintain a

formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000, Sec. 7.0 and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

8.4.1 Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a method blank should be analyzed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

8.4.2 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

8.4.3 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.4.4 See Method 8000, Sec. 8.0 for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0 for information on evaluating surrogate data and developing and updating surrogate limits.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the

laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 In single laboratory studies using organic-free reagent water and clay/still bottom samples, the mean recoveries presented in Tables 4 and 5 were obtained for diazomethane derivatization. The standard deviations of the percent recoveries of these measurements are also in Tables 4 and 5.

9.2 Table 6 presents relative recoveries of the target analytes obtained using the PFBBr derivatization procedure with spiked water samples.

10.0 REFERENCES

1. Goerlitz, D.G., Lamar, W.L., "Determination of Phenoxy Acid Herbicides in Water by Electron Capture and Microcoulometric Gas Chromatography", U.S. Geol. Survey Water Supply Paper 1967, 1817-C.

2. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis: Some Practical Aspects", J. Assoc. Off. Anal. Chem. (JAOAC), 1965, 48, 1037.

3. "Extraction and Cleanup Procedures for the Determination of Phenoxy Acid Herbicides in Sediment", U.S. Environmental Protection Agency, EPA Toxicant and Analysis Center, Bay St. Louis, MS, 1972.

4. Shore, F.L., Amick, E.N., Pan, S.T., "Single Laboratory Validation of EPA Method 8151 for the Analysis of Chlorinated Herbicides in Hazardous Waste", U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Office of Research and Development, Las Vegas, NV, 1985; EPA-60014-85-060.

5. Method 515.1, "Determination of Chlorinated Acids in Water by Gas Chromatography with an Electron Capture Detector", Revision 4.0, U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, Cincinnati, OH.

6. Gurka, D.F, Shore, F.L., Pan, S.T., "Single Laboratory Validation of EPA Method 8150 for Determination of Chlorinated Herbicides in Hazardous Waste", JAOAC, 69, 970, 1986.

TABLE 1

ESTIMATED METHOD DETECTION LIMITS FOR
DIAZOMETHANE DERIVATIZATION

Compound	Aqueous Samples GC/ECD Estimated Detection Limit[a] (µg/L)	Soil Samples GC/ECD Estimated Detection Limit[b] (µg/kg)	Soil Samples GC/MS Estimated Identification Limit[c] (ng)
Acifluorfen	0.096	-	-
Bentazon	0.2	-	-
Chloramben	0.093	4.0	1.7
2,4-D	0.2	0.11	1.25
Dalapon	1.3	0.12	0.5
2,4-DB	0.8	-	-
DCPA diacid[e]	0.02	-	-
Dicamba	0.081	-	-
3,5-Dichlorobenzoic acid	0.061	0.38	0.65
Dichloroprop	0.26	-	-
Dinoseb	0.19	-	-
5-Hydroxydicamba	0.04	-	-
MCPP	0.09[d]	66	0.43
MCPA	0.056[d]	43	0.3
4-Nitrophenol	0.13	0.34	0.44
Pentachlorophenol	0.076	0.16	1.3
Picloram	0.14	-	-
2,4,5-T	0.08	-	-
2,4,5-TP	0.075	0.28	4.5

[a] EDL = estimated detection limit; defined as either the MDL, or a concentration of analyte in a sample yielding a peak in the final extract with signal-to-noise ratio of approximately 5, whichever value is higher.

[b] Detection limits determined from standard solutions corrected back to 50-g samples, extracted and concentrated to 10 mL, with 5 µL injected. Chromatography using narrow-bore capillary column, 0.25 µm film, 5% phenyl/95% methyl silicone.

[c] The minimum amount of analyte to give a Finnigan INCOS FIT value of 800 as the methyl derivative vs. the spectrum obtained from 50 ng of the respective free acid herbicide.

[d] From Method 1658, "The Determination of Phenoxy-Acid Herbicides in Municipal and Industrial Wastewater", Methods for the Determination of Nonconventional Pesticides in Municipal and Industrial Wastewater, EPA-821-R-93-010-A, the USEPA Office of Water, Engineering and Analysis Division. MDLs were obtained with an electrolytic conductivity detector.

[e] DCPA monoacid and diacid metabolites included in method scope; DCPA diacid metabolite used for validation studies. DCPA is a dimethyl ester.

TABLE 2

RETENTION TIMES (MINUTES) OF METHYL DERIVATIVES OF CHLORINATED HERBICIDES

Analyte	Narrow Bore Columns		Wide-bore Columns	
	Primary[a] Column	Confirmation[a] Column	Primary[b] Column	Confirmation[b] Column
Dalapon	3.4	4.7	-	-
3,5-Dichlorobenzoic acid	18.6	17.7	-	-
4-Nitrophenol	18.6	20.5	-	-
DCAA (surrogate)	22.0	14.9	-	-
Dicamba	22.1	22.6	4.39	4.39
Dichloroprop	25.0	25.6	5.15	5.46
2,4-D	25.5	27.0	5.85	6.05
DBOB (internal std.)	27.5	27.6	-	-
Pentachlorophenol	28.3	27.0	-	-
Chloramben	29.7	32.8	-	-
2,4,5-TP	29.7	29.5	6.97	7.37
5-Hydroxydicamba	30.0	30.7	-	-
2,4,5-T	30.5	30.9	7.92	8.20
2,4-DB	32.2	32.2	8.74	9.02
Dinoseb	32.4	34.1	-	-
Bentazon	33.3	34.6	-	-
Picloram	34.4	37.5	-	-
DCPA diacid[c]	35.8	37.8	-	-
Acifluorfen	41.5	42.8	-	-
MCPP	-	-	4.24	4.55
MCPA	-	-	4.74	4.94

[a] Primary Column: 5% phenyl/95% methyl silicone
Confirmation Column: 14% cyanopropyl phenyl silicone
Temperature program: 60°C to 300°C, at 4°C/min
Helium carrier flow: 30 cm/sec
Injection volume: 2 µL, splitless, 45 sec delay
Injector temperature: 250°C
Detector temperature: 320°C

[b] Primary Column: DB-608
Confirmatory Column: 14% cyanopropyl phenyl silicone
Temperature program: 0.5 minute at 150°C, 150°C to 270°C, at 5°C/min
Helium carrier flow: 7 mL/min
Injection volume: 1 µL

[c] DCPA monoacid and diacid metabolites included in method scope; DCPA diacid metabolite used for validation studies. DCPA is a dimethyl ester.

TABLE 3

RETENTION TIMES (MINUTES) OF PFB DERIVATIVES OF CHLORINATED HERBICIDES

	Gas Chromatographic Column		
Compound	Thin-film DB-5[a]	SP-2250[b]	Thick-film DB-5[c]
Dalapon	10.41	12.94	13.54
MCPP	18.22	22.30	22.98
Dicamba	18.73	23.57	23.94
MCPA	18.88	23.95	24.18
Dichloroprop	19.10	24.10	24.70
2,4-D	19.84	26.33	26.20
Silvex	21.00	27.90	29.02
2,4,5-T	22.03	31.45	31.36
Dinoseb	22.11	28.93	31.57
2,4-DB	23.85	35.61	35.97

[a] DB-5 capillary column, 0.25 µm film thickness, 0.25 mm ID x 30 m long. Column programmed: 70°C for 1 minute, program 10°C/min. to 240°C, hold for 17 minutes.

[b] SP-2550 capillary column, 0.25 µm film thickness, 0.25 mm ID x 30 m long. Column programmed: 70°C for 1 minute, program 10°C/min. to 240°C, hold for 10 minutes.

[c] DB-5 capillary column, 1.0 µm film thickness, 0.32 mm ID x 30 m long. Column programmed: 70°C for 1 minute, program 10°C/min. to 240°C, hold for 10 minutes.

TABLE 4

ACCURACY AND PRECISION FOR DIAZOMETHANE DERIVATIZATION
ORGANIC-FREE REAGENT WATER MATRIX

Compound	Spike Concentration (µg/L)	Mean[a] Percent Recovery	Standard Deviation of Percent Recovery
Acifluorfen	0.2	121	15.7
Bentazon	1	120	16.8
Chloramben	0.4	111	14.4
2,4-D	1	131	27.5
Dalapon	10	100	20.0
2,4-DB	4	87	13.1
DCPA diacid[b]	0.2	74	9.7
Dicamba	0.4	135	32.4
3,5-Dichlorobenzoic acid	0.6	102	16.3
Dichloroprop	2	107	20.3
Dinoseb	0.4	42	14.3
5-Hydroxydicamba	0.2	103	16.5
4-Nitrophenol	1	131	23.6
Pentachlorophenol	0.04	130	31.2
Picloram	0.6	91	15.5
2,4,5-TP	0.4	117	16.4
2,4,5-T	0.2	134	30.8

[a] Mean percent recovery calculated from 7-8 determinations of spiked organic-free reagent water.

[b] DCPA monoacid and diacid metabolites included in method scope; DCPA diacid metabolite used for validation studies. DCPA is a dimethyl ester.

TABLE 5

ACCURACY AND PRECISION FOR DIAZOMETHANE DERIVATIZATION
CLAY MATRIX

Compound	Mean Percent Recovery[a]	Linear Concentration Range[b] (ng/g)	Percent Relative Standard Deviation[c] (n=20)
Dicamba	95.7	0.52 - 104	7.5
MCPP	98.3	620 - 61,800	3.4
MCPA	96.9	620 - 61,200	5.3
Dichloroprop	97.3	1.5 - 3,000	5.0
2,4-D	84.3	1.2 - 2,440	5.3
2,4,5-TP	94.5	0.42 - 828	5.7
2,4,5-T	83.1	0.42 - 828	7.3
2,4-DB	90.7	4.0 - 8,060	7.6
Dinoseb	93.7	0.82 - 1,620	8.7

[a] Mean percent recovery calculated from 10 determinations of spiked clay and clay/still bottom samples over the linear concentration range.

[b] Linear concentration range was determined using standard solutions and corrected to 50 g solid samples.

[c] Percent relative standard deviation was calculated using standard solutions, 10 samples high in the linear concentration range, and 10 samples low in the range.

TABLE 6

RELATIVE RECOVERIES OF PFB DERIVATIVES OF HERBICIDES*

Compound	Standard Concentration mg/L	Percent Recoveries 1	2	3	4	5	6	7	8	Mean
MCPP	5.1	95.6	88.8	97.1	100	95.5	97.2	98.1	98.2	96.3
Dicamba	3.9	91.4	99.2	100	92.7	84.0	93.0	91.1	90.1	92.7
MCPA	10.1	89.6	79.7	87.0	100	89.5	84.9	92.3	98.6	90.2
Dichloroprop	8.0	88.4	80.3	89.5	100	85.2	87.9	84.5	90.5	88.3
2,4-D	9.8	55.6	90.3	100	65.9	58.3	61.6	60.8	67.6	70.0
Silvex	10.4	95.3	85.8	91.5	100	91.3	95.0	91.1	96.0	93.3
2,4,5-T	12.8	78.6	65.6	69.2	100	81.6	90.1	84.3	98.5	83.5
2,4-DB	20.1	99.8	96.3	100	88.4	97.1	92.4	91.6	91.6	95.0
Mean		86.8	85.7	91.8	93.4	85.3	89.0	87.1	91.4	

*Percent recovery determinations made using eight spiked water samples.

FIGURE 1
DIAZOMETHANE GENERATOR

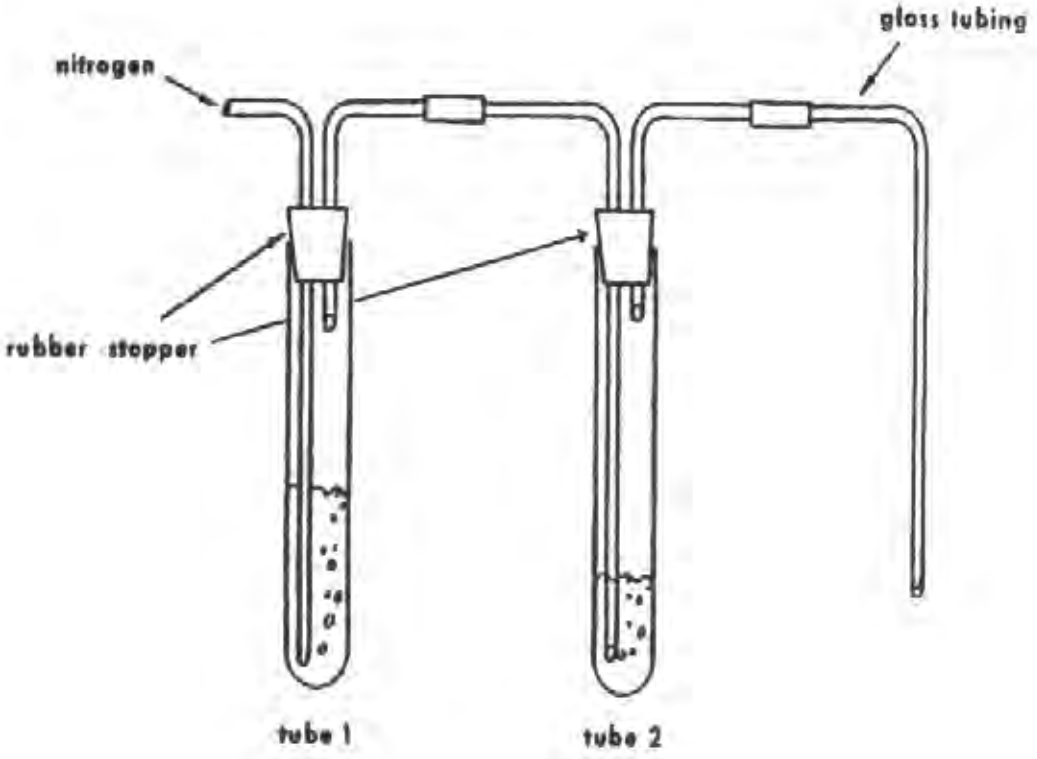
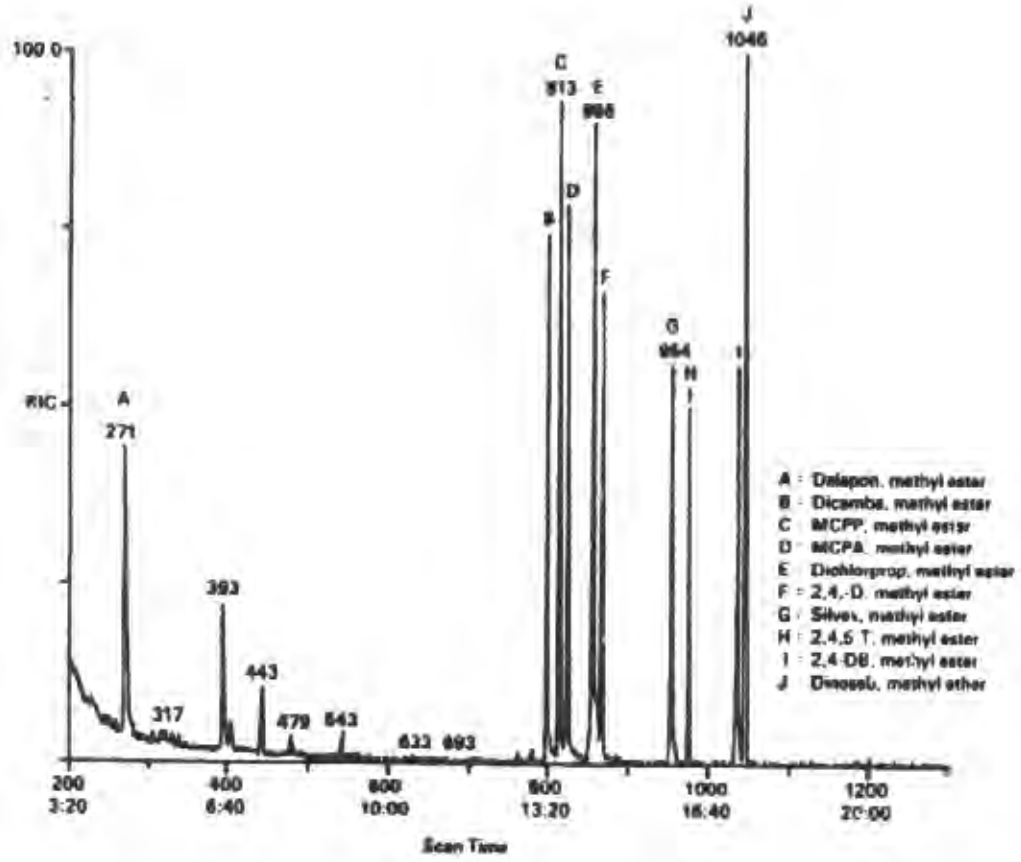
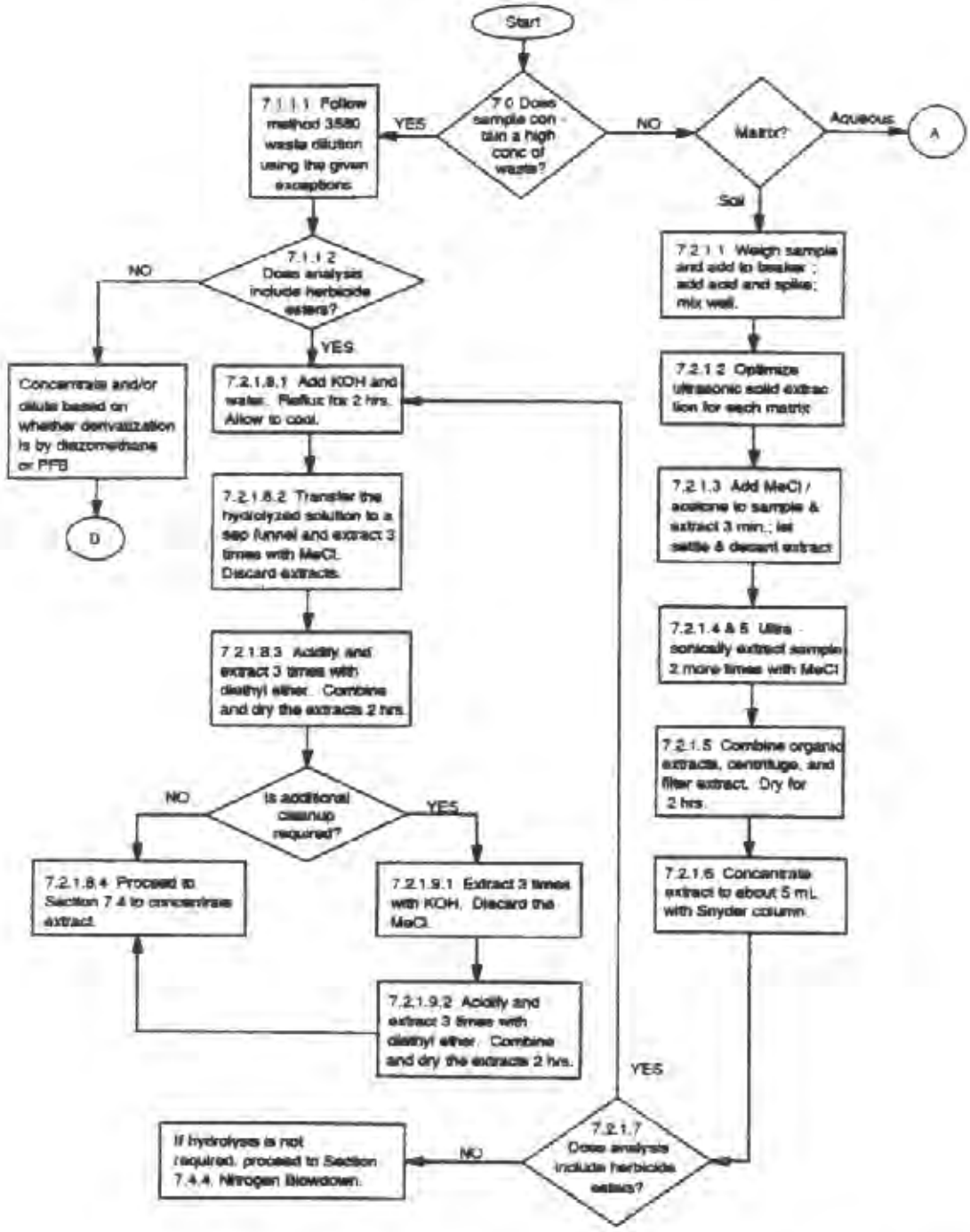


FIGURE 2
CHROMATOGRAM OF METHYL ESTERS OF CHLOROPHENOXYACIDS

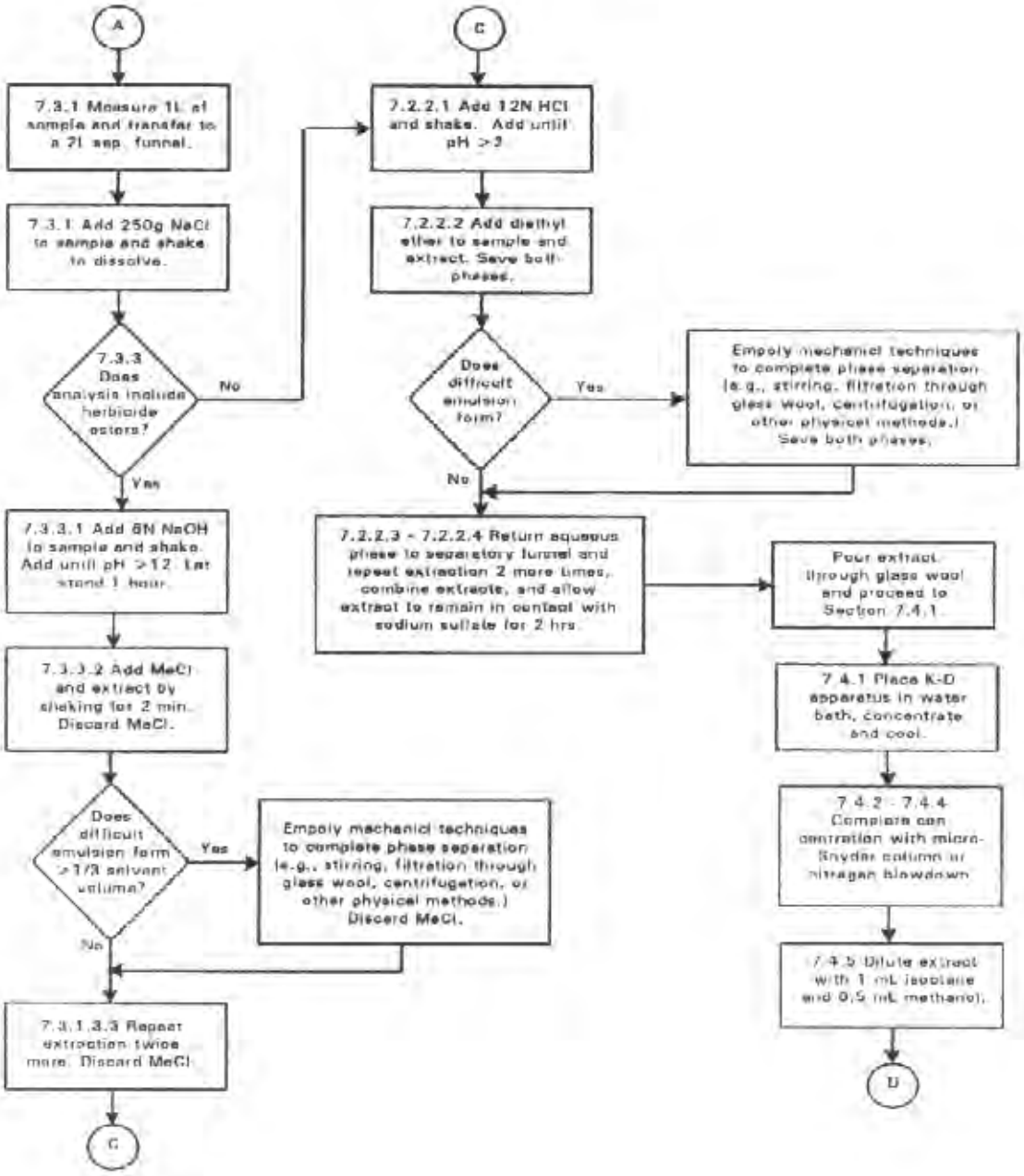


CHLORINATED HERBICIDES BY GC USING METHYLATION OR PENTAFLUOROBENZYLATION DERIVATIZATION

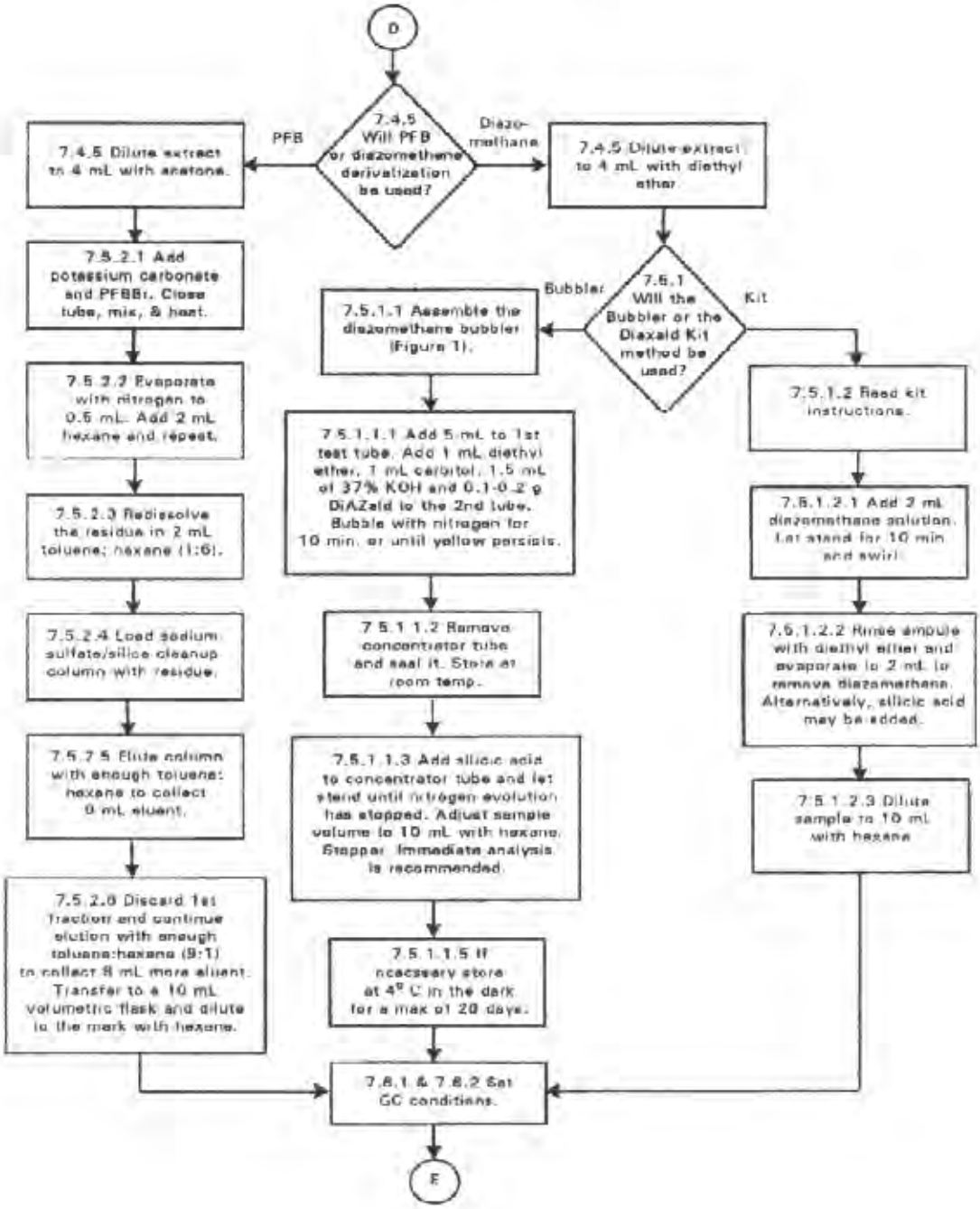
Extraction/Hydrolysis of Waste and Soil Samples



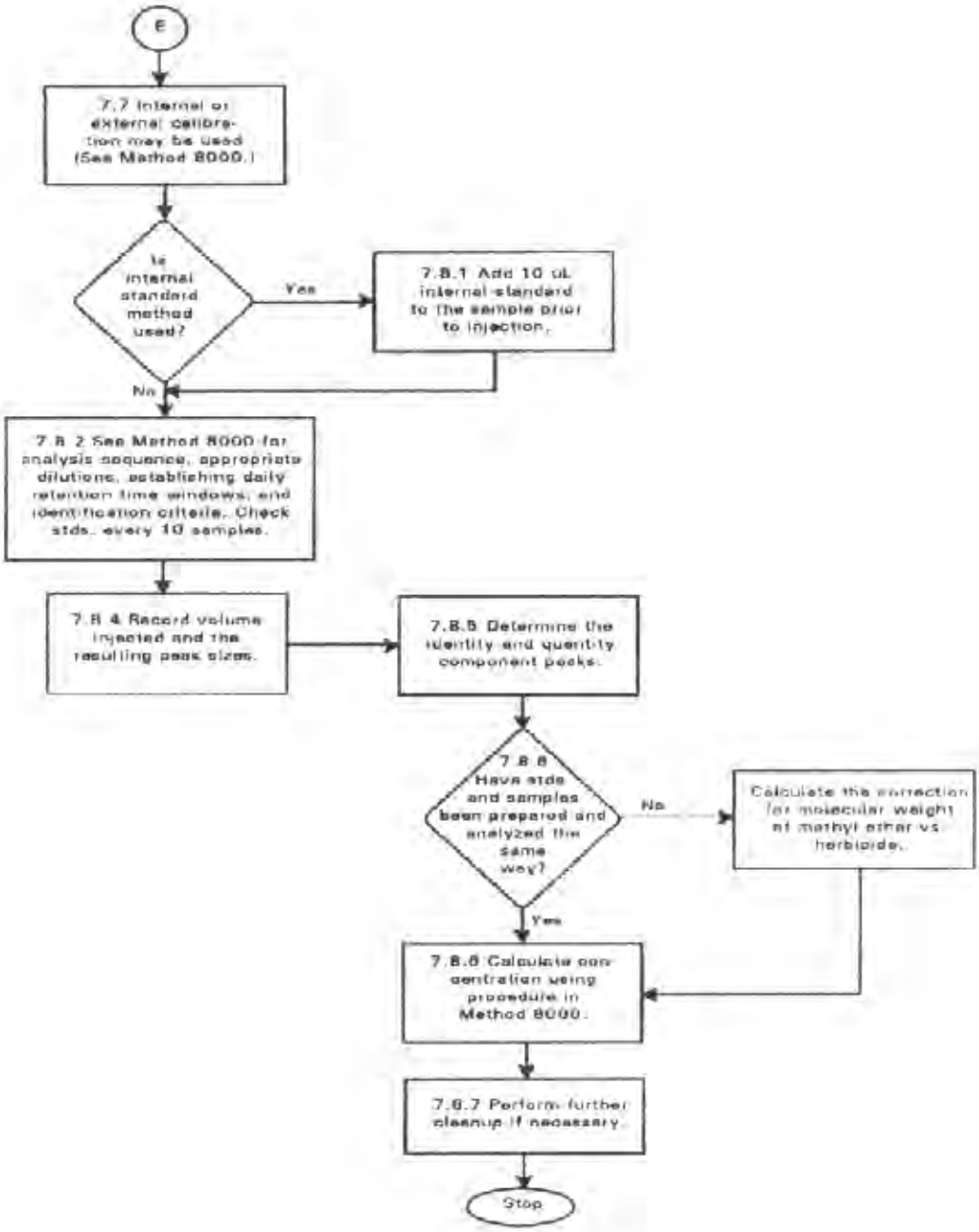
Extraction/Hydrolysis of Aqueous Samples and Extract Concentration



Extract Derivatization



Analysis by Gas Chromatography



Analytical Methods

Cyanide

9010B/9013/9014

METHOD 9010B

TOTAL AND AMENABLE CYANIDE: DISTILLATION

1.0 SCOPE AND APPLICATION

1.1 Method 9010 is reflux-distillation procedure used to extract soluble cyanide salts and many insoluble cyanide complexes from wastes and leachates. It is based on the decomposition of nearly all cyanides by a reflux distillation procedure using a strong acid and a magnesium catalyst. Cyanide, in the form of hydrocyanic acid (HCN) is purged from the sample and captured into an alkaline scrubber solution. The concentration of cyanide in the scrubber solution is then determined by Method 9014 or Method 9213. Method 9010 may be used as a reflux-distillation procedure for both total cyanide and cyanide amenable to chlorination. The "reactive" cyanide content of a waste, that is, the cyanide content that could generate toxic fumes when exposed to mild acidic conditions, is not determined by this method. Refer to Chapter Seven of SW-846 for the additional information on reactive cyanide.

1.2 This method was designed to address the problem of "trace" analyses (<1000 ppm). The method may also be used for "minor" (1000 ppm - 10,000 ppm) and "major" (>10,000 ppm) analyses by adapting the appropriate sample dilution. However, the amount of sodium hydroxide in the standards and the sample analyzed must be the same.

2.0 SUMMARY OF METHOD

2.1 The cyanide, as hydrocyanic acid (HCN), is released from samples containing cyanide by means of a reflux-distillation operation under acidic conditions and absorbed in a scrubber containing sodium hydroxide solution. The cyanide concentration in the absorbing solution is then determined colorimetrically or titrametrically by Method 9014 or by ion-selective electrode by Method 9213.

3.0 INTERFERENCES

3.1 Interferences are eliminated or reduced by using the distillation procedure. Chlorine and sulfide are interferences in Method 9010.

3.2 Oxidizing agents such as chlorine decompose most cyanides. Chlorine interferences can be removed by adding an excess of sodium arsenite to the waste prior to preservation and storage of the sample to reduce the chlorine to chloride which does not interfere.

3.3 Sulfide interference can be removed by adding an excess of bismuth nitrate to the waste (to precipitate the sulfide) before distillation. Samples that contain hydrogen sulfide, metal sulfides, or other compounds that may produce hydrogen sulfide during the distillation should be treated by the addition of bismuth nitrate.

3.4 High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation, nitrate and nitrite will form nitrous acid, which will react with some organic compounds to form oximes. These compounds once formed will decompose under test conditions to generate HCN. The possibility of interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid just before distillation. Nitrate and nitrite are interferences when present at levels higher than 10 mg/L and in conjunction with certain organic compounds.

3.5 Thiocyanate is reported to be an interference when present at very high levels. Levels of 10 mg/L were not found to interfere.

3.6 Fatty acids, detergents, surfactants, and other compounds may cause foaming during the distillation when they are present in high concentrations and may make the endpoint for the titrimetric determination difficult to detect. Refer to Sec. 6.8 for an extraction procedure to eliminate this interference.

4.0 APPARATUS AND MATERIALS

4.1 Reflux distillation apparatus such as shown in Figure 1 or Figure 2. The boiling flask should be of one liter size with inlet tube and provision for condenser. The gas scrubber may be a 270-mL Fisher-Milligan scrubber (Fisher, Part No. 07-513) or equivalent. The reflux apparatus may be a Wheaton 377160 distillation unit or equivalent.

4.2 Hot plate stirrer/heating mantle.

4.3 pH meter.

4.4 Amber light.

4.5 Vacuum source.

4.6 Refrigerator.

4.7 Erlenmeyer flask - 500 mL.

4.8 KI starch paper.

4.9 Class A volumetric flasks-1000,250, and 100 mL.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Reagents for sample collection, preservation, and handling.

5.3.1 Sodium arsenite (0.1N), $NaAsO_2$. Dissolve 3.2 g $NaAsO_2$ in 250 mL water.

5.3.2 Ascorbic acid, $C_6H_8O_6$.

5.3.3 Sodium hydroxide solution (50%), NaOH. Commercially available.

5.3.4 Acetic acid (1.6M) CH_3COOH. Dilute one part of concentrated acetic acid with 9 parts of water.

5.3.5 2,2,4-Trimethylpentane, C_8H_{18}.

5.3.6 Hexane, C_6H_{14}.

5.3.7 Chloroform, $CHCl_3$.

5.4 Reagents for cyanides amenable to chlorination

5.4.1 Calcium hypochlorite solution (0.35M), $Ca(OCl)_2$. Combine 5 g of calcium hypochlorite and 100 mL of water. Shake before using.

5.4.2 Sodium hydroxide solution (1.25N), NaOH. Dissolve 50 g of NaOH in 1 liter of water.

5.4.3 Sodium arsenite (0.1N). See Section 5.3.1.

5.4.4 Potassium iodide starch paper.

5.5 Reagents for distillation

5.5.1 Sodium hydroxide (1.25N). See Section 5.4.2.

5.5.2 Bismuth nitrate (0.062M), $Bi(NO_3)_3 \cdot 5H_2O$. Dissolve 30 g $Bi(NO_3)_3 \cdot 5H_2O$ in 100 mL of water. While stirring, add 250 mL of glacial acetic acid, CH_3COOH. Stir until dissolved and dilute to 1 liter with water.

5.5.3 Sulfamic acid (0.4N), H_2NSO_3H. Dissolve 40 g H_2NSO_3H in 1 liter of water.

5.5.4 Sulfuric acid (18N), H_2SO_4. Slowly and carefully add 500 mL of concentrated H_2SO_4 to 500 mL of water.

5.5.5 Magnesium chloride solution (2.5M), $MgCl_2 \cdot 6H_2O$. Dissolve 510 g of $MgCl_2 \cdot 6H_2O$ in 1 liter of water.

5.5.6 Lead acetate paper.

5.5.7 Stock potassium cyanide solutions - Refer to Method 9014 for the preparation of stock cyanide solutions and calibration standards.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine.

6.2 Samples should be collected in plastic or glass containers. All containers must be thoroughly cleaned and rinsed.

6.3 Oxidizing agents such as chlorine decompose most cyanides. To determine whether oxidizing agents are present, test a drop of the sample with potassium iodide-starch test paper. A blue color indicates the need for treatment. Add 0.1N sodium arsenite solution a few mL at a time until a drop of sample produces no color on the indicator paper. Add an additional 5 mL of sodium arsenite solution for each liter of sample. Ascorbic acid can be used as an alternative although it is not as effective as arsenite. Add a few crystals of ascorbic acid at a time until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume.

6.4 Aqueous samples must be preserved by adding 50% sodium hydroxide until the pH is greater than or equal to 12 at the time of collection.

6.5 Samples should be chilled to 4°C.

6.6 When properly preserved, cyanide samples can be stored for up to 14 days prior to sample preparation steps.

6.7 Solid and oily wastes may be extracted prior to analysis by method 9013. It uses a dilute NaOH solution (pH = 12) as the extractant. This yields extractable cyanide.

6.8 If fatty acids, detergents, and surfactants are a problem, they may be extracted using the following procedure. Acidify the sample with acetic acid (1.6M) to pH 6.0 to 7.0.

CAUTION: This procedure can produce lethal HCN gas.

Extract with isooctane, hexane, or chloroform (preference in order named) with solvent volume equal to 20% of the sample volume. One extraction is usually adequate to reduce the compounds below the interference level. Avoid multiple extractions or a long contact time at low pH in order to keep the loss of HCN at a minimum. When the extraction is completed, immediately raise the pH of the sample to above 12 with 50% NaOH solution.

7.0 PROCEDURE

7.1 Pretreatment for cyanides amenable to chlorination

7.1.1 This test must be performed under amber light. $K_3[Fe(CN)_6]$ may decompose under UV light and hence will test positive for cyanide amenable to chlorination if exposed to fluorescent lighting or sunlight. Two identical sample aliquots are required to determine cyanides amenable to chlorination.

7.1.2 To one 500 mL sample or to a sample diluted to 500 mL, add calcium hypochlorite solution dropwise while agitating and maintaining the pH between 11 and 12 with 1.25N sodium hydroxide until an excess of chlorine is present as indicated by KI-starch paper turning blue. The sample will be subjected to alkaline chlorination by this step.

CAUTION: The initial reaction product of alkaline chlorination is the very toxic gas cyanogen chloride; therefore, it is necessary that this reaction be performed in a hood.

7.1.3 Test for excess chlorine with KI-starch paper and maintain this excess for one hour with continuous agitation. A distinct blue color on the test paper indicates a sufficient chlorine level. If necessary, add additional calcium hypochlorite solution.

7.1.4 After one hour, add 1 mL portions of 0.1N sodium arsenite until KI-starch paper shows no residual chlorine. Add 5 mL of excess sodium arsenite to ensure the presence of excess reducing agent.

7.1.5 Analyze the total cyanide concentration of both the chlorinated and the unchlorinated samples by Method 9014 or 9213. The difference between the total cyanide concentration in the chlorinated and unchlorinated samples is equal to the cyanide amenable to chlorination.

7.2 Distillation Procedure

7.2.1 Place 500 mL of sample, or sample diluted to 500 mL in the one liter boiling flask. Pipet 50 mL of 1.25N sodium hydroxide into the gas scrubber. If the apparatus in Figure 1 is used, add water until the spiral is covered. Connect the boiling flask, condenser, gas scrubber and vacuum trap.

7.2.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately two bubbles of air per second enter the boiling flask through the air inlet tube.

7.2.3 If samples are known or suspected to contain sulfide, add 50 mL of 0.062M bismuth nitrate solution through the air inlet tube. Mix for three minutes. Use lead acetate paper to check the sample for the presence of sulfide. A positive test is indicated by a black color on the paper.

7.2.4 If samples are known or suspected to contain nitrate or nitrite, or if bismuth nitrate was added to the sample, add 50 mL of 0.4N sulfamic acid solution through the air inlet tube. Mix for three minutes.

Note: Excessive use of sulfamic acid could create method bias.

7.2.5 Slowly add 50 mL of 18N sulfuric acid through the air inlet tube. Rinse the tube with water and allow the airflow to mix the flask contents for three minutes. Add 20 mL of 2.5M magnesium chloride through the air inlet and wash the inlet tube with a stream of water.

7.2.6 Heat the solution to boiling. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, and closing the vacuum source, disconnect the gas scrubber.

7.2.7 Transfer the solution from the scrubber into a 250-mL volumetric flask. Rinse the scrubber into the volumetric flask. Dilute to volume with water.

7.2.8 Proceed to the cyanide determinative methods given in Methods 9014 or 9213. If the distillates are not analyzed immediately, they should be stored at 4°C in tightly sealed flasks.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one reagent blank per analytical batch or one in every 20 samples to determine if contamination or any memory effects are occurring.

8.3 Analyze check standards with every analytical batch of samples. If the standards are not within 15% of the expected value, then the samples must be reanalyzed.

8.4 Run one replicate sample for every 20 samples. A replicate sample is a sample brought through the entire sample preparation and analytical process. The CV of the replicates should be 20% or less. If this criterion is not met, the samples should be reanalyzed.

8.5 Run one matrix spiked sample every 20 samples to check the efficiency of sample distillation by adding cyanide from the working standard or intermediate standard to 500 mL of sample to ensure a concentration of approximately 40 µg/L. The matrix spiked sample is brought through the entire sample preparation and analytical process.

8.6 It is recommended that at least two standards (a high and a low) be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. If distilled standards do not agree within ± 10% of the undistilled standards, the analyst should find the cause of the apparent error before proceeding.

8.7 The method of standard additions shall be used for the analysis of all samples that suffer from matrix interferences such as samples which contain sulfides.

9.0 METHOD PERFORMANCE

9.1 The titration procedure using silver nitrate is used for measuring concentrations of cyanide exceeding 0.1 mg/L. The colorimetric procedure is used for concentrations below 1 mg/L of cyanide and is sensitive to about 0.02 mg/L.

9.2 EPA Method 335.2 (sample distillation with titration) reports that in a single laboratory using mixed industrial and domestic waste samples at concentrations of 0.06 to 0.62 mg/L CN^-, the standard deviations for precision were ± 0.005 to ± 0.094, respectively. In a single laboratory using mixed industrial and domestic waste samples at concentrations of 0.28 and 0.62 mg/L CN^-, recoveries (accuracy) were 85% and 102%, respectively.

9.3 In two additional studies using surface water, ground water, and landfill leachate samples, the titration procedure was further evaluated. The concentration range used in these studies was 0.5 to 10 mg/L cyanide. The detection limit was found to be 0.2 mg/L for both total and amenable cyanide determinations. The precision (CV) was 6.9 and 2.6 for total cyanide determinations and 18.6 and 9.1 for amenable cyanide determinations. The mean recoveries were 94% and 98.9% for total cyanide, and 86.7% and 97.4% for amenable cyanide.

10.0 REFERENCES

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FIGURE 1.
APPARATUS FOR CYANIDE DISTILLATION

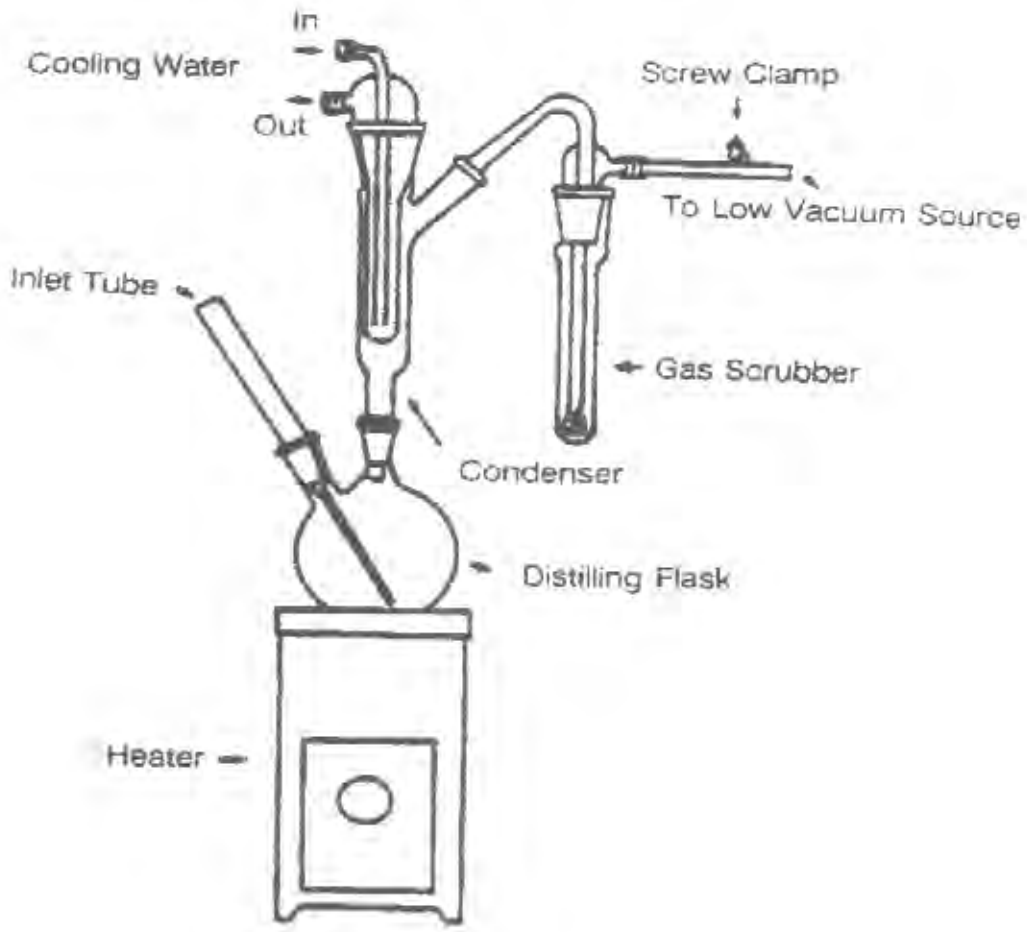
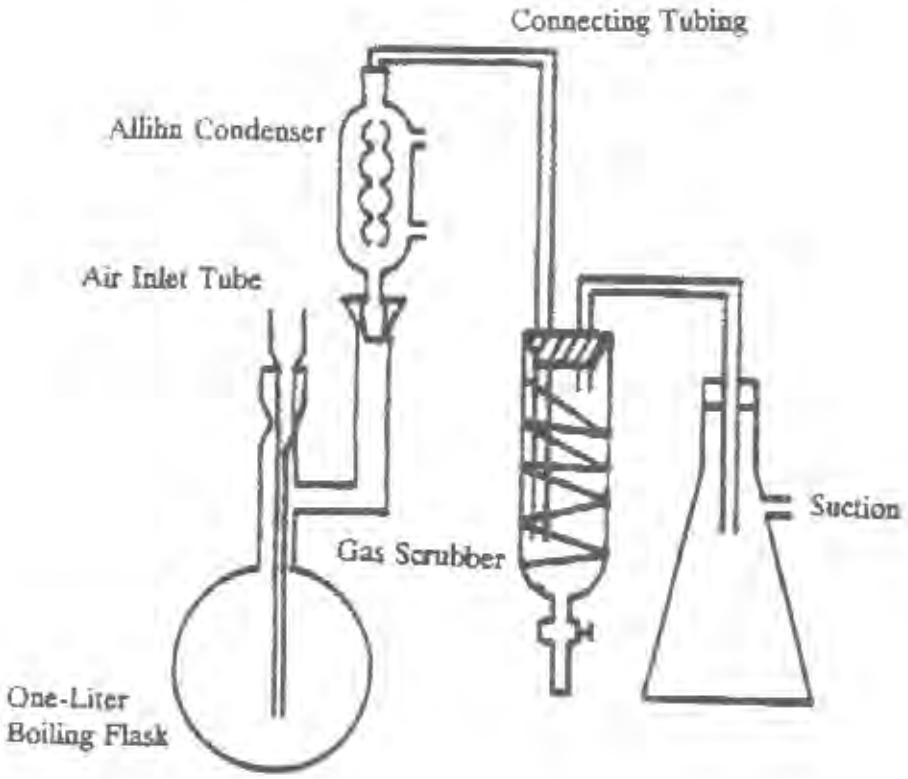
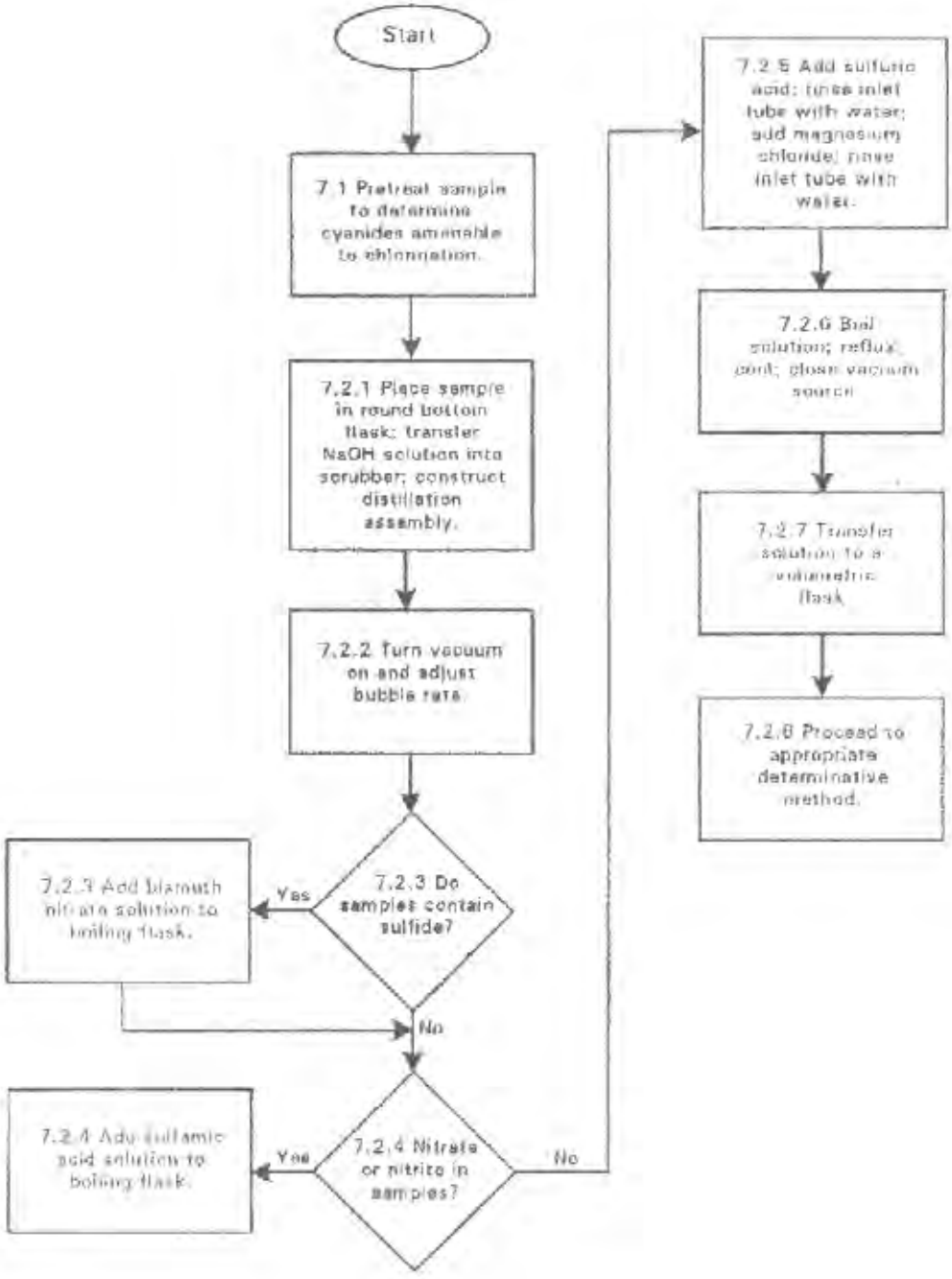


FIGURE 2
APPARATUS FOR CYANIDE DISTILLATION



TOTAL AND AMENABLE CYANIDE DISTILLATION



METHOD 9013
(APPENDIX TO METHOD 9010)

CYANIDE EXTRACTION PROCEDURE FOR SOLIDS AND OILS

1.0 SCOPE AND APPLICATION

1.1 The extraction procedure described in this method is designed for the extraction of soluble cyanides from solid and oil wastes. The method is applicable to oil, solid, and multiphasic samples. This method is not applicable to samples containing insoluble cyanide compounds.

2.0 SUMMARY OF METHOD

2.1 If the waste sample contains so much solid, or solids of such a size as to interfere with agitation and homogenization of the sample mixture in the distillation flask, or so much oil or grease as to interfere with the formation of a homogeneous emulsion, the sample may be extracted with water at pH 10 or greater, and the extract distilled and analyzed by Method 9010. Samples that contain free water are filtered and separated into an aqueous component and a combined oil and solid component. The nonaqueous component may then be extracted, and an aliquot of the extract combined with an aliquot of the filtrate in proportion to the composition of the sample. Alternatively, the components may be analyzed separately, and cyanide levels reported for each component. However, if the sample solids are known to contain sufficient levels of cyanide (about 50 µg/g) as to be well above the limit of detection, the extraction step may be deleted and the solids analyzed directly by Method 9010. This can be accomplished by diluting a small aliquot of the waste solid (1-10 g) in 500 mL water in the distillation flask and suspending the slurry during distillation with a magnetic stir-bar.

3.0 INTERFERENCES

3.1 Potential interferences that may be encountered during analysis are discussed in Method 9010.

4.0 APPARATUS AND MATERIALS

4.1 Extractor - Any suitable device that sufficiently agitates a sealed container of one liter volume or greater. For the purpose of this analysis, agitation is sufficient when:

1. All sample surfaces are continuously brought into contact with extraction fluid, and

2. The agitation prevents stratification of the sample and fluid.

4.2 Buchner funnel apparatus

4.2.1 Buchner funnel - 500-mL capacity, with 1-liter vacuum filtration flask.

4.2.2 Glass wool - Suitable for filtering, 0.8 µm diameter such as Corning Pyrex 3950.

4.2.3 Vacuum source - Preferably a water driven aspirator. A valve or stopcock to release vacuum is required.

4.3 Top loading balance - capable of weighing 0.1 g.

4.4 Separatory funnels - 500 mL.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Sodium hydroxide (50% w/v), NaOH. Commercially available.

5.4 n-Hexane, C_6H_{14}.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a plan that addresses the considerations discussed in Chapter 4 of this manual. See Section 6.0 of Method 9010 for additional guidance.

7.0 PROCEDURE

7.1 If the waste does not contain any free aqueous phase, go to Step 7.5. If the sample is a homogeneous fluid or slurry that does not separate or settle in the distillation flask when using a teflon coated magnetic stirring bar but mixes so that the solids are entirely suspended, then the sample may be analyzed by Method 9010 without an extraction step.

7.2 Assemble Buchner funnel apparatus. Unroll glass filtering fiber and fold the fiber over itself several times to make a pad about 1 cm thick when lightly compressed. Cut the pad to fit the Buchner funnel. Weigh the pad, then place it in the funnel. Turn the aspirator on and wet the pad with a known amount of water.

7.3 Transfer the sample to the Buchner funnel in small aliquots, first decanting the fluid. Rinse the sample container with known amounts of water and add the rinses to the Buchner funnel. When no free water remains in the funnel, slowly open the stopcock to allow air to enter the vacuum flask. A small amount of sediment may have passed through the glass fiber pad. This will not interfere with the analysis.

7.4 Transfer the solid and the glass fiber pad to a tared weighing dish. Since most greases and oils will not pass through the fiber pad, solids, oils, and greases will be extracted together. If the filtrate includes an oil phase, transfer the filtrate to a separatory funnel. Collect and measure the volume of the aqueous phase. Transfer the oil phase to the weighing dish with the solid.

7.5 Weigh the dish containing solid, oil (if any), and filter pad. Subtract the weight of the dry filter pad. Calculate the net volume of water present in the original sample by subtracting the total volume of rinses used from the measured volume of the filtrate.

7.6 Place the following in a 1-liter wide-mouthed bottle:

500 mL water
5 mL 50% w/v NaOH
50 mL n-Hexane (if a heavy grease is present)

If the weight of the solids (Step 7.5) is greater than 25 g, weigh out a representative aliquot of 25 g and add it to the bottle; otherwise add all of the solids. Cap the bottle.

7.7 The pH of the extract must be maintained above 10 throughout the extraction step and subsequent filtration. Since some samples may release acid, the pH must be monitored as follows. Shake the extraction bottle and after one minute, check the pH. If the pH is below 12, add 50% NaOH in 5 mL increments until it is at least 12. Recap the bottle, and repeat the procedure until the pH does not drop.

7.8 Place the bottle or bottles in the tumbler, making sure there is enough foam insulation to cushion the bottle. Turn the tumbler on and allow the extraction to run for about 16 hours.

7.9 Prepare a Buchner funnel apparatus as in Step 7.2 with a glass fiber pad filter.

7.10 Decant the extract to the Buchner funnel. Full recovery of the extract is not necessary.

7.11 If the extract contains an oil phase, separate the aqueous phase using a separatory funnel. Neither the separation nor the filtration are critical, but are necessary to be able to measure the volume of the aliquot of the aqueous extract analyzed. Small amounts of suspended solids and oil emulsions will not interfere.

7.12 At this point, an aliquot of the filtrate of the original sample may be combined with an aliquot of the extract in a proportion representative of the sample. Alternatively, they may be distilled and analyzed separately and concentrations given for each phase. This is described by the following equation:

$$\frac{\text{Liquid Sample Aliquot(mL)}}{\text{Extract Aliquot(mL)}} - \frac{\text{Solid Extracted(g)}^a}{\text{Total Solid(g)}^b} \cdot \frac{\text{Total Sample Filtrate(mL)}^c}{\text{Total Extraction Fluid(mL)}^d}$$

[4]From Step 7.6. Weight of solid sample used for extraction.

[5]From Step 7.5. Weight of solids and oil phase with the dry weight of filter and tared dish subtracted.

[6]Includes volume of all rinses added to the filtrate (Steps 7.2 and 7.3).

[7]500 mL water plus total volume of NaOH solution. Does not include hexane, which is subsequently removed (Step 7.11).

Alternatively, the aliquots may be distilled and analyzed separately, concentrations for each phase reported separately, and the amounts of each phase present in the sample reported separately.

8.0 QUALITY CONTROL

8.1 Refer to Method 9010.

9.0 METHOD PERFORMANCE

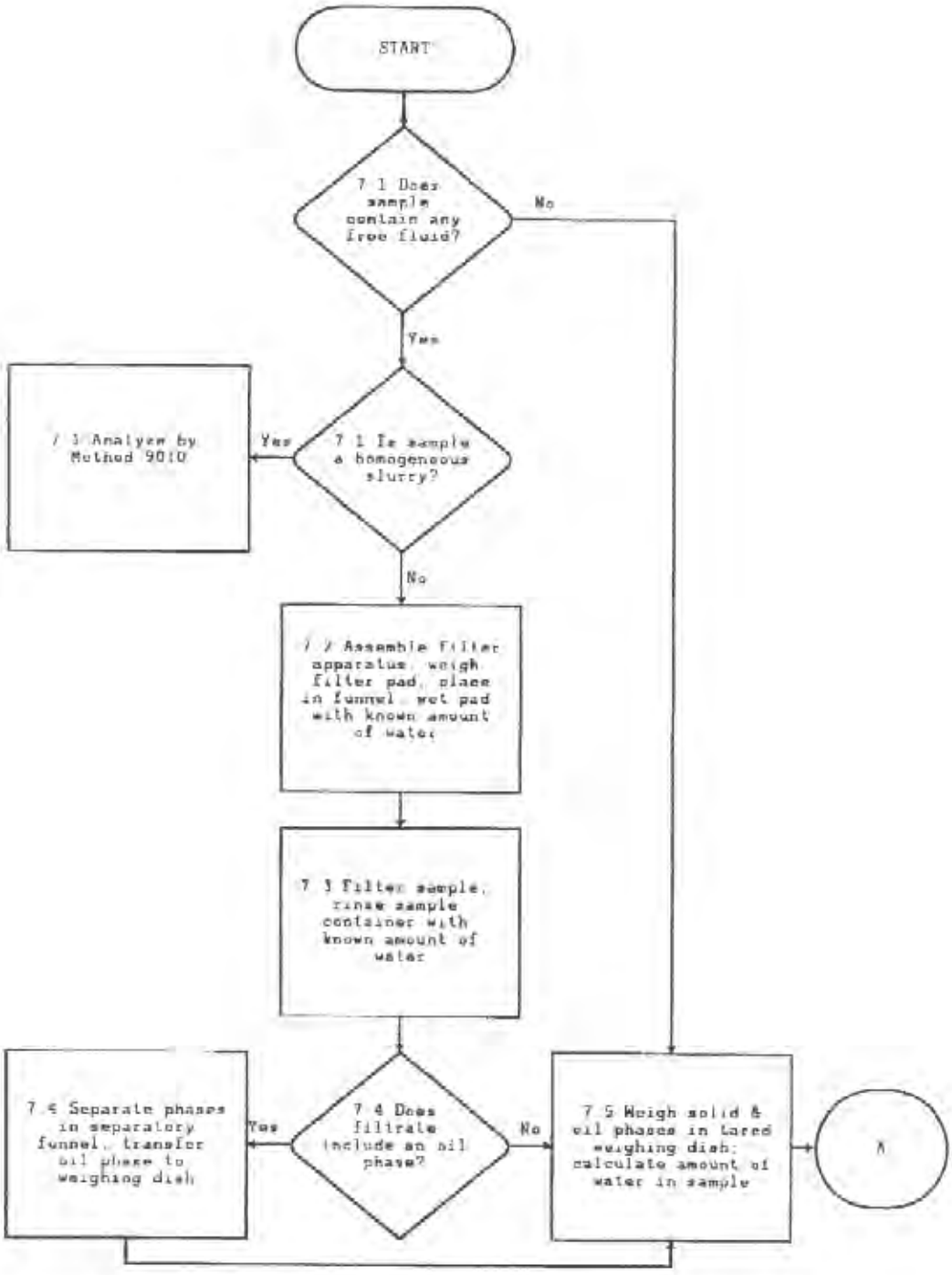
9.1 In a single laboratory study, recoveries of 60 to 90% are reported for solids and 88 to 92% for oils. The reported CVs are less than 13.

10.0 REFERENCES

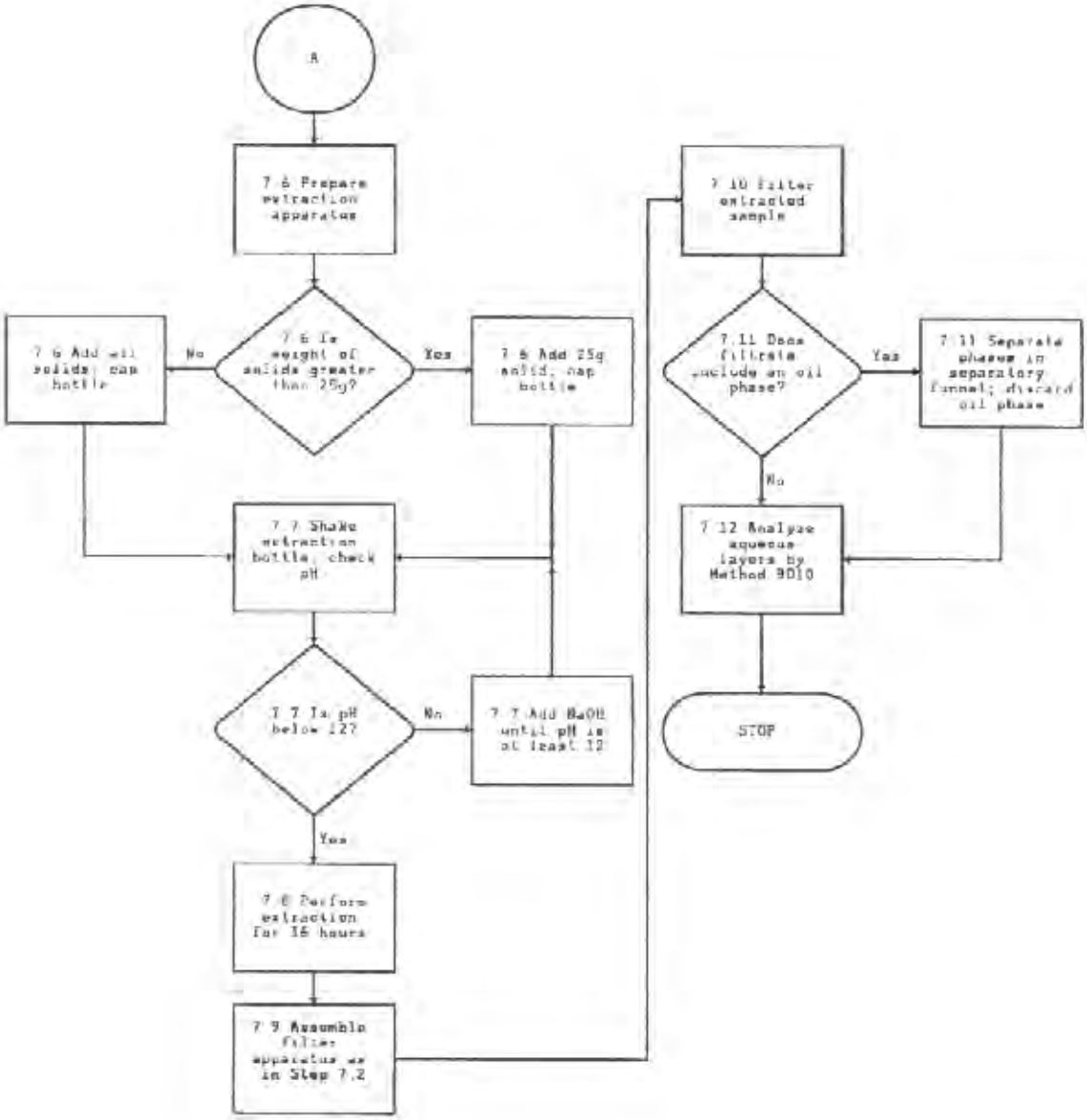
10.1 Refer to Method 9010.

METHOD 9013
(APPENDIX TO METHOD 9010)

CYANIDE EXTRACTION PROCEDURE FOR SOLIDS AND OILS



CYANIDE EXTRACTION PROCEDURE FOR SOLIDS AND OILS (CONTINUED)



METHOD 9014

TITRIMETRIC AND MANUAL SPECTROPHOTOMETRIC DETERMINATIVE METHODS FOR CYANIDE

1.0 SCOPE AND APPLICATION

1.1 This method can be used for measuring free (non-complexed) cyanide and hydrocyanic acid in drinking water, natural surface waters, domestic and industrial wastewaters, and in soil extracts. This method may also be used as a determinative step for quantifying total and amenable cyanide in the alkaline distillates from Method 9010.

1.2 The titration procedure using silver nitrate with p-dimethylamino-benzal-rhodanine indicator is used for measuring concentrations of cyanide exceeding 0.1 mg/L (0.025 mg/250 mL of absorbing liquid).

1.3 The colorimetric procedure is used for concentrations below 1 mg/L of cyanide and is sensitive to about 0.02 mg/L.

2.0 SUMMARY OF METHOD

2.1 In the colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCl) by reaction of cyanide with chloramine-T at a pH less than 8. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent. The absorbance is read at 578 nm for the complex formed with pyridine-barbituric acid reagent and CNCl. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

2.2 The titration measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

3.0 INTERFERENCES

3.1 Interferences are eliminated or reduced by using the distillation procedure provided in Method 9010.

3.2 Refer to Method 9010 for a discussion of potential cyanide interferences.

4.0 APPARATUS AND MATERIALS

4.1 Spectrophotometer - Suitable for measurements at 578 nm with a 1.0 cm cell or larger.

4.2 Hot plate stirrer/heating mantle.

4.3 pH meter.

4.4 Refrigerator.

4.5 5 mL microburette.

4.6 Class A volumetric flasks - 1000, 250, and 100 mL.

4.7 Erlenmeyer flask - 500 mL.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Reagents for spectrophotometric determination

5.3.1 Sodium hydroxide solution (0.25N), NaOH. Dissolve 10 g NaOH in 1 liter of water.

5.3.2 Sodium phosphate monobasic (1M), $NaH_2PO_4 \cdot H_2O$. Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in 1 liter of water. Refrigerate this solution.

5.3.3 Chloramine-T solution (0.44%), $C_7H_7ClNNaO_2S$. Dissolve 1.0 g of white, water soluble chloramine-T in 100 mL of water and refrigerate until ready to use.

5.3.4 Pyridine-Barbituric acid reagent, $C_5H_5N \cdot C_4H_4N_2O_3$. Place 15 g of barbituric acid in a 250-mL volumetric flask and add just enough water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of concentrated hydrochloric acid (HCl), mix, and cool to room temperature. Dilute to 250 mL with water. This reagent is stable for approximately six months if stored in a cool, dark place.

5.3.5 Stock potassium cyanide solution (1 mL = 1000 µg CN^-), KCN. Dissolve 2.51 g of KCN and 2 g KOH in 900 mL of water. Standardize with 0.0192N silver nitrate, $AgNO_3$. Dilute to appropriate concentration to achieve 1 mL = 1000 µg of CN^-.

NOTE: Detailed procedure for $AgNO_3$ standardization is described in "Standard Methods for the Examination of Water and Wastewater", 18th Edition, (1992), Methods 4500-CN D.

5.3.6 Intermediate standard potassium cyanide solution, (1 mL = 100 µg CN^-), KCN. Dilute 100 mL of stock potassium cyanide solution (1 mL = 1000 µg CN^-) to 1000 mL with water.

5.3.7 Working standard potassium cyanide solution, (1 mL = 10 µg CN^-), KCN. Prepare fresh daily by diluting 100 mL of intermediate standard potassium cyanide solution and 10 mL of 1N NaOH to 1 liter with water.

5.4 Reagents for titration procedure

5.4.1 Rhodanine indicator - Dissolve 20 mg of p-dimethylamino- benzal-rhodanine, $C_{11}H_{12}N_2OS_2$, in 100 mL of acetone.

5.4.2 Standard silver nitrate solution (0.0192N), $AgNO_3$. Prepare by crushing approximately 5 g $AgNO_3$ and drying to constant weight at 40°C. Weigh out 3.2647 g of dried $AgNO_3$. Dissolve in 1 liter of water.

NOTE: Detailed procedure for $AgNO_3$ standardization is described in "Standard Methods for the Examination of Water and Wastewater", 18th Edition, (1992), Method 4500-CN D.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to Method 9010 for guidance on sample collection, preservation, and handling.

6.2 Distillates that are not analyzed immediately should be stored in tightly sealed flasks at 4 °C.

7.0 PROCEDURE

7.1 If the manual spectrophotometric determination will be performed, proceed to Section 7.2. If the titration procedure will be performed, proceed to Section 7.6.

7.2 Manual spectrophotometric determination

7.2.1 Pipet 50 mL of sample or 50 mL of the scrubber solution obtained from the distillation procedure in Method 9010 into a 100-mL volumetric flask. If the sample is later found to be beyond the linear range of the colorimetric determination and redistillation of a smaller sample is not feasible, a smaller aliquot may be taken. If less than 50 mL is taken, dilute to 50 mL with 0.25N sodium hydroxide solution.

NOTE: Temperature of reagents and spiking solution can affect the response factor of the colorimetric determination. The reagents stored in the refrigerator should be warmed to ambient temperature before use. Samples should not be left in a warm instrument to develop color, but instead they should be aliquoted to a cuvette immediately prior to reading the absorbance.

7.2.2 Add 15 mL of 1M sodium phosphate solution and mix. Add 2 mL of chloramine-T and mix. Some distillates may contain compounds that have chlorine demand. One minute after the addition of chloramine-T, test for excess chlorine with KI-starch paper. If the test is negative, add 0.5 mL chloramine-T. After one minute recheck with KI-starch paper. Continue to add chloramine-T in 0.5 mL increments until an excess is maintained. After 1 to 2 minutes, add 5 mL of pyridine-barbituric acid solution and mix.

7.2.3 Dilute to 100 mL with water and mix again. Allow 8 minutes for color development and then read the absorbance at 578 nm in a 1-cm cell within 15 minutes. The sodium hydroxide concentration will be 0.125N.

7.3 Standard curve for samples without sulfide

7.3.1 Prepare a series of standards by pipetting suitable volumes of working standard potassium cyanide solution into 250-mL volumetric flasks. To each flask, add 50 mL of 1.25N sodium hydroxide and dilute to 250 mL with water. Prepare using the following table. The sodium hydroxide concentration will be 0.25N.

mL of Working Standard Solution (1 mL = 10 µg CN^-)	Concentration (µg CN^-/L)
0	Blank
1.0	40
2.0	80
5.0	200
10.0	400
15.0	600
20.0	800

7.3.2 After the standard solutions have been prepared according to the table above, pipet 50 mL of each standard solution into a 100-mL volumetric flask and proceed to Sections 7.2.2 and 7.2.3 to obtain absorbance values for the standard curve. The final concentrations for the standard curve will be one half of the amounts in the above table (final concentrations ranging from 20 to 400 µg/L).

7.3.3 Prepare a standard curve ranging from 20 to 400 µg/L by plotting absorbance of standard versus the cyanide concentration

7.4 Standard curve for samples with sulfide

7.4.1 It is imperative that all standards be distilled in the same manner as the samples using the method of standard additions. Standards distilled by this method will give a linear curve, at low concentrations, but as the concentration increases, the recovery decreases. It is recommended that at least five standards be distilled.

7.4.2 Prepare a series of standards similar in concentration to those mentioned in Section 7.3.1 and analyze as in Section 7.2. Prepare a standard curve by plotting absorbance of standard versus the cyanide concentration.

7.5 Calculation - If the spectrophotometric procedure is used, calculate the cyanide, in µg/L, in the original sample as follows.

$$CN^- \ (\mu g/L) = \frac{A \times B \times C}{D \times E}$$

where:

A = µg/L CN^- read from standard curve
B = mL of sample after preparation of colorimetric analysis (100 mL recommended).

C = mL of sample after distillation (250 mL recommended).
D = mL of original sample for distillation (500 mL recommended).
E = mL used for colorimetric analysis (50 mL recommended).

7.6 Titration Procedure

7.6.1 Transfer the gas scrubber solution or a suitable aliquot from the 250-mL volumetric flask to a 500-mL Erlenmeyer flask. Add 10-12 drops of the rhodanine indicator.

7.6.2 Titrate with standard 0.0192N silver nitrate to the first change in color from yellow to brownish-pink. The titration must be performed slowly with constant stirring. Titrate a water blank using the same amount of sodium hydroxide and indicator as in the sample. The analyst should be familiar with the endpoint of the titration and the amount of indicator to be used before actually titrating the samples. A 5-mL buret may be conveniently used to obtain a precise titration.

NOTE: The titration is based on the following reaction:

$$Ag^{+} + 2CN^{-} \rightarrow [Ag(CN)_2]^{-}$$

When all of the cyanide has complexed and more silver nitrate is added, the excess silver combines with the rhodanine indicator to turn the solution yellow and then brownish-pink.

7.6.3 Calculation - If the titrimetric procedure is used, calculate concentration of CN^- in µg/L in the original sample as follows:

$$CN^{-}\ (\mu g/L) = \frac{(A-B)}{C} \times D \times \frac{E}{F} \times \frac{2\ mole\ CN^{-}}{1\ eq.\ AgNO_3} \times \frac{26.02\ g\ CN^{-}}{1\ mole\ CN^{-}} \times \frac{1 \times 10^{6} \mu g}{1\ g}$$

where:

A = mL of $AgNO_3$ for titration of sample.
B = mL of $AgNO_3$ for titration of blank.
C = mL of sample titrated (250 recommended).
D = actual normality of $AgNO_3$ (0.0192N recommended).
E = mL of sample after distillation (250 recommended).
F = mL of original sample before distillation (500 recommended).

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Refer to the quality control section of Method 9010A for the method requirements for blanks, matrix duplicates, and matrix spikes. Each QC sample must be processed through the reflux-distillation steps contained in Method 9010 prior to analysis by this method.

8.3 Analyze check standards with every analytical batch of samples. If the standards are not within 15% of the expected value, then the samples must be reanalyzed.

8.4 Analyze one replicate sample for every 20 samples. The CV of the replicates should be 20% or less. If this criterion is not met, the samples should be reanalyzed.

8.5 Analyze one matrix spiked sample every 20 samples to check the efficiency of sample distillation procedure and to monitor potential matrix interference.

8.6 The method of standard additions shall be used for the analysis of all samples that suffer from matrix interferences such as samples which contain sulfides.

9.0 METHOD PERFORMANCE

9.1 The titration procedure using silver nitrate is used for measuring concentrations of cyanide exceeding 0.1 mg/L. The colorimetric procedure is used for concentrations below 1 mg/L of cyanide and is sensitive to about 0.02 mg/L.

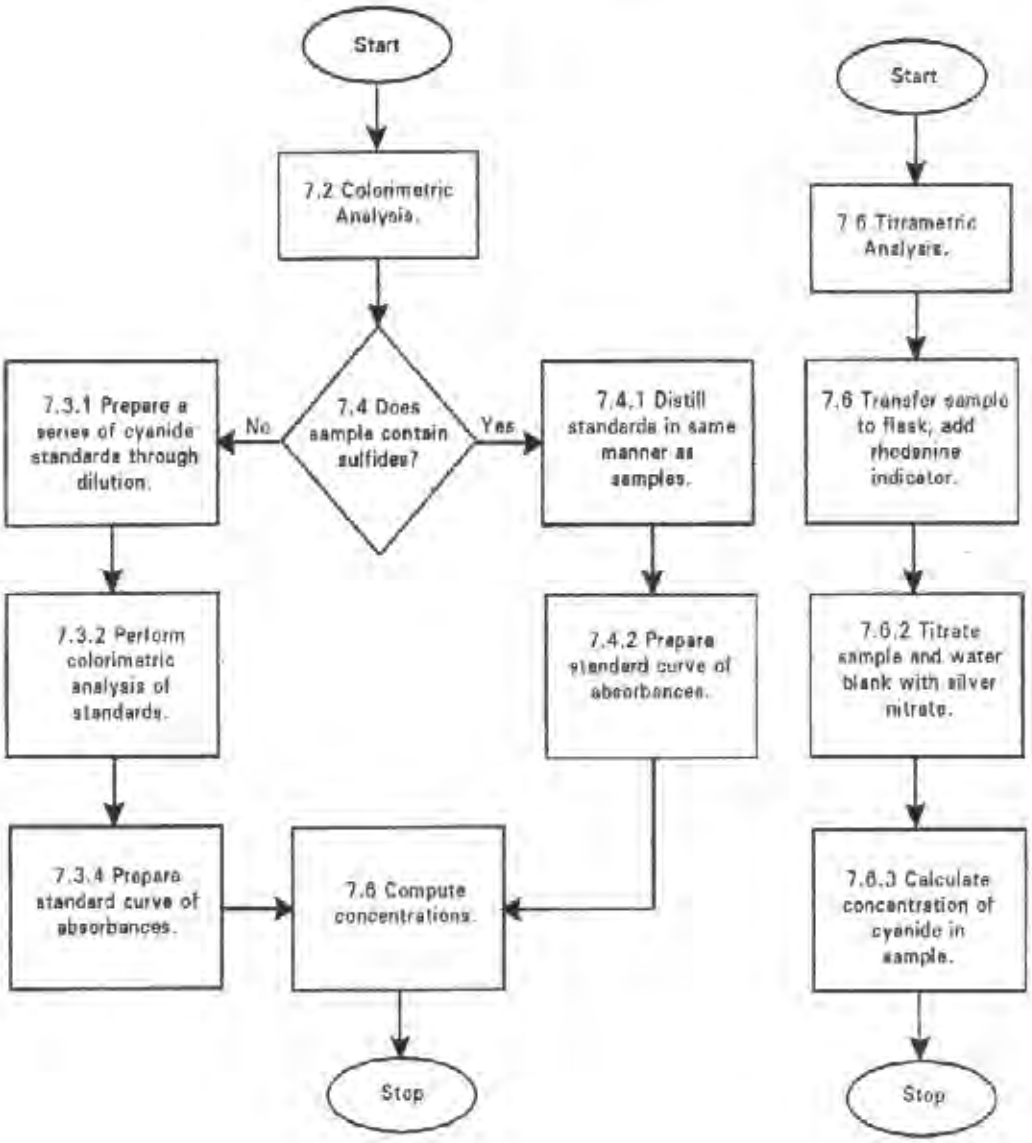
9.2 EPA Method 335.2 (sample distillation with titration) reports that in a single laboratory using mixed industrial and domestic waste samples at concentrations of 0.08 to 0.82 mg/L CN^-, the standard deviations for precision were $\pm$ 0.005 to $\pm$ 0.094, respectively. In a single laboratory using mixed industrial and domestic waste samples at concentrations of 0.28 and 0.82 mg/L CN^-, recoveries (accuracy) were 85% and 102%, respectively.

9.3 In two additional studies using surface water, ground water, and landfill leachate samples, the titration procedure was further evaluated. The concentration range used in these studies was 0.5 to 10 mg/L cyanide. The detection limit was found to be 0.2 mg/L for both total and amenable cyanide determinations. The precision (CV) was 6.9 and 2.6 for total cyanide determinations and 18.6 and 9.1 for amenable cyanide determinations. The mean recoveries were 94% and 98.9% for total cyanide, and 86.7% and 97.4% for amenable cyanide.

10.0 REFERENCES

10.1 Refer to Method 9010 for references on total and amenable cyanide.

TITRIMETRIC AND MANUAL SPECTROPHOTOMETRIC DETERMINATIVE METHODS FOR CYANIDE



Analytical Methods

Dioxins/Furans

1613B

Method 1613

Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS

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Disclaimer

This method has been reviewed by the Engineering and Analysis Division, U.S. Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Introduction

Method 1613 was developed by the United States Environmental Protection Agency's Office of Science and Technology for isomer-specific determination of the 2,3,7,8-substituted, tetra- through octa-chlorinated, dibenzo-*p*-dioxins and dibenzofurans in aqueous, solid, and tissue matrices by isotope dilution, high resolution capillary column gas chromatography (HRGC)/high resolution mass spectrometry (HRMS).

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Method 1613, Revision B
Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS

1.0 Scope and Application

1.1 This method is for determination of tetra- through octa-chlorinated dibenzo-*p*-dioxins (CDDs) and dibenzofurans (CDFs) in water, soil, sediment, sludge, tissue, and other sample matrices by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The method is for use in EPA's data gathering and monitoring programs associated with the Clean Water Act, the Resource Conservation and Recovery Act, the Comprehensive Environmental Response, Compensation and Liability Act, and the Safe Drinking Water Act. The method is based on a compilation of EPA, industry, commercial laboratory, and academic methods (References 1-6).

1.2 The seventeen 2,3,7,8-substituted CDDs/CDFs listed in Table 1 may be determined by this method. Specifications are also provided for separate determination of 2,3,7,8-tetrachloro-dibenzo-*p*-dioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachloro-dibenzofuran (2,3,7,8-TCDF).

1.3 The detection limits and quantitation levels in this method are usually dependent on the level of interferences rather than instrumental limitations. The minimum levels (MLs) in Table 2 are the levels at which the CDDs/CDFs can be determined with no interferences present. The Method Detection Limit (MDL) for 2,3,7,8-TCDD has been determined as 4.4 pg/L (parts-per-quadrillion) using this method.

1.4 The GC/MS portions of this method are for use only by analysts experienced with HRGC/HRMS or under the close supervision of such qualified persons. Each laboratory that uses this method must demonstrate the ability to generate acceptable results using the procedure in Section 9.2.

1.5 This method is "performance-based". The analyst is permitted to modify the method to overcome interferences or lower the cost of measurements, provided that all performance criteria in this method are met. The requirements for establishing method equivalency are given in Section 9.1.2.

1.6 Any modification of this method, beyond those expressly permitted, shall be considered a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

2.0 Summary of Method

Flow charts that summarize procedures for sample preparation, extraction, and analysis are given in Figure 1 for aqueous and solid samples, Figure 2 for multi-phase samples, and Figure 3 for tissue samples.

2.1 Extraction

2.1.1 Aqueous samples (samples containing less than 1% solids)—Stable isotopically labeled analogs of 15 of the 2,3,7,8-substituted CDDs/CDFs are spiked into a 1 L sample, and the sample is extracted by one of three procedures:

2.1.1.1 Samples containing no visible particles are extracted with methylene chloride in a separatory funnel or by the solid-phase extraction technique summarized in Section 2.1.1.3. The extract is concentrated for cleanup.

2.1.1.2 Samples containing visible particles are vacuum filtered through a glass-fiber filter. The filter is extracted in a Soxhlet/Dean-Stark (SDS) extractor (Reference 7), and the filtrate is extracted with methylene chloride in a separatory funnel. The methylene chloride extract is concentrated and combined with the SDS extract prior to cleanup.

2.1.1.3 The sample is vacuum filtered through a glass-fiber filter on top of a solid-phase extraction (SPE) disk. The filter and disk are extracted in an SDS extractor, and the extract is concentrated for cleanup.

2.1.2 Solid, semi-solid, and multi-phase samples (but not tissue)—The labeled compounds are spiked into a sample containing 10 g (dry weight) of solids. Samples containing multiple phases are pressure filtered and any aqueous liquid is discarded. Coarse solids are ground or homogenized. Any non-aqueous liquid from multi-phase samples is combined with the solids and extracted in an SDS extractor. The extract is concentrated for cleanup.

2.1.3 Fish and other tissue—The sample is extracted by one of two procedures:

2.1.3.1 Soxhlet or SDS extraction—A 20 g aliquot of sample is homogenized, and a 10 g aliquot is spiked with the labeled compounds. The sample is mixed with sodium sulfate, allowed to dry for 12-24 hours, and extracted for 18-24 hours using methylene chloride:hexane (1:1) in a Soxhlet extractor. The extract is evaporated to dryness, and the lipid content is determined.

2.1.3.2 HCl digestion—A 20 g aliquot is homogenized, and a 10 g aliquot is placed in a bottle and spiked with the labeled compounds. After equilibration, 200 mL of hydrochloric acid and 200 mL of methylene chloride:hexane (1:1) are added, and the bottle is agitated for 12-24 hours. The extract is evaporated to dryness, and the lipid content is determined.

2.2 After extraction, $^{37}Cl_4$-labeled 2,3,7,8-TCDD is added to each extract to measure the efficiency of the cleanup process. Sample cleanups may include back-extraction with acid and/or base, and gel permeation, alumina, silica gel, Florisil and activated carbon chromatography. High-performance liquid chromatography (HPLC) can be used for further isolation of the 2,3,7,8-isomers or other specific isomers or congeners. Prior to the cleanup procedures cited above, tissue extracts are cleaned up using an anthropogenic isolation column, a batch silica gel adsorption, or sulfuric acid and base back-extraction, depending on the tissue extraction procedure used.

2.3 After cleanup, the extract is concentrated to near dryness. Immediately prior to injection, internal standards are added to each extract, and an aliquot of the extract is injected into the gas chromatograph. The analytes are separated by the GC and detected by a high-resolution (≥10,000) mass spectrometer. Two exact m/z's are monitored for each analyte.

2.4 An individual CDD/CDF is identified by comparing the GC retention time and ion-abundance ratio of two exact m/z's with the corresponding retention time of an authentic standard and the theoretical or acquired ion-abundance ratio of the two exact m/z's. The non-2,3,7,8 substituted isomers and congeners are identified when retention times and ion-abundance ratios agree within predefined limits. Isomer specificity for 2,3,7,8-TCDD and 2,3,7,8-TCDF is achieved using GC columns that resolve these isomers from the other tetra-isomers.

2.5 Quantitative analysis is performed using selected ion current profile (SICP) areas, in one of three ways:

2.5.1 For the 15 2,3,7,8-substituted CDDs/CDFs with labeled analogs (see Table 1), the GC/MS system is calibrated, and the concentration of each compound is determined using the isotope dilution technique.

2.5.2 For 1,2,3,7,8,9-HxCDD, OCDF, and the labeled compounds, the GC/MS system is calibrated and the concentration of each compound is determined using the internal standard technique.

2.5.3 For non-2,3,7,8-substituted isomers and for all isomers at a given level of chlorination (i.e., total TCDD), concentrations are determined using response factors from calibration of the CDDs/CDFs at the same level of chlorination.

2.6 The quality of the analysis is assured through reproducible calibration and testing of the extraction, cleanup, and GC/MS systems.

3.0 Definitions

Definitions are given in the glossary at the end of this method.

4.0 Contamination and Interferences

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines causing misinterpretation of chromatograms (References 8 9). Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Where possible, reagents are cleaned by extraction or solvent rinse.

4.2 Proper cleaning of glassware is extremely important, because glassware may not only contaminate the samples but may also remove the analytes of interest by adsorption on the glass surface.

4.2.1 Glassware should be rinsed with solvent and washed with a detergent solution as soon after use as is practical. Sonication of glassware containing a detergent solution for approximately 30 seconds may aid in cleaning. Glassware with

removable parts, particularly separatory funnels with fluoropolymer stopcocks, must be disassembled prior to detergent washing.

4.2.2 After detergent washing, glassware should be rinsed immediately, first with methanol, then with hot tap water. The tap water rinse is followed by another methanol rinse, then acetone, and then methylene chloride.

4.2.3 Do not bake reusable glassware in an oven as a routine part of cleaning. Baking may be warranted after particularly dirty samples are encountered but should be minimized, as repeated baking of glassware may cause active sites on the glass surface that will irreversibly adsorb CDDs/CDFs.

4.2.4 Immediately prior to use, the Soxhlet apparatus should be pre-extracted with toluene for approximately three hours (see Sections 12.3.1 through 12.3.3). Separatory funnels should be shaken with methylene chloride/toluene (80/20 mixture) for two minutes, drained, and then shaken with pure methylene chloride for two minutes.

4.3 All materials used in the analysis shall be demonstrated to be free from interferences by running reference matrix method blanks initially and with each sample batch (samples started through the extraction process on a given 12-hour shift, to a maximum of 20 samples).

4.3.1 The reference matrix must simulate, as closely as possible, the sample matrix under test. Ideally, the reference matrix should not contain the CDDs/CDFs in detectable amounts, but should contain potential interferents in the concentrations expected to be found in the samples to be analyzed. For example, a reference sample of human adipose tissue containing pentachloronaphthalene can be used to exercise the cleanup systems when samples containing pentachloronaphthalene are expected.

4.3.2 When a reference matrix that simulates the sample matrix under test is not available, reagent water (Section 7.6.1) can be used to simulate water samples; playground sand (Section 7.6.2) or white quartz sand (Section 7.3.2) can be used to simulate soils; filter paper (Section 7.6.3) can be used to simulate papers and similar materials; and corn oil (Section 7.6.4) can be used to simulate tissues.

4.4 Interferences coextracted from samples will vary considerably from source to source, depending on the diversity of the site being sampled. Interfering compounds may be present at concentrations several orders of magnitude higher than the CDDs/CDFs. The most frequently encountered interferences are chlorinated biphenyls, methoxy biphenyls, hydroxydiphenyl ethers, benzylphenyl ethers, polynuclear aromatics, and pesticides. Because very low levels of CDDs/CDFs are measured by this method, the elimination of interferences is essential. The cleanup steps given in Section 13 can be used to reduce or eliminate these interferences and thereby permit reliable determination of the CDDs/CDFs at the levels shown in Table 2.

4.5 Each piece of reusable glassware should be numbered to associate that glassware with the processing of a particular sample. This will assist the laboratory in tracking possible sources of contamination for individual samples, identifying glassware associated with

highly contaminated samples that may require extra cleaning, and determining when glassware should be discarded.

4.6 Cleanup of tissue—The natural lipid content of tissue can interfere in the analysis of tissue samples for the CDDs/CDFs. The lipid contents of different species and portions of tissue can vary widely. Lipids are soluble to varying degrees in various organic solvents and may be present in sufficient quantity to overwhelm the column chromatographic cleanup procedures used for cleanup of sample extracts. Lipids must be removed by the lipid removal procedures in Section 13.7, followed by alumina (Section 13.4) or Florisil (Section 13.8), and carbon (Section 13.5) as minimum additional cleanup steps. If chlorodiphenyl ethers are detected, as indicated by the presence of peaks at the exact m/z's monitored for these interferents, alumina and/or Florisil cleanup must be employed to eliminate these interferences.

5.0 Safety

5.1 The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely determined; however, each chemical compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level.

5.1.1 The 2,3,7,8-TCDD isomer has been found to be acnegenic, carcinogenic, and teratogenic in laboratory animal studies. It is soluble in water to approximately 200 ppt and in organic solvents to 0.14%. On the basis of the available toxicological and physical properties of 2,3,7,8-TCDD, all of the CDDs/CDFs should be handled only by highly trained personnel thoroughly familiar with handling and cautionary procedures and the associated risks.

5.1.2 It is recommended that the laboratory purchase dilute standard solutions of the analytes in this method. However, if primary solutions are prepared, they shall be prepared in a hood, and a NIOSH/MESA approved toxic gas respirator shall be worn when high concentrations are handled.

5.2 The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should also be made available to all personnel involved in these analyses. It is also suggested that the laboratory perform personal hygiene monitoring of each analyst who uses this method and that the results of this monitoring be made available to the analyst. Additional information on laboratory safety can be found in References 10-13. The references and bibliography at the end of Reference 13 are particularly comprehensive in dealing with the general subject of laboratory safety.

5.3 The CDDs/CDFs and samples suspected to contain these compounds are handled using essentially the same techniques employed in handling radioactive or infectious materials. Well-ventilated, controlled access laboratories are required. Assistance in evaluating the health hazards of particular laboratory conditions may be obtained from certain consulting laboratories and from State Departments of Health or Labor, many of which have an industrial health service. The CDDs/CDFs are extremely toxic to laboratory animals. Each laboratory must develop a strict safety program for handling these compounds. The practices in References 2 and 14 are highly recommended.

5.3.1 Facility—When finely divided samples (dusts, soils, dry chemicals) are handled, all operations (including removal of samples from sample containers, weighing, transferring, and mixing) should be performed in a glove box demonstrated to be leak tight or in a fume hood demonstrated to have adequate air flow. Gross losses to the laboratory ventilation system must not be allowed. Handling of the dilute solutions normally used in analytical and animal work presents no inhalation hazards except in the case of an accident.

5.3.2 Protective equipment—Disposable plastic gloves, apron or lab coat, safety glasses or mask, and a glove box or fume hood adequate for radioactive work should be used. During analytical operations that may give rise to aerosols or dusts, personnel should wear respirators equipped with activated carbon filters. Eye protection equipment (preferably full face shields) must be worn while working with exposed samples or pure analytical standards. Latex gloves are commonly used to reduce exposure of the hands. When handling samples suspected or known to contain high concentrations of the CDDs/CDFs, an additional set of gloves can also be worn beneath the latex gloves.

5.3.3 Training—Workers must be trained in the proper method of removing contaminated gloves and clothing without contacting the exterior surfaces.

5.3.4 Personal hygiene—Hands and forearms should be washed thoroughly after each manipulation and before breaks (coffee, lunch, and shift).

5.3.5 Confinement—Isolated work areas posted with signs, segregated glassware and tools, and plastic absorbent paper on bench tops will aid in confining contamination.

5.3.6 Effluent vapors—The effluents of sample splitters from the gas chromatograph (GC) and from roughing pumps on the mass spectrometer (MS) should pass through either a column of activated charcoal or be bubbled through a trap containing oil or high boiling alcohols to condense CDD/CDF vapors.

5.3.7 Waste Handling—Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans. Janitors and other personnel must be trained in the safe handling of waste.

5.3.8 Decontamination

5.3.8.1 Decontamination of personnel—Use any mild soap with plenty of scrubbing action.

5.3.8.2 Glassware, tools, and surfaces—Chlorothene NU Solvent is the least toxic solvent shown to be effective. Satisfactory cleaning may be accomplished by rinsing with Chlorothene, then washing with any detergent and water. If glassware is first rinsed with solvent, then the dish water may be disposed of in the sewer. Given the cost of disposal, it is prudent to minimize solvent wastes.

5.3.9 Laundry—Clothing known to be contaminated should be collected in plastic bags. Persons who convey the bags and launder the clothing should be advised of the

hazard and trained in proper handling. The clothing may be put into a washer without contact if the launderer knows of the potential problem. The washer should be run through a cycle before being used again for other clothing.

5.3.10 Wipe tests—A useful method of determining cleanliness of work surfaces and tools is to wipe the surface with a piece of filter paper. Extraction and analysis by GC with an electron capture detector (ECD) can achieve a limit of detection of 0.1 µg per wipe; analysis using this method can achieve an even lower detection limit. Less than 0.1 µg per wipe indicates acceptable cleanliness; anything higher warrants further cleaning. More than 10 µg on a wipe constitutes an acute hazard and requires prompt cleaning before further use of the equipment or work space, and indicates that unacceptable work practices have been employed.

5.3.11 Table or wrist-action shaker—The use of a table or wrist-action shaker for extraction of tissues presents the possibility of breakage of the extraction bottle and spillage of acid and flammable organic solvent. A secondary containment system around the shaker is suggested to prevent the spread of acid and solvents in the event of such a breakage. The speed and intensity of shaking action should also be adjusted to minimize the possibility of breakage.

6.0 Apparatus and Materials

NOTE: Brand names, suppliers, and part numbers are for illustration purposes only and no endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here. Meeting the performance requirements of this method is the responsibility of the laboratory.

6.1 Sampling Equipment for Discrete or Composite Sampling

6.1.1 Sample bottles and caps

6.1.1.1 Liquid samples (waters, sludges and similar materials containing 5% solids or less)—Sample bottle, amber glass, 1.1 L minimum, with screw cap.

6.1.1.2 Solid samples (soils, sediments, sludges, paper pulps, filter cake, compost, and similar materials that contain more than 5% solids)—Sample bottle, wide mouth, amber glass, 500 mL minimum.

6.1.1.3 If amber bottles are not available, samples shall be protected from light.

6.1.1.4 Bottle caps—Threaded to fit sample bottles. Caps shall be lined with fluoropolymer.

6.1.1.5 Cleaning

6.1.1.5.1 Bottles are detergent water washed, then solvent rinsed before use.

6.1.1.5.2 Liners are detergent water washed, rinsed with reagent water (Section 7.6.1) followed by solvent, and baked at approximately 200°C for a minimum of 1 hour prior to use.

6.1.2 Compositing equipment—Automatic or manual compositing system incorporating glass containers cleaned per bottle cleaning procedure above. Only glass or fluoropolymer tubing shall be used. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used in the pump only. Before use, the tubing shall be thoroughly rinsed with methanol, followed by repeated rinsing with reagent water to minimize sample contamination. An integrating flow meter is used to collect proportional composite samples.

6.2 Equipment for Glassware Cleaning—Laboratory sink with overhead fume hood.

6.3 Equipment for Sample Preparation

6.3.1 Laboratory fume hood of sufficient size to contain the sample preparation equipment listed below.

6.3.2 Glove box (optional).

6.3.3 Tissue homogenizer—VirTis Model 45 Macro homogenizer (American Scientific Products H-3515, or equivalent) with stainless steel Macro-shaft and Turbo-shear blade.

6.3.4 Meat grinder—Hobart, or equivalent, with 3-5 mm holes in inner plate.

6.3.5 Equipment for determining percent moisture

6.3.5.1 Oven—Capable of maintaining a temperature of 110 ±5°C.

6.3.5.2 Dessicator.

6.3.6 Balances

6.3.6.1 Analytical—Capable of weighing 0.1 mg.

6.3.6.2 Top loading—Capable of weighing 10 mg.

6.4 Extraction Apparatus

6.4.1 Water samples

6.4.1.1 pH meter, with combination glass electrode.

6.4.1.2 pH paper, wide range (Hydrion Papers, or equivalent).

6.4.1.3 Graduated cylinder, 1 L capacity.

6.4.1.4 Liquid/liquid extraction—Separatory funnels, 250 mL, 500 mL, and 2000 mL, with fluoropolymer stopcocks.

6.4.1.5 Solid-phase extraction

6.4.1.5.1 One liter filtration apparatus, including glass funnel, glass frit support, clamp, adapter, stopper, filtration flask, and vacuum tubing (Figure 4). For wastewater samples, the apparatus should accept 90 or 144 mm disks. For drinking water or other samples containing low solids, smaller disks may be used.

6.4.1.5.2 Vacuum source capable of maintaining 25 in. Hg, equipped with shutoff valve and vacuum gauge.

6.4.1.5.3 Glass-fiber filter—Whatman GMF 150 (or equivalent), 1 micron pore size, to fit filtration apparatus in Section 6.4.1.5.1.

6.4.1.5.4 Solid-phase extraction disk containing octadecyl (C_{18}) bonded silica uniformly enmeshed in an inert matrix—Fisher Scientific 14-378F (or equivalent), to fit filtration apparatus in Section 6.4.1.5.1.

6.4.2 Soxhlet/Dean-Stark (SDS) extractor (Figure 5). For filters and solid/sludge samples.

6.4.2.1 Soxhlet—50 mm ID, 200 mL capacity with 500 mL flask. (Cal-Glass LG-6900, or equivalent, except substitute 500 mL round-bottom flask for 300 mL flat-bottom flask).

6.4.2.2 Thimble—43 x 123 to fit Soxhlet (Cal-Glass LG-6901-122, or equivalent).

6.4.2.3 Moisture trap—Dean Stark or Barret with fluoropolymer stopcock, to fit Soxhlet.

6.4.2.4 Heating mantle—Hemispherical, to fit 500 mL round-bottom flask (Cal-Glass LG-8801-112, or equivalent).

6.4.2.5 Variable transformer—Powerstat (or equivalent), 110 volt, 10 amp.

6.4.3 Apparatus for extraction of tissue.

6.4.3.1 Bottle for extraction (if digestion/extraction using HCl is used)—500-600 mL wide-mouth clear glass, with fluoropolymer-lined cap.

6.4.3.2 Bottle for back-extraction—100-200 mL narrow-mouth clear glass with fluoropolymer-lined cap.

6.4.3.3 Mechanical shaker—Wrist-action or platform-type rotary shaker that produces vigorous agitation (Sybron Thermolyne Model I.E "Big Bill" rotator/shaker, or equivalent).

6.4.3.4 Rack attached to shaker table to permit agitation of four to nine samples simultaneously.

6.4.4 Beakers—400-500 mL.

6.4.5 Spatulas—Stainless steel.

6.5 Filtration Apparatus

6.5.1 Pyrex glass wool—Solvent-extracted by SDS for three hours minimum.

NOTE: Baking glass wool may cause active sites that will irreversibly adsorb CDDs/CDFs.

6.5.2 Glass funnel—125-250 mL.

6.5.3 Glass-fiber filter paper—Whatman CF/D (or equivalent), to fit glass funnel in Section 6.5.2.

6.5.4 Drying column—15-20 mm ID Pyrex chromatographic column equipped with coarse-glass frit or glass-wool plug.

6.5.5 Buchner funnel—15 cm.

6.5.6 Glass-fiber filter paper—to fit Buchner funnel in Section 6.5.5.

6.5.7 Filtration flasks—1.5-2.0 L, with side arm.

6.5.8 Pressure filtration apparatus—Millipore YT30 142 HW, or equivalent.

6.6 Centrifuge Apparatus

6.6.1 Centrifuge—Capable of rotating 500 mL centrifuge bottles or 15 mL centrifuge tubes at 5,000 rpm minimum.

6.6.2 Centrifuge bottles—500 mL, with screw-caps, to fit centrifuge.

6.6.3 Centrifuge tubes—12-15 mL, with screw-caps, to fit centrifuge.

6.7 Cleanup Apparatus

6.7.1 Automated gel permeation chromatograph (Analytical Biochemical Labs, Inc, Columbia, MO, Model GPC Autoprep 1002, or equivalent).

6.7.1.1 Column—600-700 mm long x 25 mm ID, packed with 70 g of SX-3 Bio-beads (Bio-Rad Laboratories, Richmond, CA, or equivalent).

6.7.1.2 Syringe—10 mL, with Luer fitting.

6.7.1.3 Syringe filter holder—stainless steel, and glass-fiber or fluoropolymer filters (Gelman 4310, or equivalent).

6.7.1.4 UV detectors—254 nm, preparative or semi-preparative flow cell (Isco, Inc., Type 6; Schmadzu, 5 mm path length; Beckman Altex 152W, 8 µL micro-prep flow cell, 2 mm path; Pharmacia UV-1, 3 mm flow cell; LDC Milton-Roy UV-3, monitor #1203, or equivalent).

6.7.2 Reverse-phase high-performance liquid chromatograph.

6.7.2.1 Column oven and detector—Perkin-Elmer Model LC-65T (or equivalent) operated at 0.02 AUFS at 235 nm.

6.7.2.2 Injector—Rheodyne 7120 (or equivalent) with 50 µL sample loop.

6.7.2.3 Column—Two 6.2 mm x 250 mm Zorbax-ODS columns in series (DuPont Instruments Division, Wilmington, DE, or equivalent), operated at 50°C with 2.0 mL/min methanol isocratic effluent.

6.7.2.4 Pump—Altex 110A (or equivalent).

6.7.3 Pipets

6.7.3.1 Disposable, pasteur—150 mm long x 5-mm ID (Fisher Scientific 13-678-6A, or equivalent).

6.7.3.2 Disposable, serological—10 mL (6 mm ID).

6.7.4 Glass chromatographic columns

6.7.4.1 150 mm long x 8-mm ID, (Kontes K-420155, or equivalent) with coarse-glass frit or glass-wool plug and 250 mL reservoir.

6.7.4.2 200 mm long x 15 mm ID, with coarse-glass frit or glass-wool plug and 250 mL reservoir.

6.7.4.3 300 mm long x 25 mm ID, with 300 mL reservoir and glass or fluoropolymer stopcock.

6.7.5 Stirring apparatus for batch silica cleanup of tissue extracts.

6.7.5.1 Mechanical stirrer—Corning Model 320, or equivalent.

6.7.5.2 Bottle—500-600 mL wide-mouth clear glass.

6.7.6 Oven—For baking and storage of adsorbents, capable of maintaining a constant temperature (±5°C) in the range of 105-250°C.

6.8 Concentration Apparatus

6.8.1 Rotary evaporator—Buchi/Brinkman-American Scientific No. E5045-10 or equivalent, equipped with a variable temperature water bath.

6.8.1.1 Vacuum source for rotary evaporator equipped with shutoff valve at the evaporator and vacuum gauge.

6.8.1.2 A recirculating water pump and chiller are recommended, as use of tap water for cooling the evaporator wastes large volumes of water and can lead to inconsistent performance as water temperatures and pressures vary.

6.8.1.3 Round-bottom flask—100 mL and 500 mL or larger, with ground-glass fitting compatible with the rotary evaporator.

6.8.2 Kuderna-Danish (K-D) Concentrator

6.8.2.1 Concentrator tube—10 mL, graduated (Kontes K-570050-1025, or equivalent) with calibration verified. Ground-glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

6.8.2.2 Evaporation flask—500 mL (Kontes K 570001 0500, or equivalent), attached to concentrator tube with springs (Kontes K-662750-0012 or equivalent).

6.8.2.3 Snyder column—Three-ball macro (Kontes K-503000-0232, or equivalent).

6.8.2.4 Boiling chips

6.8.2.4.1 Glass or silicon carbide—Approximately 10/40 mesh, extracted with methylene chloride and baked at 450°C for one hour minimum.

6.8.2.4.2 Fluoropolymer (optional)—Extracted with methylene chloride.

6.8.2.5 Water bath—Heated, with concentric ring cover, capable of maintaining a temperature within ±2°C, installed in a fume hood.

6.8.3 Nitrogen blowdown apparatus—Equipped with water bath controlled in the range of 30-60°C (N-Evap, Organomation Associates, Inc., South Berlin, MA, or equivalent), installed in a fume hood.

6.8.4 Sample vials

6.8.4.1 Amber glass—2-5 mL with fluoropolymer lined screw cap.

6.8.4.2 Glass—0.3 mL, conical, with fluoropolymer-lined screw or crimp cap.

6.9 Gas Chromatograph—Shall have splitless or on-column injection port for capillary column, temperature program with isothermal hold, and shall meet all of the performance specifications in Section 10.

6.9.1 GC column for CDDs/CDFs and for isomer specificity for 2,3,7,8-TCDD—60 ±5 m long x 0.32 ±0.02 mm ID; 0.25 µm 5% phenyl, 94% methyl, 1% vinyl silicone bonded-phase fused-silica capillary column (J&W DB-5, or equivalent).

6.9.2 GC column for isomer specificity for 2,3,7,8-TCDF—30 ±5 m long x 0.32 ±0.02 mm ID, 0.25 µm bonded-phase fused-silica capillary column (J&W DB-225, or equivalent).

6.10 Mass Spectrometer—28-40 eV electron impact ionization, shall be capable of repetitively selectively monitoring 12 exact m/z's minimum at high resolution (≥10,000) during a period of approximately one second, and shall meet all of the performance specifications in Section 10.

6.11 GC/MS Interface—The mass spectrometer (MS) shall be interfaced to the GC such that the end of the capillary column terminates within 1 cm of the ion source but does not intercept the electron or ion beams.

6.12 Data System—Capable of collecting, recording, and storing MS data.

7.0 Reagents and Standards

7.1 pH Adjustment and Back-Extraction

7.1.1 Potassium hydroxide—Dissolve 20 g reagent grade KOH in 100 mL reagent water.

7.1.2 Sulfuric acid—Reagent grade (specific gravity 1.84).

7.1.3 Hydrochloric acid—Reagent grade, 6N.

7.1.4 Sodium chloride—Reagent grade, prepare at 5% (w/v) solution in reagent water.

7.2 Solution Drying and Evaporation

7.2.1 Solution drying—Sodium sulfate, reagent grade, granular, anhydrous (Baker 3375, or equivalent), rinsed with methylene chloride (20 mL/g), baked at 400°C for one hour minimum, cooled in a dessicator, and stored in a pre-cleaned glass bottle with screw-cap that prevents moisture from entering. If, after heating, the sodium sulfate develops a noticeable grayish cast (due to the presence of carbon in the crystal matrix), that batch of reagent is not suitable for use and should be discarded. Extraction with methylene chloride (as opposed to simple rinsing) and baking at a lower temperature may produce sodium sulfate that is suitable for use.

7.2.2 Tissue drying—Sodium sulfate, reagent grade, powdered, treated and stored as above.

7.2.3 Prepurified nitrogen.

7.3 Extraction

7.3.1 Solvents—Acetone, toluene, cyclohexane, hexane, methanol, methylene chloride, and nonane; distilled in glass, pesticide quality, lot-certified to be free of interferences.

7.3.2 White quartz sand, 60/70 mesh—For Soxhlet/Dean-Stark extraction (Aldrich Chemical, Cat. No. 27-437-9, or equivalent). Bake at 450°C for four hours minimum.

7.4 GPC Calibration Solution—Prepare a solution containing 300 mg/mL corn oil, 15 mg/mL bis(2-ethylhexyl) phthalate, 1.4 mg/mL pentachlorophenol, 0.1 mg/mL perylene, and 0.5 mg/mL sulfur.

7.5 Adsorbents for Sample Cleanup

7.5.1 Silica gel

7.5.1.1 Activated silica gel—100-200 mesh, Supelco 1-3651 (or equivalent), rinsed with methylene chloride, baked at 180°C for a minimum of one hour, cooled in a dessicator, and stored in a precleaned glass bottle with screw-cap that prevents moisture from entering.

7.5.1.2 Acid silica gel (30% w/w)—Thoroughly mix 44.0 g of concentrated sulfuric acid with 100.0 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a bottle with a fluoropolymer-lined screw-cap.

7.5.1.3 Basic silica gel—Thoroughly mix 30 g of 1N sodium hydroxide with 100 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a bottle with a fluoropolymer-lined screw-cap.

7.5.1.4 Potassium silicate

7.5.1.4.1 Dissolve 56 g of high purity potassium hydroxide (Aldrich, or equivalent) in 300 mL of methanol in a 750-1000 mL flat-bottom flask.

7.5.1.4.2 Add 100 g of silica gel and a stirring bar, and stir on a hot plate at 60-70°C for one to two hours.

7.5.1.4.3 Decant the liquid and rinse the potassium silicate twice with 100 mL portions of methanol, followed by a single rinse with 100 mL of methylene chloride.

7.5.1.4.4 Spread the potassium silicate on solvent-rinsed aluminum foil and dry for two to four hours in a hood.

7.5.1.4.5 Activate overnight at 200-250°C.

7.5.2 Alumina—Either one of two types of alumina, acid or basic, may be used in the cleanup of sample extracts, provided that the laboratory can meet the performance specifications for the recovery of labeled compounds described in Section 9.3. The same type of alumina must be used for all samples, including those used to demonstrate initial precision and recovery (Section 9.2) and ongoing precision and recovery (Section 15.5).

7.5.2.1 Acid alumina—Supelco 19996-6C (or equivalent). Activate by heating to 130°C for a minimum of 12 hours.

7.5.2.2 Basic alumina—Supelco 19944-6C (or equivalent). Activate by heating to 600°C for a minimum of 24 hours. Alternatively, activate by heating in a tube furnace at 650-700°C under an air flow rate of approximately 400 cc/minute. Do not heat over 700°C, as this can lead to reduced capacity for retaining the analytes. Store at 130°C in a covered flask. Use within five days of baking.

7.5.3 Carbon

7.5.3.1 Carbopak C—(Supelco 1-0258, or equivalent).

7.5.3.2 Celite 545—(Supelco 2-0199, or equivalent).

7.5.3.3 Thoroughly mix 9.0 g Carbopak C and 41.0 g Celite 545 to produce an 18% w/w mixture. Activate the mixture at 130°C for a minimum of six hours. Store in a dessicator.

7.5.4 Anthropogenic isolation column—Pack the column in Section 6.7.4.3 from bottom to top with the following:

7.5.4.1 2 g silica gel (Section 7.5.1.1).

7.5.4.2 2 g potassium silicate (Section 7.5.1.4).

7.5.4.3 2 g granular anhydrous sodium sulfate (Section 7.2.1).

7.5.4.4 10 g acid silica gel (Section 7.5.1.2).

7.5.4.5 2 g granular anhydrous sodium sulfate.

7.5.5 Florisil column

7.5.5.1 Florisil—60-100 mesh, Floridin Corp (or equivalent). Soxhlet extract in 500 g portions for 24 hours.

7.5.5.2 Insert a glass wool plug into the tapered end of a graduated serological pipet (Section 6.7.3.2). Pack with 1.5 g (approx 2 mL) of Florisil topped with approx 1 mL of sodium sulfate (Section 7.2.1) and a glass wool plug.

7.5.5.3 Activate in an oven at 130-150°C for a minimum of 24 hours and cool for 30 minutes. Use within 90 minutes of cooling.

7.6 Reference Matrices—Matrices in which the CDDs/CDFs and interfering compounds are not detected by this method.

7.6.1 Reagent water—Bottled water purchased locally, or prepared by passage through activated carbon.

7.6.2 High-solids reference matrix—Playground sand or similar material. Prepared by extraction with methylene chloride and/or baking at 450°C for a minimum of four hours.

7.6.3 Paper reference matrix—Glass-fiber filter, Gelman Type A, or equivalent. Cut paper to simulate the surface area of the paper sample being tested.

7.6.4 Tissue reference matrix—Corn or other vegetable oil. May be prepared by extraction with methylene chloride.

7.6.5 Other matrices—This method may be verified on any reference matrix by performing the tests given in Section 9.2. Ideally, the matrix should be free of the CDDs/CDFs, but in no case shall the background level of the CDDs/CDFs in the reference matrix exceed three times the minimum levels in Table 2. If low background levels of the CDDs/CDFs are present in the reference matrix, the spike level of the analytes used in Section 9.2 should be increased to provide a spike-to-background ratio in the range of 1:1 to 5:1 (Reference 15).

7.7 Standard Solutions—Purchased as solutions or mixtures with certification to their purity, concentration, and authenticity, or prepared from materials of known purity and composition. If the chemical purity is 98% or greater, the weight may be used without correction to compute the concentration of the standard. When not being used, standards are stored in the dark at room temperature in screw-capped vials with fluoropolymer lined caps. A mark is placed on the vial at the level of the solution so that solvent loss by evaporation can be detected. If solvent loss has occurred, the solution should be replaced.

7.8 Stock Solutions

7.8.1 Preparation—Prepare in nonane per the steps below or purchase as dilute solutions (Cambridge Isotope Laboratories (CIL), Woburn, MA, or equivalent). Observe the safety precautions in Section 5, and the recommendation in Section 5.1.2.

7.8.2 Dissolve an appropriate amount of assayed reference material in solvent. For example, weigh 1-2 mg of 2,3,7,8-TCDD to three significant figures in a 10 mL ground-glass-stoppered volumetric flask and fill to the mark with nonane. After the TCDD is completely dissolved, transfer the solution to a clean 15 mL vial with fluoropolymer-lined cap.

7.8.3 Stock standard solutions should be checked for signs of degradation prior to the preparation of calibration or performance test standards. Reference standards that can be used to determine the accuracy of calibration standards are available from CIL and may be available from other vendors.

7.9 PAR Stock Solution

7.9.1 All CDDs/CDFs—Using the solutions in Section 7.8, prepare the PAR stock solution to contain the CDDs/CDFs at the concentrations shown in Table 3. When diluted, the solution will become the PAR (Section 7.14).

7.9.2 If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, prepare the PAR stock solution to contain these compounds only.

7.10 Labeled-Compound Spiking Solution

7.10.1 All CDDs/CDFs—From stock solutions, or from purchased mixtures, prepare this solution to contain the labeled compounds in nonane at the concentrations shown in Table 3. This solution is diluted with acetone prior to use (Section 7.10.3).

7.10.2 If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, prepare the labeled-compound solution to contain these compounds only. This solution is diluted with acetone prior to use (Section 7.10.3).

7.10.3 Dilute a sufficient volume of the labeled compound solution (Section 7.10.1 or 7.10.2) by a factor of 50 with acetone to prepare a diluted spiking solution. Each sample requires 1.0 mL of the diluted solution, but no more solution should be prepared than can be used in one day.

7.11 Cleanup Standard—Prepare $^{37}Cl_4$-2,3,7,8-TCDD in nonane at the concentration shown in Table 3. The cleanup standard is added to all extracts prior to cleanup to measure the efficiency of the cleanup process.

7.12 Internal Standard(s)

7.12.1 All CDDs/CDFs—Prepare the internal standard solution to contain $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD in nonane at the concentration shown in Table 3.

7.12.2 If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, prepare the internal standard solution to contain $^{13}C_{12}$-1,2,3,4-TCDD only.

7.13 Calibration Standards (CS1 through CS5)—Combine the solutions in Sections 7.9 through 7.12 to produce the five calibration solutions shown in Table 4 in nonane. These solutions permit the relative response (labeled to native) and response factor to be measured as a function of concentration. The CS3 standard is used for calibration verification (VER). If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, combine the solutions appropriate to these compounds.

7.14 Precision and Recovery (PAR) Standard—Used for determination of initial (Section 9.2) and ongoing (Section 15.5) precision and recovery. Dilute 10 µL of the precision and recovery standard (Section 7.9.1 or 7.9.2) to 2.0 mL with acetone for each sample matrix for each sample batch. One mL each are required for the blank and OPR with each matrix in each batch.

7.15 GC Retention Time Window Defining Solution and Isomer Specificity Test Standard—Used to define the beginning and ending retention times for the dioxin and furan isomers and to demonstrate isomer specificity of the GC columns employed for determination of 2,3,7,8-TCDD and 2,3,7,8-TCDF. The standard must contain the compounds listed in Table 5 (CIL EDF-4006, or equivalent), at a minimum. It is not necessary to monitor the window-defining compounds if only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be

determined. In this case, an isomer-specificity test standard containing the most closely eluted isomers listed in Table 5 (CIL EDF-4033, or equivalent) may be used.

7.16 QC Check Sample—A QC Check Sample should be obtained from a source independent of the calibration standards. Ideally, this check sample would be a certified reference material containing the CDDs/CDFs in known concentrations in a sample matrix similar to the matrix under test.

7.17 Stability of Solutions—Standard solutions used for quantitative purposes (Sections 7.9 through 7.15) should be analyzed periodically, and should be assayed against reference standards (Section 7.8.3) before further use.

8.0 Sample Collection, Preservation, Storage, and Holding Times

8.1 Collect samples in amber glass containers following conventional sampling practices (Reference 16). Aqueous samples that flow freely are collected in refrigerated bottles using automatic sampling equipment. Solid samples are collected as grab samples using wide-mouth jars.

8.2 Maintain aqueous samples in the dark at 0-4°C from the time of collection until receipt at the laboratory. If residual chlorine is present in aqueous samples, add 80 mg sodium thiosulfate per liter of water. EPA Methods 330.4 and 330.5 may be used to measure residual chlorine (Reference 17). If sample pH is greater than 9, adjust to pH 7-9 with sulfuric acid.

Maintain solid, semi-solid, oily, and mixed-phase samples in the dark at <4°C from the time of collection until receipt at the laboratory.

Store aqueous samples in the dark at 0-4°C. Store solid, semi-solid, oily, mixed-phase, and tissue samples in the dark at <-10°C.

8.3 Fish and Tissue Samples

8.3.1 Fish may be cleaned, filleted, or processed in other ways in the field, such that the laboratory may expect to receive whole fish, fish fillets, or other tissues for analysis.

8.3.2 Fish collected in the field should be wrapped in aluminum foil, and must be maintained at a temperature less than 4°C from the time of collection until receipt at the laboratory.

8.3.3 Samples must be frozen upon receipt at the laboratory and maintained in the dark at <-10°C until prepared. Maintain unused sample in the dark at <-10°C.

8.4 Holding Times

8.4.1 There are no demonstrated maximum holding times associated with CDDs/CDFs in aqueous, solid, semi-solid, tissues, or other sample matrices. If stored in the dark at 0-4°C and preserved as given above (if required), aqueous samples may be stored for up to one year. Similarly, if stored in the dark at <-10°C, solid, semi-solid, multi-phase, and tissue samples may be stored for up to one year.

8.4.2 Store sample extracts in the dark at <-10°C until analyzed. If stored in the dark at <-10°C, sample extracts may be stored for up to one year.

9.0 Quality Assurance/Quality Control

9.1 Each laboratory that uses this method is required to operate a formal quality assurance program (Reference 18). The minimum requirements of this program consist of an initial demonstration of laboratory capability, analysis of samples spiked with labeled compounds to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

If the method is to be applied to sample matrix other than water (e.g., soils, filter cake, compost, tissue) the most appropriate alternate matrix (Sections 7.6.2 through 7.6.5) is substituted for the reagent water matrix (Section 7.6.1) in all performance tests.

9.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 9.2.

9.1.2 In recognition of advances that are occurring in analytical technology, and to allow the analyst to overcome sample matrix interferences, the analyst is permitted certain options to improve separations or lower the costs of measurements. These options include alternate extraction, concentration, cleanup procedures, and changes in columns and detectors. Alternate determinative techniques, such as the substitution of spectroscopic or immuno-assay techniques, and changes that degrade method performance, are not allowed. If an analytical technique other than the techniques specified in this method is used, that technique must have a specificity equal to or better than the specificity of the techniques in this method for the analytes of interest.

9.1.2.1 Each time a modification is made to this method, the analyst is required to repeat the procedure in Section 9.2. If the detection limit of the method will be affected by the change, the laboratory is required to demonstrate that the MDL (40 CFR Part 136, Appendix B) is lower than one-third the regulatory compliance level or one-third the ML in this method, whichever is higher. If calibration will be affected by the change, the analyst must recalibrate the instrument per Section 10.

9.1.2.2 The laboratory is required to maintain records of modifications made to this method. These records include the following, at a minimum:

9.1.2.2.1 The names, titles, addresses, and telephone numbers of the analyst(s) who performed the analyses and modification, and of the quality control officer who witnessed and will verify the analyses and modifications.

9.1.2.2.2 A listing of pollutant(s) measured, by name and CAS Registry number.

9.1.2.2.3 A narrative stating reason(s) for the modifications.

9.1.2.2.4 Results from all quality control (QC) tests comparing the modified method to this method, including:

a) Calibration (Section 10.5 through 10.7).
b) Calibration verification (Section 15.3).
c) Initial precision and recovery (Section 9.2).
d) Labeled compound recovery (Section 9.3).
e) Analysis of blanks (Section 9.5).
f) Accuracy assessment (Section 9.4).

9.1.2.2.5 Data that will allow an independent reviewer to validate each determination by tracing the instrument output (peak height, area, or other signal) to the final result. These data are to include:

a) Sample numbers and other identifiers.
b) Extraction dates.
c) Analysis dates and times.
d) Analysis sequence/run chronology.
e) Sample weight or volume (Section 11).
f) Extract volume prior to each cleanup step (Section 13).
g) Extract volume after each cleanup step (Section 13).
h) Final extract volume prior to injection (Section 14).
I) Injection volume (Section 14.3).
j) Dilution data, differentiating between dilution of a sample or extract (Section 17.5).
k) Instrument and operating conditions.
l) Column (dimensions, liquid phase, solid support, film thickness, etc).
m) Operating conditions (temperatures, temperature program, flow rates).
n) Detector (type, operating conditions, etc).
o) Chromatograms, printer tapes, and other recordings of raw data.
p) Quantitation reports, data system outputs, and other data to link the raw data to the results reported.

9.1.3 Analyses of method blanks are required to demonstrate freedom from contamination (Section 4.3). The procedures and criteria for analysis of a method blank are described in Sections 9.5 and 15.6.

9.1.4 The laboratory shall spike all samples with labeled compounds to monitor method performance. This test is described in Section 9.3. When results of these spikes indicate atypical method performance for samples, the samples are diluted to bring method performance within acceptable limits. Procedures for dilution are given in Section 17.5.

9.1.5 The laboratory shall, on an ongoing basis, demonstrate through calibration verification and the analysis of the ongoing precision and recovery aliquot that

the analytical system is in control. These procedures are described in Sections 15.1 through 15.5.

9.1.6 The laboratory shall maintain records to define the quality of data that is generated. Development of accuracy statements is described in Section 9.4.

9.2 Initial Precision and Recovery (IPR)—To establish the ability to generate acceptable precision and recovery, the analyst shall perform the following operations.

9.2.1 For low solids (aqueous) samples, extract, concentrate, and analyze four 1 L aliquots of reagent water spiked with the diluted labeled compound spiking solution (Section 7.10.3) and the precision and recovery standard (Section 7.14) according to the procedures in Sections 11 through 18. For an alternative sample matrix, four aliquots of the alternative reference matrix (Section 7.6) are used. All sample processing steps that are to be used for processing samples, including preparation (Section 11), extraction (Section 12), and cleanup (Section 13), shall be included in this test.

9.2.2 Using results of the set of four analyses, compute the average concentration (X) of the extracts in ng/mL and the standard deviation of the concentration (s) in ng/mL for each compound, by isotope dilution for CDDs/CDFs with a labeled analog, and by internal standard for 1,2,3,7,8,9-HxCDD, OCDF, and the labeled compounds.

9.2.3 For each CDD/CDF and labeled compound, compare s and X with the corresponding limits for initial precision and recovery in Table 6. If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, compare s and X with the corresponding limits for initial precision and recovery in Table 6a. If s and X for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, any individual s exceeds the precision limit or any individual X falls outside the range for accuracy, system performance is unacceptable for that compound. Correct the problem and repeat the test (Section 9.2).

9.3 The laboratory shall spike all samples with the diluted labeled compound spiking solution (Section 7.10.3) to assess method performance on the sample matrix.

9.3.1 Analyze each sample according to the procedures in Sections 11 through 18.

9.3.2 Compute the percent recovery of the labeled compounds and the cleanup standard using the internal standard method (Section 17.2).

9.3.3 The recovery of each labeled compound must be within the limits in Table 7 when all 2,3,7,8-substituted CDDs/CDFs are determined, and within the limits in Table 7a when only 2,3,7,8-TCDD and 2,3,7,8-TCDF are determined. If the recovery of any compound falls outside of these limits, method performance is unacceptable for that compound in that sample. To overcome such difficulties, water samples are diluted and smaller amounts of soils, sludges, sediments, and other matrices are reanalyzed per Section 18.4.

9.4 Recovery of labeled compounds from samples should be assessed and records should be maintained.

9.4.1 After the analysis of five samples of a given matrix type (water, soil, sludge, pulp, etc.) for which the labeled compounds pass the tests in Section 9.3, compute the average percent recovery (R) and the standard deviation of the percent recovery (S_R) for the labeled compounds only. Express the assessment as a percent recovery interval from $R-2S_R$ to $R+2S_R$ for each matrix. For example, if R = 90% and S_R = 10% for five analyses of pulp, the recovery interval is expressed as 70-110%.

9.4.2 Update the accuracy assessment for each labeled compound in each matrix on a regular basis (e.g., after each 5-10 new measurements).

9.5 Method Blanks—Reference matrix method blanks are analyzed to demonstrate freedom from contamination (Section 4.3).

9.5.1 Prepare, extract, clean up, and concentrate a method blank with each sample batch (samples of the same matrix started through the extraction process on the same 12-hour shift, to a maximum of 20 samples). The matrix for the method blank shall be similar to sample matrix for the batch, e.g., a 1 L reagent water blank (Section 7.6.1), high-solids reference matrix blank (Section 7.6.2), paper matrix blank (Section 7.6.3); tissue blank (Section 7.6.4) or alternative reference matrix blank (Section 7.6.5). Analyze the blank immediately after analysis of the OPR (Section 15.5) to demonstrate freedom from contamination.

9.5.2 If any 2,3,7,8-substituted CDD/CDF (Table 1) is found in the blank at greater than the minimum level (Table 2) or one-third the regulatory compliance level, whichever is greater; or if any potentially interfering compound is found in the blank at the minimum level for each level of chlorination given in Table 2 (assuming a response factor of 1 relative to the $^{13}C_{12}$-1,2,3,4-TCDD internal standard for compounds not listed in Table 1), analysis of samples is halted until the blank associated with the sample batch shows no evidence of contamination at this level. All samples must be associated with an uncontaminated method blank before the results for those samples may be reported for regulatory compliance purposes.

9.6 QC Check Sample—Analyze the QC Check Sample (Section 7.16) periodically to assure the accuracy of calibration standards and the overall reliability of the analytical process. It is suggested that the QC Check Sample be analyzed at least quarterly.

9.7 The specifications contained in this method can be met if the apparatus used is calibrated properly and then maintained in a calibrated state. The standards used for calibration (Section 10), calibration verification (Section 15.3), and for initial (Section 9.2) and ongoing (Section 15.5) precision and recovery should be identical, so that the most precise results will be obtained. A GC/MS instrument will provide the most reproducible results if dedicated to the settings and conditions required for the analyses of CDDs/CDFs by this method.

9.8 Depending on specific program requirements, field replicates may be collected to determine the precision of the sampling technique, and spiked samples may be required to determine the accuracy of the analysis when the internal standard method is used.

10.0 Calibration

10.1 Establish the operating conditions necessary to meet the minimum retention times for the internal standards in Section 10.2.4 and the relative retention times for the CDDs/CDFs in Table 2.

10.1.1 Suggested GC operating conditions:

Injector temperature:	270°C
Interface temperature:	290°C
Initial temperature:	200°C
Initial time:	Two minutes
Temperature program:	200-220°C, at 5°C/minute
	220°C for 16 minutes
	220-235°C, at 5°C/minute
	235°C for seven minutes
	235-330°C, at 5°C/minute

NOTE: All portions of the column that connect the GC to the ion source shall remain at or above the interface temperature specified above during analysis to preclude condensation of less volatile compounds.

Optimize GC conditions for compound separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, blanks, IPR and OPR aliquots, and samples.

10.1.2 Mass spectrometer (MS) resolution—Obtain a selected ion current profile (SICP) of each analyte in Table 3 at the two exact m/z's specified in Table 8 and at ≥10,000 resolving power by injecting an authentic standard of the CDDs/CDFs either singly or as part of a mixture in which there is no interference between closely eluted components.

10.1.2.1 The analysis time for CDDs/CDFs may exceed the long-term mass stability of the mass spectrometer. Because the instrument is operated in the high-resolution mode, mass drifts of a few ppm (e.g., 5 ppm in mass) can have serious adverse effects on instrument performance. Therefore, a mass drift correction is mandatory and a lock-mass m/z from PFK is used for drift correction. The lock-mass m/z is dependent on the exact m/z's monitored within each descriptor, as shown in Table 8. The level of PFK metered into the HRMS during analyses should be adjusted so that the amplitude of the most intense selected lock-mass m/z signal (regardless of the descriptor number) does not exceed 10% of the full-scale deflection for a given set of detector parameters. Under those conditions, sensitivity changes that might occur during the analysis can be more effectively monitored.

NOTE: Excessive PFK (or any other reference substance) may cause noise problems and contamination of the ion source necessitating increased frequency of source cleaning.

10.1.2.2 If the HRMS has the capability to monitor resolution during the analysis, it is acceptable to terminate the analysis when the resolution falls below 10,000 to save reanalysis time.

10.1.2.3 Using a PFK molecular leak, tune the instrument to meet the minimum required resolving power of 10,000 (10% valley) at m/z 304.9824 (PFK) or any other reference signal close to m/z 304 (from TCDF). For each descriptor (Table 8), monitor and record the resolution and exact m/z's of three to five reference peaks covering the mass range of the descriptor. The resolution must be greater than or equal to 10,000, and the deviation between the exact m/z and the theoretical m/z (Table 8) for each exact m/z monitored must be less than 5 ppm.

10.2 Ion Abundance Ratios, Minimum Levels, Signal-to-Noise Ratios, and Absolute Retention Times—Choose an injection volume of either 1 µL or 2 µL, consistent with the capability of the HRGC/HRMS instrument. Inject a 1 µL or 2 µL aliquot of the CS1 calibration solution (Table 4) using the GC conditions from Section 10.1.1. If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, the operating conditions and specifications below apply to analysis of those compounds only.

10.2.1 Measure the SICP areas for each analyte, and compute the ion abundance ratios at the exact m/z's specified in Table 8. Compare the computed ratio to the theoretical ratio given in Table 9.

10.2.1.1 The exact m/z's to be monitored in each descriptor are shown in Table 8. Each group or descriptor shall be monitored in succession as a function of GC retention time to ensure that all CDDs/CDFs are detected. Additional m/z's may be monitored in each descriptor, and the m/z's may be divided among more than the five descriptors listed in Table 8, provided that the laboratory is able to monitor the m/z's of all the CDDs/CDFs that may elute from the GC in a given retention-time window. If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, the descriptors may be modified to include only the exact m/z's for the tetra- and penta-isomers, the diphenyl ethers, and the lock m/z's.

10.2.1.2 The mass spectrometer shall be operated in a mass-drift correction mode, using perfluorokerosene (PFK) to provide lock m/z's. The lock-mass for each group of m/z's is shown in Table 8. Each lock mass shall be monitored and shall not vary by more than ±20% throughout its respective retention time window. Variations of the lock mass by more than 20% indicate the presence of coeluting interferences that may significantly reduce the sensitivity of the mass spectrometer. Reinjection of another aliquot of the sample extract will not resolve the problem. Additional cleanup of the extract may be required to remove the interferences.

10.2.2 All CDDs/CDFs and labeled compounds in the CS1 standard shall be within the QC limits in Table 9 for their respective ion abundance ratios; otherwise, the mass spectrometer shall be adjusted and this test repeated until the m/z ratios fall within the limits specified. If the adjustment alters the resolution of the mass spectrometer, resolution shall be verified (Section 10.1.2) prior to repeat of the test.

10.2.3 Verify that the HRGC/HRMS instrument meets the minimum levels in Table 2. The peaks representing the CDDs/CDFs and labeled compounds in the CS1 calibration standard must have signal-to-noise ratios (S/N) greater than or equal to 10.0. Otherwise, the mass spectrometer shall be adjusted and this test repeated until the minimum levels in Table 2 are met.

10.2.4 The absolute retention time of $^{13}C_{12}$-1,2,3,4-TCDD (Section 7.12) shall exceed 25.0 minutes on the DB-5 column, and the retention time of $^{13}C_{12}$-1,2,3,4-TCDD shall exceed 15.0 minutes on the DB-225 column; otherwise, the GC temperature program shall be adjusted and this test repeated until the above-stated minimum retention time criteria are met.

10.3 Retention-Time Windows—Analyze the window defining mixtures (Section 7.15) using the optimized temperature program in Section 10.1. Table 5 gives the elution order (first/last) of the window-defining compounds. If 2,3,7,8-TCDD and 2,3,7,8-TCDF only are to be analyzed, this test is not required.

10.4 Isomer Specificity

10.4.1 Analyze the isomer specificity test standards (Section 7.15) using the procedure in Section 14 and the optimized conditions for sample analysis (Section 10.1.1).

10.4.2 Compute the percent valley between the GC peaks that elute most closely to the 2,3,7,8-TCDD and TCDF isomers, on their respective columns, per Figures 6 and 7.

10.4.3 Verify that the height of the valley between the most closely eluted isomers and the 2,3,7,8-substituted isomers is less than 25% (computed as 100 x/y in Figures 6 and 7). If the valley exceeds 25%, adjust the analytical conditions and repeat the test or replace the GC column and recalibrate (Sections 10.1.2 through 10.7).

10.5 Calibration by Isotope Dilution—Isotope dilution calibration is used for the 15 2,3,7,8-substituted CDDs/CDFs for which labeled compounds are added to samples prior to extraction. The reference compound for each CDD/CDF compound is shown in Table 2.

10.5.1 A calibration curve encompassing the concentration range is prepared for each compound to be determined. The relative response (RR) (labeled to native) vs. concentration in standard solutions is plotted or computed using a linear regression. Relative response is determined according to the procedures described below. Five calibration points are employed.

10.5.2 The response of each CDD/CDF relative to its labeled analog is determined using the area responses of both the primary and secondary exact m/z's specified in Table 8, for each calibration standard, as follows:

$$RR = \frac{(A1_n + A2_n)\ C_l}{(A1_l + A2_l)\ C_n}$$

where,

$A1_n$ and $A2_n$ = The areas of the primary and secondary m/z's for the CDD/CDF.

$A1_l$ and $A2_l$ = The areas of the primary and secondary m/z's for the labeled compound.

C_l = The concentration of the labeled compound in the calibration standard (Table 4).

C_n = The concentration of the native compound in the calibration standard (Table 4).

10.5.3 To calibrate the analytical system by isotope dilution, inject a volume of calibration standards CS1 through CS5 (Section 7.13 and Table 4) identical to the volume chosen in Section 10.2, using the procedure in Section 14 and the conditions in Section 10.1.1 and Table 2. Compute the relative response (RR) at each concentration.

10.5.4 Linearity—If the relative response for any compound is constant (less than 20% coefficient of variation) over the five-point calibration range, an averaged relative response may be used for that compound; otherwise, the complete calibration curve for that compound shall be used over the five-point calibration range.

10.6 Calibration by Internal Standard—The internal standard method is applied to determination of 1,2,3,7,8,9-HxCDD (Section 17.1.2), OCDF (Section 17.1.1), the non 2,3,7,8-substituted compounds, and to the determination of labeled compounds for intralaboratory statistics (Sections 9.4 and 15.5.4).

10.6.1 Response factors—Calibration requires the determination of response factors (RF) defined by the following equation:

$$RF = \frac{(A1_s + A2_s)\ C_{is}}{(A1_{is} + A2_{is})\ C_s}$$

where,

$A1_s$ and $A2_s$ = The areas of the primary and secondary m/z's for the CDD/CDF.

$A1_{is}$ and $A2_{is}$ = The areas of the primary and secondary m/z's for the internal standard.

C_{is} = The concentration of the internal standard (Table 4).

C_s = The concentration of the compound in the calibration standard (Table 4).

NOTE: There is only one m/z for $^{37}Cl_4$-2,3,7,8-TCDD. See Table 8.

10.6.2 To calibrate the analytical system by internal standard, inject 1.0 µL or 2.0 µL of calibration standards CS1 through CS5 (Section 7.13 and Table 4) using the procedure in Section 14 and the conditions in Section 10.1.1 and Table 2. Compute the response factor (RF) at each concentration.

10.6.3 Linearity—If the response factor (RF) for any compound is constant (less than 35% coefficient of variation) over the five-point calibration range, an averaged response factor may be used for that compound; otherwise, the complete calibration curve for that compound shall be used over the five-point range.

10.7 Combined Calibration—By using calibration solutions (Section 7.13 and Table 4) containing the CDDs/CDFs and labeled compounds and the internal standards, a single set of analyses can be used to produce calibration curves for the isotope dilution and internal standard methods. These curves are verified each shift (Section 15.3) by analyzing the calibration verification standard (VER, Table 4). Recalibration is required if any of the calibration verification criteria (Section 15.3) cannot be met.

10.8 Data Storage—MS data shall be collected, recorded, and stored.

10.8.1 Data acquisition—The signal at each exact m/z shall be collected repetitively throughout the monitoring period and stored on a mass storage device.

10.8.2 Response factors and multipoint calibrations—The data system shall be used to record and maintain lists of response factors (response ratios for isotope dilution) and multipoint calibration curves. Computations of relative standard deviation (coefficient of variation) shall be used to test calibration linearity. Statistics on initial performance (Section 9.2) and ongoing performance (Section 15.5) should be computed and maintained, either on the instrument data system, or on a separate computer system.

11.0 Sample Preparation

11.1 Sample preparation involves modifying the physical form of the sample so that the CDDs/CDFs can be extracted efficiently. In general, the samples must be in a liquid form or in the form of finely divided solids in order for efficient extraction to take place. Table 10 lists the phases and suggested quantities for extraction of various sample matrices.

For samples known or expected to contain high levels of the CDDs/CDFs, the smallest sample size representative of the entire sample should be used (see Section 17.5).

For all samples, the blank and IPR/OPR aliquots must be processed through the same steps as the sample to check for contamination and losses in the preparation processes.

11.1.1 For samples that contain particles, percent solids and particle size are determined using the procedures in Sections 11.2 and 11.3, respectively.

11.1.2 Aqueous samples—Because CDDs/CDFs may be bound to suspended particles, the preparation of aqueous samples is dependent on the solids content of the sample.

11.1.2.1 Aqueous samples visibly absent particles are prepared per Section 11.4 and extracted directly using the separatory funnel or SPE techniques in Sections 12.1 or 12.2, respectively.

11.1.2.2 Aqueous samples containing visible particles and containing one percent suspended solids or less are prepared using the procedure in Section 11.4. After preparation, the sample is extracted directly using the SPE technique in 12.2 or filtered per Section 11.4.3. After filtration, the particles and filter are extracted using the SDS procedure in Section 12.3 and the filtrate is extracted using the separatory funnel procedure in Section 12.1.

11.1.2.3 For aqueous samples containing greater than one percent solids, a sample aliquot sufficient to provide 10 g of dry solids is used, as described in Section 11.5.

11.1.3 Solid samples are prepared using the procedure described in Section 11.5 followed by extraction via the SDS procedure in Section 12.3.

11.1.4 Multiphase samples—The phase(s) containing the CDDs/CDFs is separated from the non-CDD/CDF phase using pressure filtration and centrifugation, as described in Section 11.6. The CDDs/CDFs will be in the organic phase in a multiphase sample in which an organic phase exists.

11.1.5 Procedures for grinding, homogenization, and blending of various sample phases are given in Section 11.7.

11.1.6 Tissue samples—Preparation procedures for fish and other tissues are given in Section 11.8.

11.2 Determination of Percent Suspended Solids

NOTE: This aliquot is used for determining the solids content of the sample, not for determination of CDDs/CDFs.

11.2.1 Aqueous liquids and multi-phase samples consisting of mainly an aqueous phase.

11.2.1.1 Dessicate and weigh a GF/D filter (Section 6.5.3) to three significant figures.

11.2.1.2 Filter 10.0 ±0.02 mL of well-mixed sample through the filter.

11.2.1.3 Dry the filter a minimum of 12 hours at 110 ±5°C and cool in a dessicator.

11.2.1.4 Calculate percent solids as follows:

$$\%solids = \frac{weight\ of\ sample\ aliquot\ after\ drying\ (g) - weight\ of\ filter\ (g)}{10\ g} \times 100$$

11.2.2 Non-aqueous liquids, solids, semi-solid samples, and multi-phase samples in which the main phase is not aqueous; but not tissues.

11.2.2.1 Weigh 5-10 g of sample to three significant figures in a tared beaker.

11.2.2.2 Dry a minimum of 12 hours at 110 ±5°C, and cool in a dessicator.

11.2.2.3 Calculate percent solids as follows:

$$\%\ solids = \frac{weight\ of\ sample\ aliquot\ after\ drying}{weight\ of\ sample\ aliquot\ before\ drying} \times 100$$

11.3 Determination of Particle Size

11.3.1 Spread the dried sample from Section 11.2.2.2 on a piece of filter paper or aluminum foil in a fume hood or glove box.

11.3.2 Estimate the size of the particles in the sample. If the size of the largest particles is greater than 1 mm, the particle size must be reduced to 1 mm or less prior to extraction using the procedures in Section 11.7.

11.4 Preparation of Aqueous Samples Containing 1% Suspended Solids or Less

11.4.1 Aqueous samples visibly absent particles are prepared per the procedure below and extracted directly using the separatory funnel or SPE techniques in Sections 12.1 or 12.2, respectively. Aqueous samples containing visible particles and one percent suspended solids or less are prepared using the procedure below and extracted using either the SPE technique in Section 12.2 or further prepared using the filtration procedure in Section 11.4.3. The filtration procedure is followed by SDS extraction of the filter and particles (Section 12.3) and separatory funnel extraction of the filtrate (Section 12.1). The SPE procedure is followed by SDS extraction of the filter and disk.

11.4.2 Preparation of sample and QC aliquots

11.4.2.1 Mark the original level of the sample on the sample bottle for reference. Weigh the sample plus bottle to ±1 g.

11.4.2.2 Spike 1.0 mL of the diluted labeled-compound spiking solution (Section 7.10.3) into the sample bottle. Cap the bottle and mix the sample by careful shaking. Allow the sample to equilibrate for one to two hours, with occasional shaking.

11.4.2.3 For each sample or sample batch (to a maximum of 20 samples) to be extracted during the same 12-hour shift, place two 1.0 L aliquots of reagent water in clean sample bottles or flasks.

11.4.2.4 Spike 1.0 mL of the diluted labeled-compound spiking solution (Section 7.10.3) into both reagent water aliquots. One of these aliquots will serve as the method blank.

11.4.2.5 Spike 1.0 mL of the PAR standard (Section 7.14) into the remaining reagent water aliquot. This aliquot will serve as the OPR (Section 15.5).

11.4.2.6 If SPE is to be used, add 5 mL of methanol to the sample, cap and shake the sample to mix thoroughly, and proceed to Section 12.2 for extraction. If SPE is not to be used, and the sample is visibly absent particles, proceed to Section 12.1 for extraction. If SPE is not to be used and the sample contains visible particles, proceed to the following section for filtration of particles.

11.4.3 Filtration of particles

11.4.3.1 Assemble a Buchner funnel (Section 6.5.5) on top of a clean filtration flask. Apply vacuum to the flask, and pour the entire contents of the sample bottle through a glass-fiber filter (Section 6.5.6) in the Buchner funnel, swirling the sample remaining in the bottle to suspend any particles.

11.4.3.2 Rinse the sample bottle twice with approximately 5 mL portions of reagent water to transfer any remaining particles onto the filter.

11.4.3.3 Rinse any particles off the sides of the Buchner funnel with small quantities of reagent water.

11.4.3.4 Weigh the empty sample bottle to ±1 g. Determine the weight of the sample by difference. Save the bottle for further use.

11.4.3.5 Extract the filtrate using the separatory funnel procedure in Section 12.1.

11.4.3.6 Extract the filter containing the particles using the SDS procedure in Section 12.3.

11.5 Preparation of Samples Containing Greater Than 1% Solids

11.5.1 Weigh a well-mixed aliquot of each sample (of the same matrix type) sufficient to provide 10 g of dry solids (based on the solids determination in Section 11.2) into a clean beaker or glass jar.

11.5.2 Spike 1.0 mL of the diluted labeled compound spiking solution (Section 7.10.3) into the sample.

11.5.3 For each sample or sample batch (to a maximum of 20 samples) to be extracted during the same 12-hour shift, weigh two 10 g aliquots of the appropriate reference matrix (Section 7.6) into clean beakers or glass jars.

11.5.4 Spike 1.0 mL of the diluted labeled compound spiking solution (Section 7.10.3) into each reference matrix aliquot. One aliquot will serve as the method blank. Spike 1.0 mL of the PAR standard (Section 7.14) into the other reference matrix aliquot. This aliquot will serve as the OPR (Section 15.5).

11.5.5 Stir or tumble and equilibrate the aliquots for one to two hours.

11.5.6 Decant excess water. If necessary to remove water, filter the sample through a glass-fiber filter and discard the aqueous liquid.

11.5.7 If particles >1mm are present in the sample (as determined in Section 11.3.2), spread the sample on clean aluminum foil in a hood. After the sample is dry, grind to reduce the particle size (Section 11.7).

11.5.8 Extract the sample and QC aliquots using the SDS procedure in Section 12.3.

11.6 Multiphase Samples

11.6.1 Using the percent solids determined in Section 11.2.1 or 11.2.2, determine the volume of sample that will provide 10 g of solids, up to 1 L of sample.

11.6.2 Pressure filter the amount of sample determined in Section 11.6.1 through Whatman GF/D glass-fiber filter paper (Section 6.5.3). Pressure filter the blank and OPR aliquots through GF/D papers also. If necessary to separate the phases and/or settle the solids, centrifuge these aliquots prior to filtration.

11.6.3 Discard any aqueous phase (if present). Remove any non-aqueous liquid present and reserve the maximum amount filtered from the sample (Section 11.6.1) or 10 g, whichever is less, for combination with the solid phase (Section 12.3.5).

11.6.4 If particles >1mm are present in the sample (as determined in Section 11.3.2) and the sample is capable of being dried, spread the sample and QC aliquots on clean aluminum foil in a hood. After the aliquots are dry or if the sample cannot be dried, reduce the particle size using the procedures in Section 11.7 and extract the reduced particles using the SDS procedure in Section 12.3. If particles >1mm are not present, extract the particles and filter in the sample and QC aliquots directly using the SDS procedure in Section 12.3.

11.7 Sample grinding, homogenization, or blending—Samples with particle sizes greater than 1 mm (as determined in Section 11.3.2) are subjected to grinding, homogenization, or blending. The method of reducing particle size to less than 1 mm is matrix-dependent. In general, hard particles can be reduced by grinding with a mortar and pestle. Softer particles can be reduced by grinding in a Wiley mill or meat grinder, by homogenization, or in a blender.

11.7.1 Each size-reducing preparation procedure on each matrix shall be verified by running the tests in Section 9.2 before the procedure is employed routinely.

11.7.2 The grinding, homogenization, or blending procedures shall be carried out in a glove box or fume hood to prevent particles from contaminating the work environment.

11.7.3 Grinding—Certain papers and pulps, slurries, and amorphous solids can be ground in a Wiley mill or heavy duty meat grinder. In some cases, reducing the temperature of the sample to freezing or to dry ice or liquid nitrogen temperatures can aid in the grinding process. Grind the sample aliquots from Section 11.5.7 or 11.6.4 in a clean grinder. Do not allow the sample temperature

to exceed 50°C. Grind the blank and reference matrix aliquots using a clean grinder.

11.7.4 Homogenization or blending. Particles that are not ground effectively, or particles greater than 1 mm in size after grinding, can often be reduced in size by high speed homogenization or blending. Homogenize and/or blend the particles or filter from Section 11.5.7 or 11.6.4 for the sample, blank, and OPR aliquots.

11.7.5 Extract the aliquots using the SDS procedure in Section 12.3.

11.8 Fish and Other Tissues—Prior to processing tissue samples, the laboratory must determine the exact tissue to be analyzed. Common requests for analysis of fish tissue include whole fish-skin on, whole fish-skin removed, edible fish fillets (filleted in the field or by the laboratory), specific organs, and other portions. Once the appropriate tissue has been determined, the sample must be homogenized.

11.8.1 Homogenization

11.8.1.1 Samples are homogenized while still frozen, where practical. If the laboratory must dissect the whole fish to obtain the appropriate tissue for analysis, the unused tissues may be rapidly refrozen and stored in a clean glass jar for subsequent use.

11.8.1.2 Each analysis requires 10 g of tissue (wet weight). Therefore, the laboratory should homogenize at least 20 g of tissue to allow for re-extraction of a second aliquot of the same homogenized sample, if re-analysis is required. When whole fish analysis is necessary, the entire fish is homogenized.

11.8.1.3 Homogenize the sample in a tissue homogenizer (Section 6.3.3) or grind in a meat grinder (Section 6.3.4). Cut tissue too large to feed into the grinder into smaller pieces. To assure homogeneity, grind three times.

11.8.1.4 Transfer approximately 10 g (wet weight) of homogenized tissue to a clean, tared, 400-500 mL beaker. For the alternate HCl digestion/extraction, transfer the tissue to a clean, tared 500-600 mL wide-mouth bottle. Record the weight to the nearest 10 mg.

11.8.1.5 Transfer the remaining homogenized tissue to a clean jar with a fluoropolymer-lined lid. Seal the jar and store the tissue at <-10°C. Return any tissue that was not homogenized to its original container and store at <-10°C.

11.8.2 QC aliquots

11.8.2.1 Prepare a method blank by adding approximately 10 g of the oily liquid reference matrix (Section 7.6.4) to a 400-500 mL beaker. For the alternate HCl digestion/extraction, add the reference matrix to a 500-600 mL wide-mouth bottle. Record the weight to the nearest 10 mg.

11.8.2.2 Prepare a precision and recovery aliquot by adding approximately 10 g of the oily liquid reference matrix (Section 7.6.4) to a separate 400-500 mL beaker or wide-mouth bottle, depending on the extraction procedure to be used. Record the weight to the nearest 10 mg. If the initial precision and recovery test is to be performed, use four aliquots; if the ongoing precision and recovery test is to be performed, use a single aliquot.

11.8.3 Spiking

11.8.3.1 Spike 1.0 mL of the labeled compound spiking solution (Section 7.10.3) into the sample, blank, and OPR aliquot.

11.8.3.2 Spike 1.0 mL of the PAR standard (Section 7.14) into the OPR aliquot.

11.8.4 Extract the aliquots using the procedures in Section 12.4.

12.0 Extraction and Concentration

Extraction procedures include separatory funnel (Section 12.1) and solid phase (Section 12.2) for aqueous liquids; Soxhlet/Dean-Stark (Section 12.3) for solids, filters, and SPE disks; and Soxhlet extraction (Section 12.4.1) and HCl digestion (Section 12.4.2) for tissues. Acid/base back-extraction (Section 12.5) is used for initial cleanup of extracts.

Macro-concentration procedures include rotary evaporation (Section 12.6.1), heating mantle (Section 12.6.2), and Kuderna-Danish (K-D) evaporation (Section 12.6.3). Micro-concentration uses nitrogen blowdown (Section 12.7).

12.1 Separatory funnel extraction of filtrates and of aqueous samples visibly absent particles.

12.1.1 Pour the spiked sample (Section 11.4.2.2) or filtrate (Section 11.4.3.5) into a 2 L separatory funnel. Rinse the bottle or flask twice with 5 mL of reagent water and add these rinses to the separatory funnel.

12.1.2 Add 60 mL methylene chloride to the empty sample bottle (Section 12.1.1), seal, and shake 60 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting. Allow the organic layer to separate from the aqueous phase for a minimum of 10 minutes. If an emulsion forms and is more than one-third the volume of the solvent layer, employ mechanical techniques to complete the phase separation (see note below). Drain the methylene chloride extract through a solvent-rinsed glass funnel approximately one-half full of granular

anhydrous sodium sulfate (Section 7.2.1) supported on clean glass-fiber paper into a solvent-rinsed concentration device (Section 12.6).

NOTE: If an emulsion forms, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, use of phase separation paper, centrifugation, use of an ultrasonic bath with ice, addition of NaCl, or other physical methods. Alternatively, solid-phase or other extraction techniques may be used to prevent emulsion formation. Any alternative technique is acceptable so long as the requirements in Section 9 are met.

Experience with aqueous samples high in dissolved organic materials (e.g., paper mill effluents) has shown that acidification of the sample prior to extraction may reduce the formation of emulsions. Paper industry methods suggest that the addition of up to 400 mL of ethanol to a 1 L effluent sample may also reduce emulsion formation. However, studies by EPA suggest that the effect may be a result of sample dilution, and that the addition of reagent water may serve the same function. Mechanical techniques may still be necessary to complete the phase separation. If either acidification or addition of ethanol is utilized, the laboratory must perform the startup tests described in Section 9.2 using the same techniques.

12.1.3 Extract the water sample two more times with 60 mL portions of methylene chloride. Drain each portion through the sodium sulfate into the concentrator. After the third extraction, rinse the separatory funnel with at least 20 mL of methylene chloride, and drain this rinse through the sodium sulfate into the concentrator. Repeat this rinse at least twice. Set aside the funnel with sodium sulfate if the extract is to be combined with the extract from the particles.

12.1.4 Concentrate the extract using one of the macro-concentration procedures in Section 12.6.

12.1.4.1 If the extract is from a sample visibly absent particles (Section 11.1.2.1), adjust the final volume of the concentrated extract to approximately 10 mL with hexane, transfer to a 250 mL separatory funnel, and back-extract using the procedure in Section 12.5.

12.1.4.2 If the extract is from the aqueous filtrate (Section 11.4.3.5), set aside the concentration apparatus for addition of the SDS extract from the particles (Section 12.3.9.1.2).

12.2 SPE of Samples Containing Less Than 1% Solids (References 19-20)

12.2.1 Disk preparation

12.2.1.1 Place an SPE disk on the base of the filter holder (Figure 4) and wet with toluene. While holding a GMF 150 filter above the SPE disk with tweezers, wet the filter with toluene and lay the filter on the SPE disk, making sure that air is not trapped between the filter and disk. Clamp the filter and SPE disk between the 1 L glass reservoir and the vacuum filtration flask.

12.2.1.2 Rinse the sides of the filtration flask with approx 15 mL of toluene using a squeeze bottle or syringe. Apply vacuum momentarily until a few drops appear at the drip tip. Release the vacuum and allow the filter/disk to soak for approx one minute. Apply vacuum and draw all of the toluene through the filter/disk. Repeat the wash step with approx 15 mL of acetone and allow the filter/disk to air dry.

12.2.1.3 Re-wet the filter/disk with approximately 15 mL of methanol, allowing the filter/disk to soak for approximately one minute. Pull the methanol through the filter/disk using the vacuum, but retain a layer of methanol approximately 1 mm thick on the filter. Do not allow the disk to go dry from this point until the end of the extraction.

12.2.1.4 Rinse the filter/disk with two 50-mL portions of reagent water by adding the water to the reservoir and pulling most through, leaving a layer of water on the surface of the filter.

12.2.2 Extraction

12.2.2.1 Pour the spiked sample (Section 11.4.2.2), blank (Section 11.4.2.4), or IPR/OPR aliquot (Section 11.4.2.5) into the reservoir and turn on the vacuum to begin the extraction. Adjust the vacuum to complete the extraction in no less than 10 minutes. For samples containing a high concentration of particles (suspended solids), filtration times may be eight hours or longer.

12.2.2.2 Before all of the sample has been pulled through the filter/disk, rinse the sample bottle with approximately 50 mL of reagent water to remove any solids, and pour into the reservoir. Pull through the filter/disk. Use additional reagent water rinses until all visible solids are removed.

12.2.2.3 Before all of the sample and rinses have been pulled through the filter/disk, rinse the sides of the reservoir with small portions of reagent water.

12.2.2.4 Allow the filter/disk to dry, then remove the filter and disk and place in a glass Petri dish. Extract the filter and disk per Section 12.3.

12.3 SDS Extraction of Samples Containing Particles, and of Filters and/or Disks

12.3.1 Charge a clean extraction thimble (Section 6.4.2.2) with 5.0 g of 100/200 mesh silica (Section 7.5.1.1) topped with 100 g of quartz sand (Section 7.3.2).

NOTE: Do not disturb the silica layer throughout the extraction process.

12.3.2 Place the thimble in a clean extractor. Place 30-40 mL of toluene in the receiver and 200-250 mL of toluene in the flask.

12.3.3 Pre-extract the glassware by heating the flask until the toluene is boiling. When properly adjusted, one to two drops of toluene will fall per second from the condenser tip into the receiver. Extract the apparatus for a minimum of three hours.

12.3.4 After pre-extraction, cool and disassemble the apparatus. Rinse the thimble with toluene and allow to air dry.

12.3.5 Load the wet sample, filter, and/or disk from Section 11.4.3.6, 11.5.8, 11.6.4, 11.7.3, 11.7.4, or 12.2.2.4 and any nonaqueous liquid from Section 11.6.3 into the thimble and manually mix into the sand layer with a clean metal spatula, carefully breaking up any large lumps of sample.

12.3.6 Reassemble the pre-extracted SDS apparatus, and add a fresh charge of toluene to the receiver and reflux flask. Apply power to the heating mantle to begin refluxing. Adjust the reflux rate to match the rate of percolation through the sand and silica beds until water removal lessens the restriction to toluene flow. Frequently check the apparatus for foaming during the first two hours of extraction. If foaming occurs, reduce the reflux rate until foaming subsides.

12.3.7 Drain the water from the receiver at one to two hours and eight to nine hours, or sooner if the receiver fills with water. Reflux the sample for a total of 16-24 hours. Cool and disassemble the apparatus. Record the total volume of water collected.

12.3.8 Remove the distilling flask. Drain the water from the Dean-Stark receiver and add any toluene in the receiver to the extract in the flask.

12.3.9 Concentrate the extract using one of the macro-concentration procedures in Section 12.6 per the following:

12.3.9.1 Extracts from the particles in an aqueous sample containing less than 1% solids (Section 11.4.3.6).

12.3.9.1.1 Concentrate the extract to approximately 5 mL using the rotary evaporator or heating mantle procedures in Section 12.6.1 or 12.6.2.

12.3.9.1.2 Quantitatively transfer the extract through the sodium sulfate (Section 12.1.3) into the apparatus that was set aside (Section 12.1.4.2) and reconcentrate to the level of the toluene.

12.3.9.1.3 Adjust to approximately 10 mL with hexane, transfer to a 250 mL separatory funnel, and proceed with back-extraction (Section 12.5).

12.3.9.2 Extracts from particles (Sections 11.5 through 11.6) or from the SPE filter and disk (Section 12.2.2.4)—Concentrate to approximately 10 mL using the rotary evaporator or heating mantle (Section 12.6.1

or 12.6.2), transfer to a 250 mL separatory funnel, and proceed with back-extraction (Section 12.5).

12.4 Extraction of Tissue—Two procedures are provided for tissue extraction.

12.4.1 Soxhlet extraction (Reference 21)

12.4.1.1 Add 30-40 g of powdered anhydrous sodium sulfate to each of the beakers (Section 11.8.4) and mix thoroughly. Cover the beakers with aluminum foil and allow to equilibrate for 12-24 hours. Remix prior to extraction to prevent clumping.

12.4.1.2 Assemble and pre-extract the Soxhlet apparatus per Sections 12.3.1 through 12.3.4, except use the methylene chloride:hexane (1:1) mixture for the pre-extraction and rinsing and omit the quartz sand. The Dean Stark moisture trap may also be omitted, if desired.

12.4.1.3 Reassemble the pre-extracted Soxhlet apparatus and add a fresh charge of methylene chloride:hexane to the reflux flask.

12.4.1.4 Transfer the sample/sodium sulfate mixture (Section 12.4.1.1) to the Soxhlet thimble, and install the thimble in the Soxhlet apparatus.

12.4.1.5 Rinse the beaker with several portions of solvent mixture and add to the thimble. Fill the thimble/receiver with solvent. Extract for 18-24 hours.

12.4.1.6 After extraction, cool and disassemble the apparatus.

12.4.1.7 Quantitatively transfer the extract to a macro-concentration device (Section 12.6), and concentrate to near dryness. Set aside the concentration apparatus for re-use.

12.4.1.8 Complete the removal of the solvent using the nitrogen blowdown procedure (Section 12.7) and a water bath temperature of 60°C. Weigh the receiver, record the weight, and return the receiver to the blowdown apparatus, concentrating the residue until a constant weight is obtained.

12.4.1.9 Percent lipid determination—The lipid content is determined by extraction of tissue with the same solvent system (methylene chloride:hexane) that was used in EPA's National Dioxin Study (Reference 22) so that lipid contents are consistent with that study.

12.4.1.9.1 Redissolve the residue in the receiver in hexane and spike 1.0 mL of the cleanup standard (Section 7.11) into the solution.

12.4.1.9.2 Transfer the residue/hexane to the anthropogenic isolation column (Section 13.7.1) or bottle for the acidified silica gel batch cleanup (Section 13.7.2), retaining the boiling chips in the concentration apparatus. Use several rinses to assure that all material is transferred. If necessary, sonicate or heat the receiver slightly to assure that all material is re-dissolved. Allow the receiver to dry. Weigh the receiver and boiling chips.

12.4.1.9.3 Calculate the lipid content to the nearest three significant figures as follows:

$$Percent\ lipid = \frac{Weight\ of\ residue\ (g)}{Weight\ of\ tissue\ (g)} \times 100$$

12.4.1.9.4 It is not necessary to determine the lipid content of the blank, IPR, or OPR aliquots.

12.4.2 HCl digestion/extraction and concentration (References 23-26)

12.4.2.1 Add 200 mL of 6 N HCl and 200 mL of methylene chloride:hexane (1:1) to the sample and QC aliquots (Section 11.8.4).

12.4.2.2 Cap and shake each bottle one to three times. Loosen the cap in a hood to vent excess pressure. Shake each bottle for 10-30 seconds and vent.

12.4.2.3 Tightly cap and place on shaker. Adjust the shaker action and speed so that the acid, solvent, and tissue are in constant motion. However, take care to avoid such violent action that the bottle may be dislodged from the shaker. Shake for 12-24 hours.

12.4.2.4 After digestion, remove the bottles from the shaker. Allow the bottles to stand so that the solvent and acid layers separate.

12.4.2.5 Decant the solvent through a glass funnel with glass-fiber filter (Sections 6.5.2 through 6.5.3) containing approximately 10 g of granular anhydrous sodium sulfate (Section 7.2.1) into a macro-concentration apparatus (Section 12.6). Rinse the contents of the bottle with two 25 mL portions of hexane and pour through the sodium sulfate into the apparatus.

12.4.2.6 Concentrate the solvent to near dryness using a macro-concentration procedure (Section 12.6).

12.4.2.7 Complete the removal of the solvent using the nitrogen blowdown apparatus (Section 12.7) and a water bath temperature of 60°C. Weigh the receiver, record the weight, and return the receiver to the blowdown apparatus, concentrating the residue until a constant weight is obtained.

12.4.2.8 Percent lipid determination—The lipid content is determined in the same solvent system [methylene chloride:hexane (1:1)] that was used in EPA's National Dioxin Study (Reference 22) so that lipid contents are consistent with that study.

12.4.2.8.1 Redissolve the residue in the receiver in hexane and spike 1.0 mL of the cleanup standard (Section 7.11) into the solution.

12.4.2.8.2 Transfer the residue/hexane to the narrow-mouth 100-200 mL bottle retaining the boiling chips in the receiver. Use several rinses to assure that all material is transferred, to a maximum hexane volume of approximately 70 mL. Allow the receiver to dry. Weigh the receiver and boiling chips.

12.4.2.8.3 Calculate the percent lipid per Section 12.4.1.9.3. It is not necessary to determine the lipid content of the blank, IPR, or OPR aliquots.

12.4.2.9 Clean up the extract per Section 13.7.3.

12.5 Back-Extraction with Base and Acid

12.5.1 Spike 1.0 mL of the cleanup standard (Section 7.11) into the separatory funnels containing the sample and QC extracts from Section 12.1.4.1, 12.3.9.1.3, or 12.3.9.2.

12.5.2 Partition the extract against 50 mL of potassium hydroxide solution (Section 7.1.1). Shake for two minutes with periodic venting into a hood. Remove and discard the aqueous layer. Repeat the base washing until no color is visible in the aqueous layer, to a maximum of four washings. Minimize contact time between the extract and the base to prevent degradation of the CDDs/CDFs. Stronger potassium hydroxide solutions may be employed for back-extraction, provided that the laboratory meets the specifications for labeled compound recovery and demonstrates acceptable performance using the procedure in Section 9.2.

12.5.3 Partition the extract against 50 mL of sodium chloride solution (Section 7.1.4) in the same way as with base. Discard the aqueous layer.

12.5.4 Partition the extract against 50 mL of sulfuric acid (Section 7.1.2) in the same way as with base. Repeat the acid washing until no color is visible in the aqueous layer, to a maximum of four washings.

12.5.5 Repeat the partitioning against sodium chloride solution and discard the aqueous layer.

12.5.6 Pour each extract through a drying column containing 7-10 cm of granular anhydrous sodium sulfate (Section 7.2.1). Rinse the separatory funnel with 30-50 mL of solvent, and pour through the drying column. Collect each extract in a round bottom flask. Re-concentrate the sample and QC aliquots per Sections 12.6 through 12.7, and clean up the samples and QC aliquots per Section 13.

12.6 Macro-Concentration—Extracts in toluene are concentrated using a rotary evaporator or a heating mantle; extracts in methylene chloride or hexane are concentrated using a rotary evaporator, heating mantle, or Kuderna-Danish apparatus.

12.6.1 Rotary evaporation—Concentrate the extracts in separate round-bottom flasks.

12.6.1.1 Assemble the rotary evaporator according to manufacturer's instructions, and warm the water bath to 45°C. On a daily basis, preclean the rotary evaporator by concentrating 100 mL of clean extraction solvent through the system. Archive both the concentrated solvent and the solvent in the catch flask for a contamination check if necessary. Between samples, three 2-3 mL aliquots of solvent should be rinsed down the feed tube into a waste beaker.

12.6.1.2 Attach the round-bottom flask containing the sample extract to the rotary evaporator. Slowly apply vacuum to the system, and begin rotating the sample flask.

12.6.1.3 Lower the flask into the water bath, and adjust the speed of rotation and the temperature as required to complete concentration in 15-20 minutes. At the proper rate of concentration, the flow of solvent into the receiving flask will be steady, but no bumping or visible boiling of the extract will occur.

NOTE: If the rate of concentration is too fast, analyte loss may occur.

12.6.1.4 When the liquid in the concentration flask has reached an apparent volume of approximately 2 mL, remove the flask from the water bath and stop the rotation. Slowly and carefully admit air into the system. Be sure not to open the valve so quickly that the sample is blown out of the flask. Rinse the feed tube with approximately 2 mL of solvent.

12.6.1.5 Proceed to Section 12.6.4 for preparation for back-extraction or micro-concentration and solvent exchange.

12.6.2 Heating mantle—Concentrate the extracts in separate round-bottom flasks.

12.6.2.1 Add one or two clean boiling chips to the round-bottom flask, and attach a three-ball macro Snyder column. Prewet the column by adding approximately 1 mL of solvent through the top. Place the round-bottom flask in a heating mantle, and apply heat as required to complete the concentration in 15-20 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood.

12.6.2.2 When the liquid has reached an apparent volume of approximately 10 mL, remove the round-bottom flask from the heating mantle and allow the solvent to drain and cool for at least 10 minutes.

Remove the Snyder column and rinse the glass joint into the receiver with small portions of solvent.

12.6.2.3 Proceed to Section 12.6.4 for preparation for back-extraction or micro-concentration and solvent exchange.

12.6.3 Kuderna-Danish (K-D)—Concentrate the extracts in separate 500 mL K-D flasks equipped with 10 mL concentrator tubes. The K-D technique is used for solvents such as methylene chloride and hexane. Toluene is difficult to concentrate using the K-D technique unless a water bath fed by a steam generator is used.

12.6.3.1 Add one to two clean boiling chips to the receiver. Attach a three-ball macro Snyder column. Prewet the column by adding approximately 1 mL of solvent through the top. Place the K-D apparatus in a hot water bath so that the entire lower rounded surface of the flask is bathed with steam.

12.6.3.2 Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood.

12.6.3.3 When the liquid has reached an apparent volume of 1 mL, remove the K-D apparatus from the bath and allow the solvent to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of solvent. A 5 mL syringe is recommended for this operation.

12.6.3.4 Remove the three-ball Snyder column, add a fresh boiling chip, and attach a two-ball micro Snyder column to the concentrator tube. Prewet the column by adding approximately 0.5 mL of solvent through the top. Place the apparatus in the hot water bath.

12.6.3.5 Adjust the vertical position and the water temperature as required to complete the concentration in 5-10 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood.

12.6.3.6 When the liquid reaches an apparent volume of 0.5 mL, remove the apparatus from the water bath and allow to drain and cool for at least 10 minutes.

12.6.3.7 Proceed to 12.6.4 for preparation for back-extraction or micro-concentration and solvent exchange.

12.6.4 Preparation for back-extraction or micro-concentration and solvent exchange.

12.6.4.1 For back-extraction (Section 12.5), transfer the extract to a 250 mL separatory funnel. Rinse the concentration vessel with small

portions of hexane, adjust the hexane volume in the separatory funnel to 10-20 mL, and proceed to back-extraction (Section 12.5).

12.6.4.2 For determination of the weight of residue in the extract, or for clean-up procedures other than back-extraction, transfer the extract to a blowdown vial using two to three rinses of solvent. Proceed with micro-concentration and solvent exchange (Section 12.7).

12.7 Micro-Concentration and Solvent Exchange

12.7.1 Extracts to be subjected to GPC or HPLC cleanup are exchanged into methylene chloride. Extracts to be cleaned up using silica gel, alumina, carbon, and/or Florisil are exchanged into hexane.

12.7.2 Transfer the vial containing the sample extract to a nitrogen blowdown device. Adjust the flow of nitrogen so that the surface of the solvent is just visibly disturbed.

NOTE: A large vortex in the solvent may cause analyte loss.

12.7.3 Lower the vial into a 45°C water bath and continue concentrating.

12.7.3.1 If the extract is to be concentrated to dryness for weight determination (Sections 12.4.1.8, 12.4.2.7, and 13.7.1.4), blow dry until a constant weight is obtained.

12.7.3.2 If the extract is to be concentrated for injection into the GC/MS or the solvent is to be exchanged for extract cleanup, proceed as follows:

12.7.4 When the volume of the liquid is approximately 100 µL, add 2-3 mL of the desired solvent (methylene chloride for GPC and HPLC, or hexane for the other cleanups) and continue concentration to approximately 100 µL. Repeat the addition of solvent and concentrate once more.

12.7.5 If the extract is to be cleaned up by GPC, adjust the volume of the extract to 5.0 mL with methylene chloride. If the extract is to be cleaned up by HPLC, further concentrate the extract to 30 µL. Proceed with GPC or HPLC cleanup (Section 13.2 or 13.6, respectively).

12.7.6 If the extract is to be cleaned up by column chromatography (alumina, silica gel, Carbopak/Celite, or Florisil), bring the final volume to 1.0 mL with hexane. Proceed with column cleanups (Sections 13.3 through 13.5 and 13.8).

12.7.7 If the extract is to be concentrated for injection into the GC/MS (Section 14), quantitatively transfer the extract to a 0.3 mL conical vial for final concentration, rinsing the larger vial with hexane and adding the rinse to the conical vial. Reduce the volume to approximately 100 µL. Add 10 µL of nonane to the vial, and evaporate the solvent to the level of the nonane. Seal the vial and label with the sample number. Store in the dark at room temperature until ready for

GC/MS analysis. If GC/MS analysis will not be performed on the same day, store the vial at <-10°C.

13.0 Extract Cleanup

13.1 Cleanup may not be necessary for relatively clean samples (e.g., treated effluents, groundwater, drinking water). If particular circumstances require the use of a cleanup procedure, the analyst may use any or all of the procedures below or any other appropriate procedure. Before using a cleanup procedure, the analyst must demonstrate that the requirements of Section 9.2 can be met using the cleanup procedure. If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, the cleanup procedures may be optimized for isolation of these two compounds.

13.1.1 Gel permeation chromatography (Section 13.2) removes high molecular weight interferences that cause GC column performance to degrade. It should be used for all soil and sediment extracts and may be used for water extracts that are expected to contain high molecular weight organic compounds (e.g., polymeric materials, humic acids).

13.1.2 Acid, neutral, and basic silica gel (Section 13.3), alumina (Section 13.4), and Florisil (Section 13.8) are used to remove nonpolar and polar interferences. Alumina and Florisil are used to remove chlorodiphenyl ethers.

13.1.3 Carbopak/Celite (Section 13.5) is used to remove nonpolar interferences.

13.1.4 HPLC (Section 13.6) is used to provide specificity for the 2,3,7,8-substituted and other CDD and CDF isomers.

13.1.5 The anthropogenic isolation column (Section 13.7.1), acidified silica gel batch adsorption procedure (Section 13.7.2), and sulfuric acid and base back-extraction (Section 13.7.3) are used for removal of lipids from tissue samples.

13.2 Gel Permeation Chromatography (GPC)

13.2.1 Column packing

13.2.1.1 Place 70-75 g of SX-3 Bio-beads (Section 6.7.1.1) in a 400-500 mL beaker.

13.2.1.2 Cover the beads with methylene chloride and allow to swell overnight (a minimum of 12 hours).

13.2.1.3 Transfer the swelled beads to the column (Section 6.7.1.1) and pump solvent through the column, from bottom to top, at 4.5-5.5 mL/minute prior to connecting the column to the detector.

13.2.1.4 After purging the column with solvent for one to two hours, adjust the column head pressure to 7-10 psig and purge for four to five hours to remove air. Maintain a head pressure of 7-10 psig. Connect the column to the detector (Section 6.7.1.4).

13.2.2 Column calibration

13.2.2.1 Load 5 mL of the calibration solution (Section 7.4) into the sample loop.

13.2.2.2 Inject the calibration solution and record the signal from the detector. The elution pattern will be corn oil, bis(2-ethyl hexyl)phthalate, pentachlorophenol, perylene, and sulfur.

13.2.2.3 Set the "dump time" to allow >85% removal of the corn oil and >85% collection of the phthalate.

13.2.2.4 Set the "collect time" to the peak minimum between perylene and sulfur.

13.2.2.5 Verify the calibration with the calibration solution after every 20 extracts. Calibration is verified if the recovery of the pentachlorophenol is greater than 85%. If calibration is not verified, the system shall be recalibrated using the calibration solution, and the previous 20 samples shall be re-extracted and cleaned up using the calibrated GPC system.

13.2.3 Extract cleanup—GPC requires that the column not be overloaded. The column specified in this method is designed to handle a maximum of 0.5 g of high molecular weight material in a 5 mL extract. If the extract is known or expected to contain more than 0.5 g, the extract is split into aliquots for GPC, and the aliquots are combined after elution from the column. The residue content of the extract may be obtained gravimetrically by evaporating the solvent from a 50 µL aliquot.

13.2.3.1 Filter the extract or load through the filter holder (Section 6.7.1.3) to remove the particles. Load the 5.0 mL extract onto the column.

13.2.3.2 Elute the extract using the calibration data determined in Section 13.2.2. Collect the eluate in a clean 400-500 mL beaker.

13.2.3.3 Rinse the sample loading tube thoroughly with methylene chloride between extracts to prepare for the next sample.

13.2.3.4 If a particularly dirty extract is encountered, a 5.0 mL methylene chloride blank shall be run through the system to check for carry over.

13.2.3.5 Concentrate the eluate per Sections 12.6 and 12.7 for further cleanup or injection into the GC/MS.

13.3 Silica Gel Cleanup

13.3.1 Place a glass-wool plug in a 15 mm ID chromatography column (Section 6.7.4.2). Pack the column bottom to top with: 1 g silica gel (Section 7.5.1.1), 4 g basic silica gel (Section 7.5.1.3), 1 g silica gel, 8 g acid silica gel (Section 7.5.1.2), 2 g silica gel.

and 4 g granular anhydrous sodium sulfate (Section 7.2.1). Tap the column to settle the adsorbents.

13.3.2 Pre-elute the column with 50-100 mL of hexane. Close the stopcock when the hexane is within 1 mm of the sodium sulfate. Discard the eluate. Check the column for channeling. If channeling is present, discard the column and prepare another.

13.3.3 Apply the concentrated extract to the column. Open the stopcock until the extract is within 1 mm of the sodium sulfate.

13.3.4 Rinse the receiver twice with 1 mL portions of hexane, and apply separately to the column. Elute the CDDs/CDFs with 100 mL hexane, and collect the eluate.

13.3.5 Concentrate the eluate per Sections 12.6 and 12.7 for further cleanup or injection into the HPLC or GC/MS.

13.3.6 For extracts of samples known to contain large quantities of other organic compounds (such as paper mill effluents), it may be advisable to increase the capacity of the silica gel column. This may be accomplished by increasing the strengths of the acid and basic silica gels. The acid silica gel (Section 7.5.1.2) may be increased in strength to as much as 44% w/w (7.9 g sulfuric acid added to 10 g silica gel). The basic silica gel (Section 7.5.1.3) may be increased in strength to as much as 33% w/w (50 mL 1N NaOH added to 100 g silica gel), or the potassium silicate (Section 7.5.1.4) may be used.

NOTE: The use of stronger acid silica gel (44% w/w) may lead to charring of organic compounds in some extracts. The charred material may retain some of the analytes and lead to lower recoveries of CDDs/CDFs. Increasing the strengths of the acid and basic silica gel may also require different volumes of hexane than those specified above to elute the analytes off the column. Therefore, the performance of the method after such modifications must be verified by the procedure in Section 9.2.

13.4 Alumina Cleanup

13.4.1 Place a glass-wool plug in a 15 mm ID chromatography column (Section 6.7.4.2).

13.4.2 If using acid alumina, pack the column by adding 6 g acid alumina (Section 7.5.2.1). If using basic alumina, substitute 6 g basic alumina (Section 7.5.2.2). Tap the column to settle the adsorbents.

13.4.3 Pre-elute the column with 50-100 mL of hexane. Close the stopcock when the hexane is within 1 mm of the alumina.

13.4.4 Discard the eluate. Check the column for channeling. If channeling is present, discard the column and prepare another.

13.4.5 Apply the concentrated extract to the column. Open the stopcock until the extract is within 1 mm of the alumina.

13.4.6 Rinse the receiver twice with 1 mL portions of hexane and apply separately to the column. Elute the interfering compounds with 100 mL hexane and discard the eluate.

13.4.7 The choice of eluting solvents will depend on the choice of alumina (acid or basic) made in Section 13.4.2.

13.4.7.1 If using acid alumina, elute the CDDs/CDFs from the column with 20 mL methylene chloride:hexane (20:80 v/v). Collect the eluate.

13.4.7.2 If using basic alumina, elute the CDDs/CDFs from the column with 20 mL methylene chloride:hexane (50:50 v/v). Collect the eluate.

13.4.8 Concentrate the eluate per Sections 12.6 and 12.7 for further cleanup or injection into the HPLC or GC/MS.

13.5 Carbon Column

13.5.1 Cut both ends from a 10 mL disposable serological pipet (Section 6.7.3.2) to produce a 10 cm column. Fire-polish both ends and flare both ends if desired. Insert a glass-wool plug at one end, and pack the column with 0.55 g of Carbopak/Celite (Section 7.5.3.3) to form an adsorbent bed approximately 2 cm long. Insert a glass-wool plug on top of the bed to hold the adsorbent in place.

13.5.2 Pre-elute the column with 5 mL of toluene followed by 2 mL of methylene chloride: methanol:toluene (15:4:1 v/v), 1 mL of methylene chloride:cyclohexane (1:1 v/v), and 5 mL of hexane. If the flow rate of eluate exceeds 0.5 mL/minute, discard the column.

13.5.3 When the solvent is within 1 mm of the column packing, apply the sample extract to the column. Rinse the sample container twice with 1 mL portions of hexane and apply separately to the column. Apply 2 mL of hexane to complete the transfer.

13.5.4 Elute the interfering compounds with two 3 mL portions of hexane, 2 mL of methylene chloride:cyclohexane (1:1 v/v), and 2 mL of methylene chloride:methanol:toluene (15:4:1 v/v). Discard the eluate.

13.5.5 Invert the column, and elute the CDDs/CDFs with 20 mL of toluene. If carbon particles are present in the eluate, filter through glass-fiber filter paper.

13.5.6 Concentrate the eluate per Sections 12.6 and 12.7 for further cleanup or injection into the HPLC or GC/MS.

13.6 HPLC (Reference 6)

13.6.1 Column calibration

13.6.1.1 Prepare a calibration standard containing the 2,3,7,8-substituted isomers and/or other isomers of interest at a concentration of approximately 500 pg/µL in methylene chloride.

13.6.1.2 Inject 30 µL of the calibration solution into the HPLC and record the signal from the detector. Collect the eluant for reuse. The elution order will be the tetra- through octa-isomers.

13.6.1.3 Establish the collection time for the tetra-isomers and for the other isomers of interest. Following calibration, flush the injection system with copious quantities of methylene chloride, including a minimum of five 50 µL injections while the detector is monitored, to ensure that residual CDDs/CDFs are removed from the system.

13.6.1.4 Verify the calibration with the calibration solution after every 20 extracts. Calibration is verified if the recovery of the CDDs/CDFs from the calibration standard (Section 13.6.1.1) is 75-125% compared to the calibration (Section 13.6.1.2). If calibration is not verified, the system shall be recalibrated using the calibration solution, and the previous 20 samples shall be re-extracted and cleaned up using the calibrated system.

13.6.2 Extract cleanup—HPLC requires that the column not be overloaded. The column specified in this method is designed to handle a maximum of 30 µL of extract. If the extract cannot be concentrated to less than 30 µL, it is split into fractions and the fractions are combined after elution from the column.

13.6.2.1 Rinse the sides of the vial twice with 30 µL of methylene chloride and reduce to 30 µL with the evaporation apparatus (Section 12.7).

13.6.2.2 Inject the 30 µL extract into the HPLC.

13.6.2.3 Elute the extract using the calibration data determined in Section 13.6.1. Collect the fraction(s) in a clean 20 mL concentrator tube containing 5 mL of hexane:acetone (1:1 v/v).

13.6.2.4 If an extract containing greater than 100 ng/mL of total CDD or CDF is encountered, a 30 µL methylene chloride blank shall be run through the system to check for carry-over.

13.6.2.5 Concentrate the eluate per Section 12.7 for injection into the GC/MS.

13.7 Cleanup of Tissue Lipids—Lipids are removed from the Soxhlet extract using either the anthropogenic isolation column (Section 13.7.1) or acidified silica gel (Section 13.7.2), or are removed from the HCl digested extract using sulfuric acid and base back-extraction (Section 13.7.3).

13.7.1 Anthropogenic isolation column (References 22 and 27)—Used for removal of lipids from the Soxhlet/SDS extraction (Section 12.4.1).

13.7.1.1 Prepare the column as given in Section 7.5.4.

13.7.1.2 Pre-elute the column with 100 mL of hexane. Drain the hexane layer to the top of the column, but do not expose the sodium sulfate.

13.7.1.3 Load the sample and rinses (Section 12.4.1.9.2) onto the column by draining each portion to the top of the bed. Elute the CDDs/CDFs from the column into the apparatus used for concentration (Section 12.4.1.7) using 200 mL of hexane.

13.7.1.4 Concentrate the cleaned up extract (Sections 12.6 through 12.7) to constant weight per Section 12.7.3.1. If more than 500 mg of material remains, repeat the cleanup using a fresh anthropogenic isolation column.

13.7.1.5 Redissolve the extract in a solvent suitable for the additional cleanups to be used (Sections 13.2 through 13.6 and 13.8).

13.7.1.6 Spike 1.0 mL of the cleanup standard (Section 7.11) into the residue/solvent.

13.7.1.7 Clean up the extract using the procedures in Sections 13.2 through 13.6 and 13.8. Alumina (Section 13.4) or Florisil (Section 13.8) and carbon (Section 13.5) are recommended as minimum additional cleanup steps.

13.7.1.8 Following cleanup, concentrate the extract to 10 µL as described in Section 12.7 and proceed with the analysis in Section 14.

13.7.2 Acidified silica gel (Reference 28)—Procedure alternate to the anthropogenic isolation column (Section 13.7.1) that is used for removal of lipids from the Soxhlet/SDS extraction (Section 12.4.1).

13.7.2.1 Adjust the volume of hexane in the bottle (Section 12.4.1.9.2) to approximately 200 mL.

13.7.2.2 Spike 1.0 mL of the cleanup standard (Section 7.11) into the residue/solvent.

13.7.2.3 Drop the stirring bar into the bottle, place the bottle on the stirring plate, and begin stirring.

13.7.2.4 Add 30-100 g of acid silica gel (Section 7.5.1.2) to the bottle while stirring, keeping the silica gel in motion. Stir for two to three hours.

NOTE: 30 grams of silica gel should be adequate for most samples and will minimize contamination from this source.

13.7.2.5 After stirring, pour the extract through approximately 10 g of granular anhydrous sodium sulfate (Section 7.2.1) contained in a funnel with glass-fiber filter into a macro contration device (Section 12.6). Rinse the bottle and sodium sulfate with hexane to complete the transfer.

13.7.2.6 Concentrate the extract per Sections 12.6 through 12.7 and clean up the extract using the procedures in Sections 13.2 through 13.6 and 13.8. Alumina (Section 13.4) or Florisil (Section 13.8) and carbon (Section 13.5) are recommended as minimum additional cleanup steps.

13.7.3 Sulfuric acid and base back-extraction—Used with HCl digested extracts (Section 12.4.2).

13.7.3.1 Spike 1.0 mL of the cleanup standard (Section 7.11) into the residue/solvent (Section 12.4.2.8.2).

13.7.3.2 Add 10 mL of concentrated sulfuric acid to the bottle. Immediately cap and shake one to three times. Loosen cap in a hood to vent excess pressure. Cap and shake the bottle so that the residue/solvent is exposed to the acid for a total time of approximately 45 seconds.

13.7.3.3 Decant the hexane into a 250 mL separatory funnel making sure that no acid is transferred. Complete the quantitative transfer with several hexane rinses.

13.7.3.4 Back extract the solvent/residue with 50 mL of potassium hydroxide solution per Section 12.5.2, followed by two reagent water rinses.

13.7.3.5 Drain the extract through a filter funnel containing approximately 10 g of granular anhydrous sodium sulfate in a glass-fiber filter into a macro concentration device (Section 12.6).

13.7.3.6 Concentrate the cleaned up extract to a volume suitable for the additional cleanups given in Sections 13.2 through 13.6 and 13.8. Gel permeation chromatography (Section 13.2), alumina (Section 13.4) or Florisil (Section 13.8), and Carbopak/Celite (Section 13.5) are recommended as minimum additional cleanup steps.

13.7.3.7 Following cleanup, concentrate the extract to 10 µL as described in Section 12.7 and proceed with analysis per Section 14.

13.8 Florisil Cleanup (Reference 29)

13.8.1 Pre-elute the activated Florisil column (Section 7.5.3) with 10 mL of methylene chloride followed by 10 mL of hexane:methylene chloride (98:2 v/v) and discard the solvents.

13.8.2 When the solvent is within 1 mm of the packing, apply the sample extract (in hexane) to the column. Rinse the sample container twice with 1 mL portions of hexane and apply to the column.

13.8.3 Elute the interfering compounds with 20 mL of hexane:methylene chloride (98:2) and discard the eluate.

13.8.4 Elute the CDDs/CDFs with 35 mL of methylene chloride and collect the eluate. Concentrate the eluate per Sections 12.6 through 12.7 for further cleanup or for injection into the HPLC or GC/MS.

14.0 HRGC/HRMS Analysis

14.1 Establish the operating conditions given in Section 10.1.

14.2 Add 10 µL of the appropriate internal standard solution (Section 7.12) to the sample extract immediately prior to injection to minimize the possibility of loss by evaporation, adsorption, or reaction. If an extract is to be reanalyzed and evaporation has occurred, do not add more instrument internal standard solution. Rather, bring the extract back to its previous volume (e.g., 19 µL) with pure nonane only (18 µL if 2 µL injections are used).

14.3 Inject 1.0 µL or 2.0 µL of the concentrated extract containing the internal standard solution, using on-column or splitless injection. The volume injected must be identical to the volume used for calibration (Section 10). Start the GC column initial isothermal hold upon injection. Start MS data collection after the solvent peak elutes. Stop data collection after the OCDD and OCDF have eluted. If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, stop data collection after elution of these compounds. Return the column to the initial temperature for analysis of the next extract or standard.

15.0 System and Laboratory Performance

15.1 At the beginning of each 12-hour shift during which analyses are performed, GC/MS system performance and calibration are verified for all CDDs/CDFs and labeled compounds. For these tests, analysis of the CS3 calibration verification (VER) standard (Section 7.13 and Table 4) and the isomer specificity test standards (Section 7.15 and Table 5) shall be used to verify all performance criteria. Adjustment and/or recalibration (Section 10) shall be performed until all performance criteria are met. Only after all performance criteria are met may samples, blanks, IPRs, and OPRs be analyzed.

15.2 MS Resolution - A static resolving power of at least 10,000 (10% valley definition) must be demonstrated at the appropriate m/z before any analysis is performed. Static resolving power checks must be performed at the beginning and at the end of each 12-hour shift according to procedures in Section 10.1.2. Corrective actions must be implemented whenever the resolving power does not meet the requirement.

15.3 Calibration Verification

15.3.1 Inject the VER standard using the procedure in Section 14.

15.3.2 The m/z abundance ratios for all CDDs/CDFs shall be within the limits in Table 9; otherwise, the mass spectrometer shall be adjusted until the m/z abundance ratios fall within the limits specified, and the verification test shall be repeated. If the adjustment alters the resolution of the mass spectrometer, resolution shall be verified (Section 10.1.2) prior to repeat of the verification test.

15.3.3 The peaks representing each CDD/CDF and labeled compound in the VER standard must be present with S/N of at least 10; otherwise, the mass spectrometer shall be adjusted and the verification test repeated.

15.3.4 Compute the concentration of each CDD/CDF compound by isotope dilution (Section 10.5) for those compounds that have labeled analogs (Table 1). Compute the concentration of the labeled compounds by the internal standard method (Section 10.6). These concentrations are computed based on the calibration data in Section 10.

15.3.5 For each compound, compare the concentration with the calibration verification limit in Table 6. If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, compare the concentration to the limit in Table 6a. If all compounds meet the acceptance criteria, calibration has been verified and analysis of standards and sample extracts may proceed. If, however, any compound fails its respective limit, the measurement system is not performing properly for that compound. In this event, prepare a fresh calibration standard or correct the problem causing the failure and repeat the resolution (Section 15.2) and verification (Section 15.3) tests, or recalibrate (Section 10).

15.4 Retention Times and GC Resolution

15.4.1 Retention times

15.4.1.1 Absolute—The absolute retention times of the $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD GCMS internal standards in the verification test (Section 15.3) shall be within ±15 seconds of the retention times obtained during calibration (Sections 10.2.1 and 10.2.4).

15.4.1.2 Relative - The relative retention times of CDDs/CDFs and labeled compounds in the verification test (Section 15.3) shall be within the limits given in Table 2.

15.4.2 GC resolution

15.4.2.1 Inject the isomer specificity standards (Section 7.15) on their respective columns.

15.4.2.2 The valley height between 2,3,7,8-TCDD and the other tetra-dioxin isomers at m/z 319.8965, and between 2,3,7,8-TCDF and the other tetra-furan isomers at m/z 303.9016 shall not exceed 25% on their respective columns (Figures 6 and 7).

15.4.3 If the absolute retention time of any compound is not within the limits specified or if the 2,3,7,8-isomers are not resolved, the GC is not performing properly. In this event, adjust the GC and repeat the verification test (Section 15.3) or recalibrate (Section 10), or replace the GC column and either verify calibration or recalibrate.

15.5 Ongoing Precision and Recovery

15.5.1 Analyze the extract of the ongoing precision and recovery (OPR) aliquot (Section 11.4.2.5, 11.5.4, 11.6.2, 11.7.4, or 11.8.3.2) prior to analysis of samples from the same batch.

15.5.2 Compute the concentration of each CDD/CDF by isotope dilution for those compounds that have labeled analogs (Section 10.5). Compute the concentration of 1,2,3,7,8,9-HxCDD, OCDF, and each labeled compound by the internal standard method (Section 10.6).

15.5.3 For each CDD/CDF and labeled compound, compare the concentration to the OPR limits given in Table 6. If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, compare the concentration to the limits in Table 6a. If all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may proceed. If, however, any individual concentration falls outside of the range given, the extraction/concentration processes are not being performed properly for that compound. In this event, correct the problem, re-prepare, extract, and clean up the sample batch and repeat the ongoing precision and recovery test (Section 15.5).

15.5.4 Add results that pass the specifications in Section 15.5.3 to initial and previous ongoing data for each compound in each matrix. Update QC charts to form a graphic representation of continued laboratory performance. Develop a statement of laboratory accuracy for each CDD/CDF in each matrix type by calculating the average percent recovery (R) and the standard deviation of percent recovery (S_R). Express the accuracy as a recovery interval from $R-2S_R$ to $R+2S_R$. For example, if R = 95% and S_R = 5%, the accuracy is 85-105%.

15.6 Blank—Analyze the method blank extracted with each sample batch immediately following analysis of the OPR aliquot to demonstrate freedom from contamination and freedom from carryover from the OPR analysis. The results of the analysis of the blank must meet the specifications in Section 9.5.2 before sample analyses may proceed.

16.0 Qualitative Determination

A CDD, CDF, or labeled compound is identified in a standard, blank, or sample when all of the criteria in Sections 16.1 through 16.4 are met.

16.1 The signals for the two exact m/z's in Table 8 must be present and must maximize within the same two seconds.

16.2 The signal-to-noise ratio (S/N) for the GC peak at each exact m/z must be greater than or equal to 2.5 for each CDD or CDF detected in a sample extract, and greater than or equal to 10 for all CDDs/CDFs in the calibration standard (Sections 10.2.3 and 15.3.3).

16.3 The ratio of the integrated areas of the two exact m/z's specified in Table 8 must be within the limit in Table 9, or within ±10% of the ratio in the midpoint (CS3) calibration or calibration verification (VER), whichever is most recent.

16.4 The relative retention time of the peak for a 2,3,7,8-substituted CDD or CDF must be within the limit in Table 2. The retention time of peaks representing non-2,3,7,8-substituted CDDs/CDFs must be within the retention time windows established in Section 10.3.

16.5 Confirmatory Analysis—Isomer specificity for 2,3,7,8-TCDF cannot be achieved on the DB-5 column. Therefore, any sample in which 2,3,7,8-TCDF is identified by analysis on a DB-5 column must have a confirmatory analysis performed on a DB-225, SP-2330, or equivalent GC column. The operating conditions in Section 10.1.1 may be adjusted to optimize the analysis on the second GC column, but the GC/MS must meet the mass resolution and calibration specifications in Section 10.

16.6 If the criteria for identification in Sections 16.1 through16.5 are not met, the CDD or CDF has not been identified and the results may not be reported for regulatory compliance purposes. If interferences preclude identification, a new aliquot of sample must be extracted, further cleaned up, and analyzed.

17.0 Quantitative Determination

17.1 Isotope Dilution Quantitation—By adding a known amount of a labeled compound to every sample prior to extraction, correction for recovery of the CDD/CDF can be made because the CDD/CDF and its labeled analog exhibit similar effects upon extraction, concentration, and gas chromatography. Relative response (RR) values are used in conjunction with the initial calibration data described in Section 10.5 to determine concentrations directly, so long as labeled compound spiking levels are constant, using the following equation:

$$C_{ex}\ (ng/mL) = \frac{(A1_n + A2_n)\ C_l}{(A1_l + A2_l)\ RR}$$

where,

C_{ex} = The concentration of the CDD/CDF in the extract, and the other terms are as defined in Section 10.5.2.

17.1.1 Because of a potential interference, the labeled analog of OCDF is not added to the sample. Therefore, OCDF is quantitated against labeled OCDD. As a result, the concentration of OCDF is corrected for the recovery of the labeled OCDD. In instances where OCDD and OCDF behave differently during sample extraction, concentration, and cleanup procedures, this may decrease the accuracy of the OCDF results. However, given the low toxicity of this compound relative to the other dioxins and furans, the potential decrease in accuracy is not considered significant.

17.1.2 Because $^{13}C_{12}$-1,2,3,7,8,9-HxCDD is used as an instrument internal standard (i.e., not added before extraction of the sample), it cannot be used to quantitate the 1,2,3,7,8,9-HxCDD by strict isotope dilution procedures. Therefore, 1,2,3,7,8,9-HxCDD is quantitated using the averaged response of the labeled analogs of the other two 2,3,7,8-substituted HxCDD's: 1,2,3,4,7,8-HxCDD and 1,2,3,6,7,8-HxCDD. As a result, the concentration of 1,2,3,7,8,9-HxCDD is corrected for the average recovery of the other two HxCDD's.

17.1.3 Any peaks representing non-2,3,7,8-substituted CDDs/CDFs are quantitated using an average of the response factors from all of the labeled 2,3,7,8-isomers at the same level of chlorination.

17.2 Internal Standard Quantitation and Labeled Compound Recovery

17.2.1 Compute the concentrations of 1,2,3,7,8,9-HxCDD, OCDF, the ^{13}C-labeled analogs and the ^{37}C-labeled cleanup standard in the extract using the response factors determined from the initial calibration data (Section 10.6) and the following equation:

$$C_{ex}\ (ng/mL) = \frac{(A_x + A_n)\ C_{is}}{(A_{is} + A_{is})\ RF}$$

where,

C_{ex} = The concentration of the CDD/CDF in the extract, and the other terms are as defined in Section 10.6.1.

NOTE: There is only one m/z for the ^{37}Cl-labeled standard.

17.2.2 Using the concentration in the extract determined above, compute the percent recovery of the ^{13}C-labeled compounds and the ^{37}C labeled cleanup standard using the following equation:

$$Recovery\ (\%) = \frac{Concentration\ found\ (\mu g/mL)}{Concentration\ spiked\ (\mu g/mL)} \times 100$$

17.3 The concentration of a CDD/CDF in the solid phase of the sample is computed using the concentration of the compound in the extract and the weight of the solids (Section 11.5.1), as follows:

$$Concentration\ in\ solid\ (ng/kg) = \frac{(C_{ex} \times V_{ex})}{W_s}$$

where,

C_{ex} = The concentration of the compound in the extract.
V_{ex} = The extract volume in mL.
W_s = The sample weight (dry weight) in kg.

17.4 The concentration of a CDD/CDF in the aqueous phase of the sample is computed using the concentration of the compound in the extract and the volume of water extracted (Section 11.4 or 11.5), as follows:

$$\text{Concentration in aqueous phase } (pg/L) = \frac{(C_{ex} \times V_{ex})}{V_s}$$

where,

C_{ex} = The concentration of the compound in the extract.
V_{ex} = The extract volume in mL.
V_s = The sample volume in liters.

17.5 If the SICP area at either quantitation m/z for any compound exceeds the calibration range of the system, a smaller sample aliquot is extracted.

17.5.1 For aqueous samples containing 1% solids or less, dilute 100 mL, 10 mL, etc., of sample to 1 L with reagent water and re-prepare, extract, clean up, and analyze per Sections 11 through 14.

17.5.2 For samples containing greater than 1% solids, extract an amount of sample equal to 1/10, 1/100, etc., of the amount used in Section 11.5.1. Re-prepare, extract, clean up, and analyze per Sections 11 through 14.

17.5.3 If a smaller sample size will not be representative of the entire sample, dilute the sample extract by a factor of 10, adjust the concentration of the instrument internal standard to 100 pg/µL in the extract, and analyze an aliquot of this diluted extract by the internal standard method.

17.6 Results are reported to three significant figures for the CDDs/CDFs and labeled compounds found in all standards, blanks, and samples.

17.6.1 Reporting units and levels

17.6.1.1 Aqueous samples—Report results in pg/L (parts-per-quadrillion).

17.6.1.2 Samples containing greater than 1% solids (soils, sediments, filter cake, compost)—Report results in ng/kg based on the dry weight of the sample. Report the percent solids so that the result may be corrected.

17.6.1.3 Tissues—Report results in ng/kg of wet tissue, not on the basis of the lipid content of the sample. Report the percent lipid content so that the data user can calculate the concentration on a lipid basis if desired.

17.6.1.4 Reporting level

17.6.1.4.1 Standards (VER, IPR, OPR) and samples—Report results at or above the minimum level (Table 2). Report results below the minimum level as not detected or as required by the regulatory authority.

17.6.1.4.2 Blanks—Report results above one-third the ML.

17.6.2 Results for CDDs/CDFs in samples that have been diluted are reported at the least dilute level at which the areas at the quantitation m/z's are within the calibration range (Section 17.5).

17.6.3 For CDDs/CDFs having a labeled analog, results are reported at the least dilute level at which the area at the quantitation m/z is within the calibration range (Section 17.5) and the labeled compound recovery is within the normal range for the method (Section 9.3 and Tables 6, 6a, 7, and 7a).

17.6.4 Additionally, if requested, the total concentration of all isomers in an individual level of chlorination (i.e., total TCDD, total TCDF, total Paced, etc.) may be reported by summing the concentrations of all isomers identified in that level of chlorination, including both 2,3,7,8-substituted and non-2,3,7,8-substituted isomers.

18.0 Analysis of Complex Samples

18.1 Some samples may contain high levels (>10 ng/L; >1000 ng/kg) of the compounds of interest, interfering compounds, and/or polymeric materials. Some extracts will not concentrate to 10 µL (Section 12.7); others may overload the GC column and/or mass spectrometer.

18.2 Analyze a smaller aliquot of the sample (Section 17.5) when the extract will not concentrate to 10 µL after all cleanup procedures have been exhausted.

18.3 Chlorodiphenyl Ethers—If chromatographic peaks are detected at the retention time of any CDDs/CDFs in any of the m/z channels being monitored for the chlorodiphenyl ethers (Table 8), cleanup procedures must be employed until these interferences are removed. Alumina (Section 13.4) and Florisil (Section 13.8) are recommended for removal of chlorodiphenyl ethers.

18.4 Recovery of Labeled Compounds—In most samples, recoveries of the labeled compounds will be similar to those from reagent water or from the alternate matrix (Section 7.6).

18.4.1 If the recovery of any of the labeled compounds is outside of the normal range (Table 7), a diluted sample shall be analyzed (Section 17.5).

18.4.2 If the recovery of any of the labeled compounds in the diluted sample is outside of normal range, the calibration verification standard (Section 7.13) shall be analyzed and calibration verified (Section 15.3).

18.4.3 If the calibration cannot be verified, a new calibration must be performed and the original sample extract reanalyzed.

18.4.4 If the calibration is verified and the diluted sample does not meet the limits for labeled compound recovery, the method does not apply to the sample being analyzed and the result may not be reported for regulatory compliance purposes. In this case, alternate extraction and cleanup procedures in this method must be employed to resolve the interference. If all cleanup procedures in this method have been employed and labeled compound recovery remains outside of the normal range, extraction and/or cleanup procedures that are beyond this scope of this method will be required to analyze these samples.

19.0 Pollution Prevention

19.1 The solvents used in this method pose little threat to the environment when managed properly. The solvent evaporation techniques used in this method are amenable to solvent recovery, and it is recommended that the laboratory recover solvents wherever feasible.

19.2 Standards should be prepared in volumes consistent with laboratory use to minimize disposal of standards.

20.0 Waste Management

20.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations.

20.2 Samples containing HCl to pH <2 are hazardous and must be neutralized before being poured down a drain or must be handled as hazardous waste.

20.3 The CDDs/CDFs decompose above 800°C. Low-level waste such as absorbent paper, tissues, animal remains, and plastic gloves may be burned in an appropriate incinerator. Gross quantities (milligrams) should be packaged securely and disposed of through commercial or governmental channels that are capable of handling extremely toxic wastes.

20.4 Liquid or soluble waste should be dissolved in methanol or ethanol and irradiated with ultraviolet light with a wavelength shorter than 290 nm for several days. Use F40 BL or equivalent lamps. Analyze liquid wastes, and dispose of the solutions when the CDDs/CDFs can no longer be detected.

20.5 For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel" and "Less is Better-Laboratory Chemical Management for Waste Reduction," available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

21.0 Method Performance

Method performance was validated and performance specifications were developed using data from EPA's international interlaboratory validation study (References 30-31) and the

EPA/paper industry Long-Term Variability Study of discharges from the pulp and paper industry (58 FR 66078).

22.0 References

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23.0 Tables and Figures

TABLE 1. CHLORINATED DIBENZO-*P*-DIOXINS AND FURANS DETERMINED BY ISOTOPE DILUTION AND INTERNAL STANDARD HIGH RESOLUTION GAS CHROMATOGRAPHY (HRGC)/HIGH RESOLUTION MASS SPECTROMETRY (HRMS)

CDDs/CDFs [1]	CAS Registry	Labeled analog	CAS Registry
2,3,7,8-TCDD	1746-01-6	$^{13}C_{12}$-2,3,7,8-TCDD	76523-40-5
		$^{37}Cl_4$-2,3,7,8-TCDD	85508-50-5
Total TCDD	41903-57-5	—	
2,3,7,8-TCDF	51207-31-9	$^{13}C_{12}$-2,3,7,8-TCDF	89059-46-1
Total-TCDF	55722-27-5	—	—
1,2,3,7,8-PeCDD	40321-76-4	$^{13}C_{12}$-1,2,3,7,8-PeCDD	109719-79-1
Total-PeCDD	36088-22-9		—
1,2,3,7,8-PeCDF	57117-41-6	$^{13}C_{12}$-1,2,3,7,8-PeCDF	109719-77-9
2,3,4,7,8-PeCDF	57117-31-4	$^{13}C_{12}$-2,3,4,7,8-PeCDF	116843-02-8
Total-PeCDF	30402-15-4		—
1,2,3,4,7,8-HxCDD	39227-28-6	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	109719-80-4
1,2,3,6,7,8-HxCDD	57653-85-7	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	109719-81-5
1,2,3,7,8,9-HxCDD	19408-74-3	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	109719-82-6
Total-HxCDD	34465-46-8	—	—
1,2,3,4,7,8-HxCDF	70648-26-9	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	114423-98-2
1,2,3,6,7,8-HxCDF	57117-44-9	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	116843-03-9
1,2,3,7,8,9-HxCDF	72918-21-9	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	116843-04-0
2,3,4,6,7,8-HxCDF	60851-34-5	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	116843-05-1
Total-HxCDF	55684-94-1		—
1,2,3,4,6,7,8-HpCDD	35822-46-9	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	109719-83-7
Total-HpCDD	37871-00-4	—	
1,2,3,4,6,7,8-HpCDF	67562-39-4	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	109719-84-8
1,2,3,4,7,8,9-HpCDF	55673-89-7	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	109719-94-0
Total-HpCDF	38998-75-3	—	—
OCDD	3268-87-9	$^{13}C_{12}$-OCDD	114423-97-1
OCDF	39001-02-0	not used	—

[1] Chlorinated dibenzo-*p*-dioxins and chlorinated dibenzofurans

TCDD = Tetrachlorodibenzo-*p*-dioxin
PeCDD = Pentachlorodibenzo-*p*-dioxin
HxCDD = Hexachlorodibenzo-*p*-dioxin
HpCDD = Heptachlorodibenzo-*p*-dioxin
OCDD = Octachlorodibenzo-*p*-dioxin

TCDF = Tetrachlorodibenzofuran
PeCDF = Pentachlorodibenzofuran
HxCDF = Hexachlorodibenzofuran
HpCDF = Heptachlorodibenzofuran
OCDF = Octachlorodibenzofuran

TABLE 2. RETENTION TIME REFERENCES, QUANTITATION REFERENCES, RELATIVE RETENTION TIMES, AND MINIMUM LEVELS FOR CDDS AND CDFS

CDD/CDF	Retention time and quantitation reference	Relative retention time	Minimum level [1] Water (pg/L; ppq)	Solid (ng/kg; ppt)	Extract (pg/µL; ppb)
Compounds using $^{13}C_{12}$-1,2,3,4-TCDD as the injection internal standard					
2,3,7,8-TCDF	$^{13}C_{12}$-2,3,7,8-TCDF	0.999–1.003	10	1	0.5
2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD	0.999–1.002	10	1	0.5
1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF	0.999–1.002	50	5	2.5
2,3,4,7,8-PeCDF	$^{13}C_{12}$-2,3,4,7,8-PeCDF	0.999–1.002	50	5	2.5
1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDD	0.999–1.002	50	5	2.5
$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TCDD	0.923–1.103			
$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0.976–1.043			
$^{37}Cl_4$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0.989–1.052			
$^{13}C_{12}$-1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1.000–1.425			
$^{13}C_{12}$-2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1.011–1.526			
$^{13}C_{12}$-1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,4-TCDD	1.000–1.567			
Compounds using $^{13}C_{12}$-1,2,3,7,8,9-HxCDD as the injection internal standard					
1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	0.999–1.001	50	5	2.5
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	0.997–1.005	50	5	2.5
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	0.999–1.001	50	5	2.5
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	0.999–1.001	50	5	2.5
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	0.999–1.001	50	5	2.5
1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	0.998–1.004	50	5	2.5
1,2,3,7,8,9-HxCDD	—[2]	1.000–1.019	50	5	2.5
1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	0.999–1.001	50	5	2.5
1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	0.999–1.001	50	5	2.5
1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	0.999–1.001	50	5	2.5
OCDF	$^{13}C_{12}$-OCDD	0.999–1.008	100	10	5.0
OCDD	$^{13}C_{12}$-OCDD	0.999–1.001	100	10	5.0
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.944–0.970			
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.949–0.975			
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.977–1.047			
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.959–1.021			
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.977–1.000			
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.981–1.003			
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.043–1.085			

TABLE 2. RETENTION TIME REFERENCES, QUANTITATION REFERENCES, RELATIVE RETENTION TIMES, AND MINIMUM LEVELS FOR CDDS AND CDFS

CDD/CDF	Retention time and quantitation reference	Relative retention time	Minimum level [1]		
			Water (pg/L; ppq)	Solid (ng/kg; ppt)	Extract (pg/µL; ppb)
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.057–1.151			
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.086–1.110			
$^{13}C_{12}$-OCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.032–1.311			

[1]The Minimum Level (ML) for each analyte is defined as the level at which the entire analytical system must give a recognizable signal and acceptable calibration point. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

[2]The retention time reference for 1,2,3,7,8,9-HxCDD is $^{13}C_{12}$-1,2,3,6,7,8-HxCDD, and 1,2,3,7,8,9-HxCDD is quantified using the averaged responses for $^{13}C_{12}$-1,2,3,4,7,8-HxCDD and $^{13}C_{12}$-1,2,3,6,7,8-HxCDD.

TABLE 3. CONCENTRATION OF STOCK AND SPIKING SOLUTIONS CONTAINING CDDS/CDFS AND LABELED COMPOUNDS

CDD/CDF	Labeled Compound Stock Solution [1] (ng/mL)	Labeled Compound Spiking Solution [2] (ng/mL)	PAR Stock Solution [3] (ng/mL)	PAR Spiking Solution [4] (ng/mL)
2,3,7,8-TCDD	—	—	40	0.8
2,3,7,8-TCDF	—	—	40	0.8
1,2,3,7,8-PeCDD	—	—	200	4
1,2,3,7,8-PeCDF	—	—	200	4
2,3,4,7,8-PeCDF	—	—	200	4
1,2,3,4,7,8-HxCDD	—	—	200	4
1,2,3,6,7,8-HxCDD	—	—	200	4
1,2,3,7,8,9-HxCDD	—	—	200	4
1,2,3,4,7,8-HxCDF	—	—	200	4
1,2,3,6,7,8-HxCDF	—	—	200	4
1,2,3,7,8,9-HxCDF	—	—	200	4
2,3,4,6,7,8-HxCDF	—	—	200	4
1,2,3,4,6,7,8-HpCDD	—	—	200	4
1,2,3,4,6,7,8-HpCDF	—	—	200	4
1,2,3,4,7,8,9-HpCDF	—	—	200	4
OCDD	—	—	400	8
OCDF	—	—	400	8
$^{13}C_{12}$-2,3,7,8-TCDD	100	2	—	—
$^{13}C_{12}$-2,3,7,8-TCDF	100	2	—	—
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	2	—	—
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	2	—	—
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	2	—	—
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	2	—	—
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	2	—	—
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	2	—	—
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	2	—	—
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	2	—	—
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	2	—	—
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	2	—	—
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	2	—	—
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	2	—	—
$^{13}C_{12}$-OCDD	200	4	—	—

TABLE 3. CONCENTRATION OF STOCK AND SPIKING SOLUTIONS CONTAINING CDDS/CDFS AND LABELED COMPOUNDS

CDD/CDF	Labeled Compound Stock Solution [1] (ng/mL)	Labeled Compound Spiking Solution [2] (ng/mL)	PAR Stock Solution [3] (ng/mL)	PAR Spiking Solution [4] (ng/mL)
	Concentration (ng/mL)			
Cleanup Standard [5]				
$^{37}Cl_4$-2,3,7,8-TCDD	0.8			
Internal Standards [6]				
$^{13}C_{12}$-1,2,3,4-TCDD	200			
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	200			

[1] Section 7.10—prepared in nonane and diluted to prepare spiking solution.
[2] Section 7.10.3—prepared in acetone from stock solution daily.
[3] Section 7.9—prepared in nonane and diluted to prepare spiking solution.
[4] Section 7.14—prepared in acetone from stock solution daily.
[5] Section 7.11—prepared in nonane and added to extract prior to cleanup.
[6] Section 7.12—prepared in nonane and added to the concentrated extract immediately prior to injection into the GC (Section 14.2).

TABLE 4. CONCENTRATION OF CDDS/CDFS IN CALIBRATION AND CALIBRATION VERIFICATION SOLUTIONS[1] (section 15.3)

	CDD/CDF	CS2 (ng/mL)	CS3 (ng/mL)	CS4 (ng/mL)	CS5 (ng/mL)
2,3,7,8-TCDD	0.5	2	10	40	200
2,3,7,8-TCDF	0.5	2	10	40	200
1,2,3,7,8-PeCDD	2.5	10	50	200	1000
1,2,3,7,8-PeCDF	2.5	10	50	200	1000
2,3,4,7,8-PeCDF	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDD	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDD	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDD	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDF	2.5	10	50	200	1000
2,3,4,6,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDD	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDF	2.5	10	50	200	1000
1,2,3,4,7,8,9-HpCDF	2.5	10	50	200	1000
OCDD	5.0	20	100	400	2000
OCDF	5.0	20	100	400	2000
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100
$^{13}C_{12}$-PeCDF	100	100	100	100	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	100	100	100	100
$^{13}C_{12}$-OCDD	200	200	200	200	200
Cleanup Standard					
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	2	10	40	200
Internal Standards					
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

TABLE 5. GC RETENTION TIME WINDOW DEFINING SOLUTION AND ISOMER SPECIFICITY TEST STANDARD (SECTION 7.15)

DB-5 Column GC Retention-Time Window Defining Solution

CDD/CDF	First Eluted	Last Eluted
TCDF	1,3,6,8-	1,2,8,9-
TCDD	1,3,6,8-	1,2,8,9-
PeCDF	1,3,4,6,8-	1,2,3,8,9-
PeCDD	1,2,4,7,9-	1,2,3,8,9-
HxCDF	1,2,3,4,6,8-	1,2,3,4,8,9-
HxCDD	1,2,4,6,7,9-	1,2,3,4,6,7-
HpCDF	1,2,3,4,6,7,8-	1,2,3,4,7,8,9-
HpCDD	1,2,3,4,6,7,9-	1,2,3,4,6,7,8-

DB-5 Column TCDD Specificity Test Standard

1,2,3,7+1,2,3,8-TCDD
2,3,7,8-TCDD
1,2,3,9-TCDD

DB-225 Column TCDF Isomer Specificity Test Standard

2,3,4,7-TCDF
2,3,7,8-TCDF
1,2,3,9-TCDF

TABLE 6. ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS WHEN ALL CDDS/CDFS ARE TESTED [1]

CDD/CDF	Test Conc. (ng/mL)	IPR [2,3] s (ng/mL)	IPR [2,3] X (ng/mL)	OPR (ng/mL)	VER (ng/mL)
2,3,7,8-TCDD	10	2.8	8.3-12.9	6.7-15.8	7.8-12.9
2,3,7,8-TCDF	10	2.0	8.7-13.7	7.5-15.8	8.4-12.0
1,2,3,7,8-PeCDD	50	7.5	38-66	35-71	39-65
1,2,3,7,8-PeCDF	50	7.5	43-62	40-67	41-60
2,3,4,7,8-PeCDF	50	8.6	36-75	34-80	41-61
1,2,3,4,7,8-HxCDD	50	9.4	39-76	35-82	39-64
1,2,3,6,7,8-HxCDD	50	7.7	42-62	38-67	39-64
1,2,3,7,8,9-HxCDD	50	11.1	37-71	32-81	41-61
1,2,3,4,7,8-HxCDF	50	8.7	41-59	36-67	45-56
1,2,3,6,7,8-HxCDF	50	6.7	46-60	42-65	44-57
1,2,3,7,8,9-HxCDF	50	6.4	42-61	39-65	45-56
2,3,4,6,7,8-HxCDF	50	7.4	37-74	35-78	44-57
1,2,3,4,6,7,8-HpCDD	50	7.7	38-65	35-70	43-58
1,2,3,4,6,7,8-HpCDF	50	6.3	45-56	41-61	45-55
1,2,3,4,7,8,9-HpCDF	50	8.1	43-63	39-69	43-58
OCDD	100	19	89-127	78-144	79-126
OCDF	100	27	74-146	63-170	63-159
$^{13}C_{12}$-2,3,7,8-TCDD	100	37	28-134	20-175	82-121
$^{13}C_{12}$-2,3,7,8-TCDF	100	35	31-113	22-152	71-140
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	39	27-184	21-227	62-160
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	34	27-156	21-192	76-130
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	38	16-279	13-328	77-130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	41	29-147	21-193	85-117
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	38	34-122	25-163	85-118
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	43	27-152	19-202	76-131
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	35	30-122	21-159	70-143
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	40	24-157	17-205	74-135
$^{13}C_{12}$-2,3,4,6,7,8,-HxCDF	100	37	29-136	22-176	73-137
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	35	34-129	26-166	72-138
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	41	32-110	21-158	78-129
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	40	28-141	20-186	77-129
$^{13}C_{12}$-OCDD	200	95	41-276	26-397	96-415
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.6	3.9-15.4	3.1-19.1	7.9-12.7

[1] All specifications are given as concentration in the final extract, assuming a 20 µL volume.
[2] s = standard deviation of the concentration.
[3] X = average concentration.

TABLE 6A. ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS WHEN ONLY TETRA COMPOUNDS ARE TESTED [1]

CDD/CDF	Test Conc. (ng/mL)	IPR [2,3] s (ng/mL)	IPR [2,3] X (ng/mL)	OPR (ng/mL)	VER (ng/mL)
2,3,7,8-TCDD	10	2.7	8.7–12.4	7.3–14.6	8.2–12.3
2,3,7,8-TCDF	10	2.0	9.1–13.1	8.0–14.7	8.6–11.6
$^{13}C_{12}$-2,3,7,8-TCDD	100	35	32–115	25–141	85–117
$^{13}C_{12}$-2,3,7,8-TCDF	100	34	35–99	26–126	76–131
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.4	4.5–13.4	3.7–15.8	8.3–12.1

[1] All specifications are given as concentration in the final extract, assuming a 20 µL volume.
[2] s = standard deviation of the concentration.
[3] X = average concentration.

TABLE 7. LABELED COMPOUND RECOVERY IN SAMPLES WHEN ALL CDDS/CDFS ARE TESTED

Compound	Test Conc. (ng/mL)	Labeled Compound Recovery (ng/mL) [1]	Labeled Compound Recovery (%)
$^{13}C_{12}$-2,3,7,8-TCDD	100	25–164	25–164
$^{13}C_{12}$-2,3,7,8-TCDF	100	24–169	24–169
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	25–181	25–181
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	24–185	24–185
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	21–178	21–178
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	32–141	32–141
$^{13}C_{12}$-1,2,3,6,7,8,-HxCDD	100	28–130	28–130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	26–152	26–152
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	26–123	26–123
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	29–147	29–147
$^{13}C_{12}$-2,3,4,6,7,8,-HxCDF	100	28–136	28–136
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	23–140	23–140
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	28–143	28–143
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	26–138	26–138
$^{13}C_{12}$-OCDD	200	34–313	17–157
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.5–19.7	35–197

[1] Specification given as concentration in the final extract, assuming a 20-µL volume.

TABLE 7A. LABELED COMPOUND RECOVERY IN SAMPLES WHEN ONLY TETRA COMPOUNDS ARE TESTED

Compound	Test Conc. (ng/mL)	Labeled compound recovery	
		(ng/mL) [1]	(%)
$^{13}C_{12}$-2,3,7,8-TCDD	100	31-137	31-137
$^{13}C_{12}$-2,3,7,8-TCDF	100	29-140	29-140
$^{37}Cl_4$-2,3,7,8-TCDD	10	4.2-16.4	42-164

[1] Specification given as concentration in the final extract, assuming a 20 µL volume.

TABLE 8. DESCRIPTORS, EXACT M/Z's, M/Z TYPES, AND ELEMENTAL COMPOSITIONS OF THE CDDs AND CDFs

Descriptor	Exact M/Z [1]	M/Z Type	Elemental Composition	Substance [2]
1	292.9825	Lock	$C_7 F_{11}$	PFK
	303.9016	M	$C_{12} H_4 {}^{35}Cl_4 O$	TCDF
	305.8987	M+2	$C_{12} H_4 {}^{35}Cl_3 {}^{37}Cl O$	TCDF
	315.9419	M	$^{13}C_{12} H_4 {}^{35}Cl_4 O$	TCDF [3]
	317.9389	M+2	$^{13}C_{12} H_4 {}^{35}Cl_3 {}^{37}Cl O$	TCDF [3]
	319.8965	M	$C_{12} H_4 {}^{35}Cl_4 O_2$	TCDD
	321.8936	M+2	$C_{12} H_4 {}^{35}Cl_3 {}^{37}Cl O_2$	TCDD
	327.8847	M	$C_{12} H_4 {}^{37}Cl_4 O_2$	TCDD [4]
	330.9792	QC	$C_7 F_{12}$	PFK
	331.9368	M	$^{13}C_{12} H_4 {}^{35}Cl_4 O_2$	TCDD [3]
	333.9339	M+2	$^{13}C_{12} H_4 {}^{35}Cl_3 {}^{37}Cl O_2$	TCDD [3]
	375.8364	M+2	$C_{12} H_4 {}^{35}Cl_5 {}^{37}Cl O$	HxCDPE
2	339.8597	M+2	$C_{12} H_3 {}^{35}Cl_3 {}^{37}Cl O$	PeCDF
	341.8567	M+4	$C_{12} H_3 {}^{35}Cl_2 {}^{37}Cl_2 O$	PeCDF
	351.9000	M+2	$^{13}C_{12} H_3 {}^{35}Cl_3 {}^{37}Cl O$	PeCDF
	353.8970	M+4	$^{13}C_{12} H_3 {}^{35}Cl_2 {}^{37}Cl_2 O$	PeCDF [3]
	354.9792	Lock	$C_9 F_{12}$	PFK
	355.8546	M+2	$C_{12} H_3 {}^{35}Cl_4 {}^{37}Cl O_2$	PeCDD
	357.8516	M+4	$C_{12} H_3 {}^{35}Cl_3 {}^{37}Cl_2 O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12} H_3 {}^{35}Cl_4 {}^{37}Cl O_2$	PeCDD [3]
	369.8919	M+4	$^{13}C_{12} H_3 {}^{35}Cl_3 {}^{37}Cl_2 O_2$	PeCDD [3]
	409.7974	M+2	$C_{12} H_3 {}^{35}Cl_6 {}^{37}Cl O$	HpCDPE
3	373.8208	M+2	$C_{12} H_2 {}^{35}Cl_5 {}^{37}Cl O$	HxCDF
	375.8178	M+4	$C_{12} H_2 {}^{35}Cl_4 {}^{37}Cl_2 O$	HxCDF
	383.8639	M	$^{13}C_{12} H_2 {}^{35}Cl_6 O$	HxCDF [3]
	385.8610	M+2	$^{13}C_{12} H_2 {}^{35}Cl_5 {}^{37}Cl O$	HxCDF [3]
	389.8157	M+2	$C_{12} H_2 {}^{35}Cl_5 {}^{37}Cl O_2$	HxCDD
	391.8127	M+4	$C_{12} H_2 {}^{35}Cl_4 {}^{37}Cl_2 O_2$	HxCDD

TABLE 8. DESCRIPTORS, EXACT M/Z's, M/Z TYPES, AND ELEMENTAL COMPOSITIONS OF THE CDDs AND CDFs

Descriptor	Exact M/Z [1]	M/Z Type	Elemental Composition	Substance [2]
	392.9760	Lock	C_8F_{15}	PFK
	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDD [3]
	403.8529	M+4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDD [3]
	430.9729	QC	C_9F_{17}	PFK
	445.7555	M+4	$C_{12}H_2{}^{35}Cl_5{}^{37}Cl_2O$	OCDPE
4	407.7818	M+2	$C_{12}H{}^{35}Cl_5{}^{37}ClO$	HpCDF
	409.7789	M+4	$C_{12}H{}^{35}Cl_3{}^{37}Cl_2O$	HpCDF
	417.8253	M	$^{13}C_{12}H{}^{35}Cl_7O$	HpCDF [3]
	419.8220	M+2	$^{13}C_{12}H{}^{35}Cl_6{}^{37}ClO$	HpCDF [3]
	423.7766	M+2	$C_{12}H{}^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M+4	$C_{12}H{}^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	430.9729	Lock	C_9F_{17}	PFK
	435.8169	M+2	$^{13}C_{12}H{}^{35}Cl_6{}^{37}ClO_2$	HpCDD [3]
	437.8140	M+4	$^{13}C_{12}H{}^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD [3]
	479.7165	M+4	$C_{12}H{}^{35}Cl_6{}^{37}Cl_2O$	NCDPE
5	441.7428	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	442.9728	Lock	$C_{10}F_{17}$	PFK
	443.7399	M+4	$C_{12}{}^{35}Cl_5{}^{37}Cl_2O$	OCDF
	457.7377	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7779	M+2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD [3]
	471.7750	M+4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD [3]
	513.6775	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	DCDPE

[1] Nuclidic masses used:

H = 1.007825 C = 12.00000 ^{13}C = 13.003355 F = 18.9984
O = 15.994915 ^{35}Cl = 34.968853 ^{37}Cl = 36.965903

[2] TCDD = Tetrachlorodibenzo-*p*-dioxin; TCDF = Tetrachlorodibenzofuran
PeCDD = Pentachlorodibenzo-*p*-dioxin; PeCDF = Pentachlorodibenzofuran
HxCDD = Hexachlorodibenzo-*p*-dioxin; HxCDF = Hexachlorodibenzofuran
HpCDD = Heptachlorodibenzo-*p*-dioxin; HpCDF = Heptachlorodibenzofuran
OCDD = Octachlorodibenzo-*p*-dioxin; OCDF = Octachlorodibenzofuran
HxCDPE = Hexachlorodiphenyl ether; HpCDPE = Heptachlorodiphenyl ether
OCDPE = Octachlorodiphenyl ether; NCDPE = Nonachlorodiphenyl ether
DCDPE = Decachlorodiphenyl ether; PFK = Perfluorokerosene

[3] Labeled compound.

[4] There is only one m/z for $^{37}Cl_4$-2,3,7,8,-TCDD (cleanup standard).

TABLE 9. THEORETICAL ION ABUNDANCE RATIOS AND QC LIMITS

Number of Chlorine Atoms	M/Z's Forming Ratio	Theoretical Ratio	QC Limit [1]	
			Lower	Upper
4 [2]	M/(M+2)	0.77	0.65	0.89
5	(M+2)/(M+4)	1.55	1.32	1.78
6	(M+2)/(M+4)	1.24	1.05	1.43
6 [3]	M/(M+2)	0.51	0.43	0.59
7	(M+2)/(M+4)	1.05	0.88	1.20
7 [4]	M/(M+2)	0.44	0.37	0.51
8	(M+2)/(M+4)	0.89	0.76	1.02

[1] QC limits represent ±15% windows around the theoretical ion abundance ratios.
[2] Does not apply to $^{37}Cl_4$-2,3,7,8-TCDD (cleanup standard).
[3] Used for $^{13}C_{12}$-HxCDF only.
[4] Used for $^{13}C_{12}$-HpCDF only.

TABLE 10. SUGGESTED SAMPLE QUANTITIES TO BE EXTRACTED FOR VARIOUS MATRICES [1]

Sample Matrix [2]	Example	Percent Solids	Phase	Quantity Extracted
Single-phase				
Aqueous	Drinking water Groundwater Treated wastewater	<1	—[3]	1000 mL
Solid	Dry soil Compost Ash	>20	Solid	10 g
Organic	Waste solvent Waste oil Organic polymer	<1	Organic	10 g
Tissue	Fish Human adipose	—	Organic	10 g
Multi-phase				
Liquid/Solid				
Aqueous/Solid	Wet soil Untreated effluent Digested municipal sludge Filter cake Paper pulp	1–30	Solid	10 g
Organic/solid	Industrial sludge Oily waste	1–100	Both	10 g
Liquid/Liquid				
Aqueous/organic	In-process effluent Untreated effluent Drum waste	<1	Organic	10 g
Aqueous/organic/solid	Untreated effluent Drum waste	>1	Organic & solid	10 g

[1] The quantitity of sample to be extracted is adjusted to provide 10 g of solids (dry weight). One liter of aqueous samples containing 1% solids will contain 10 g of solids. For aqueous samples containing greater than 1% solids, a lesser volume is used so that 10 g of solids (dry weight) will be extracted.

[2] The sample matrix may be amorphous for some samples. In general, when the CDDs/CDFs are in contact with a multiphase system in which one of the phases is water, they will be preferentially dispersed in or adsorbed on the alternate phase because of their low solubility in water.

[3] Aqueous samples are filtered after spiking with the labeled compounds. The filtrate and the materials trapped on the filter are extracted separately, and the extracts are combined for cleanup and analysis.

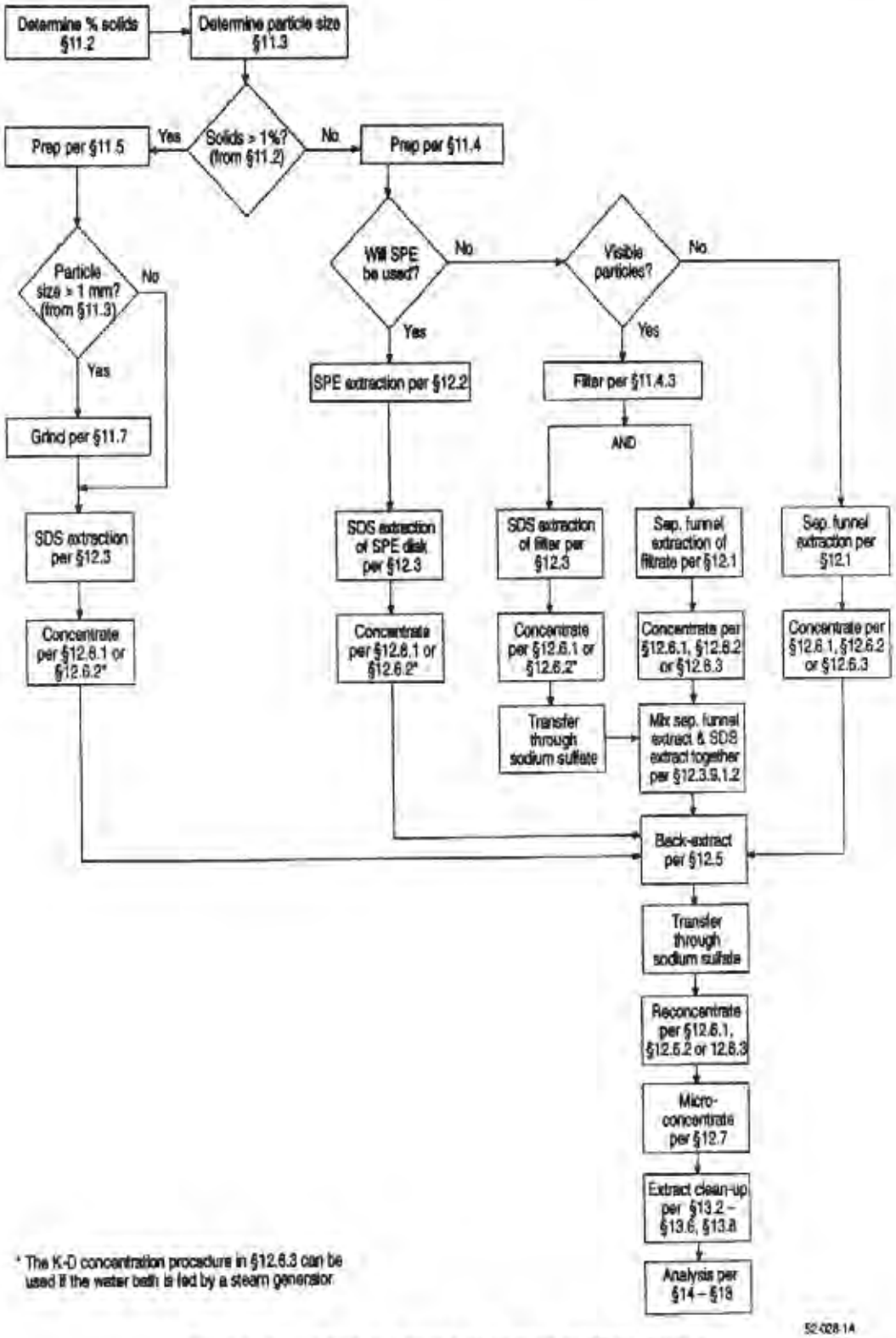


Figure 1. Flow Chart for Analysis of Aqueous and Solid Samples

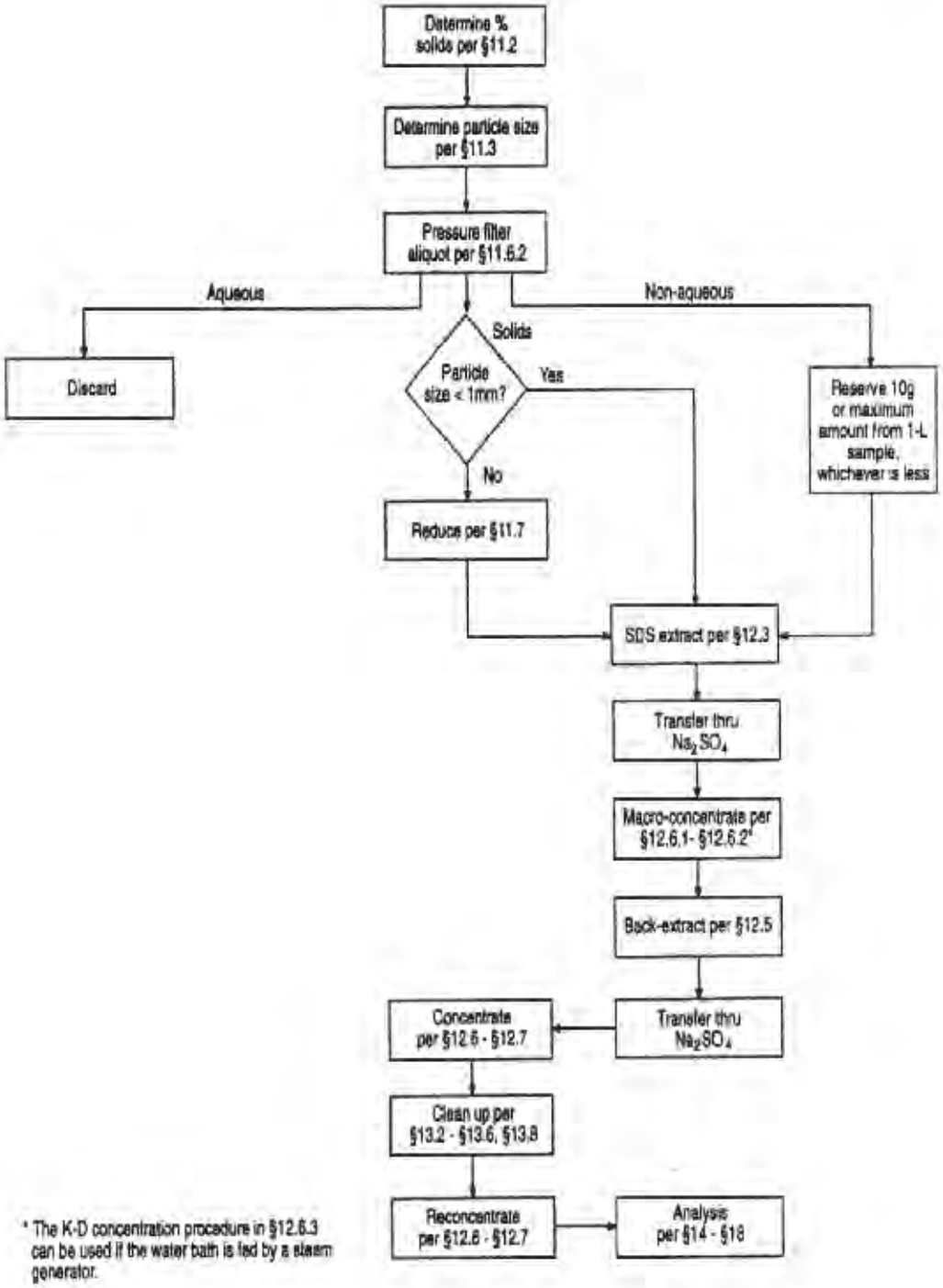


Figure 2. Flow Chart for Analysis of Multi-Phase Samples

52-028-2A

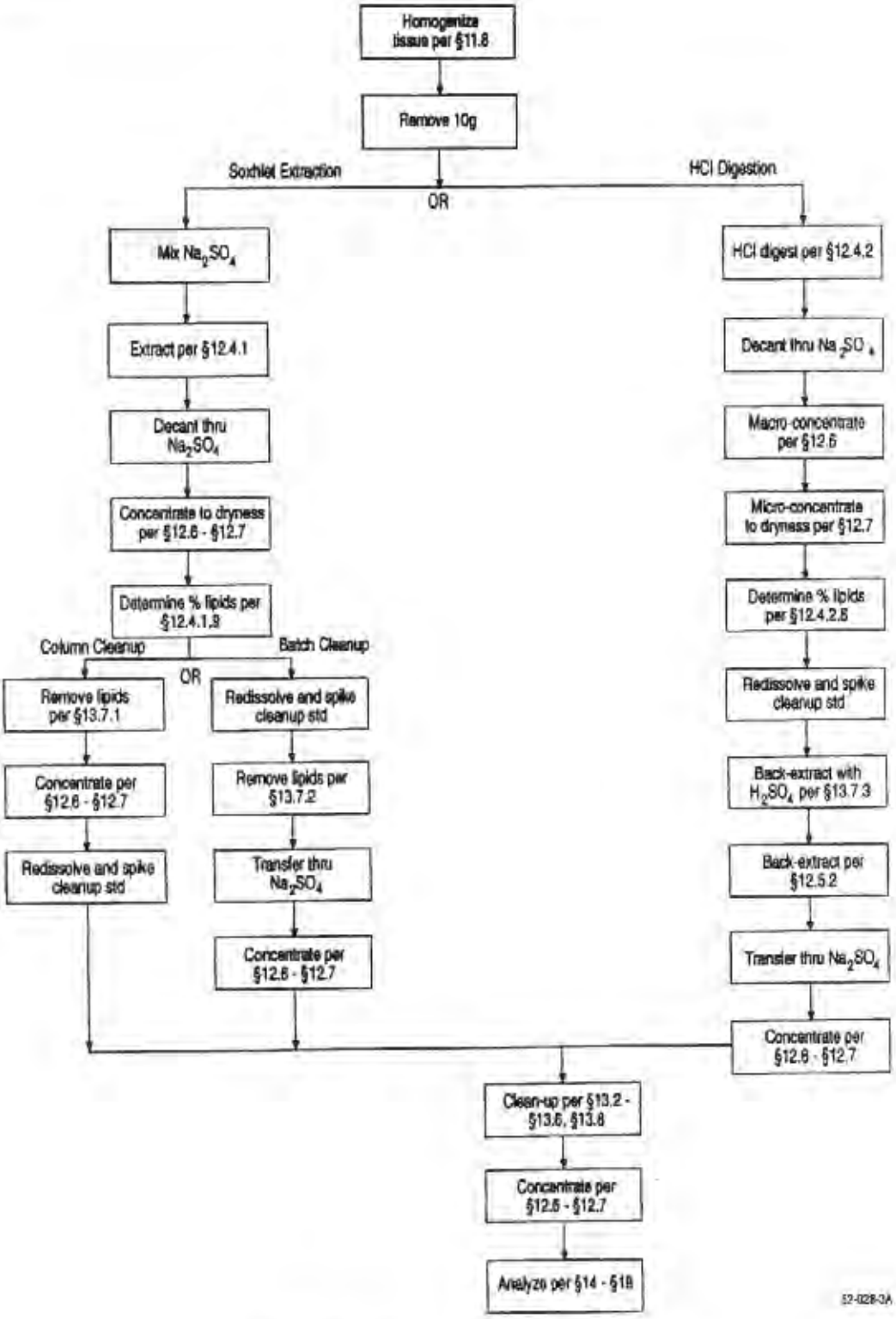


Figure 3. Flow Chart for Analysis of Tissue Samples

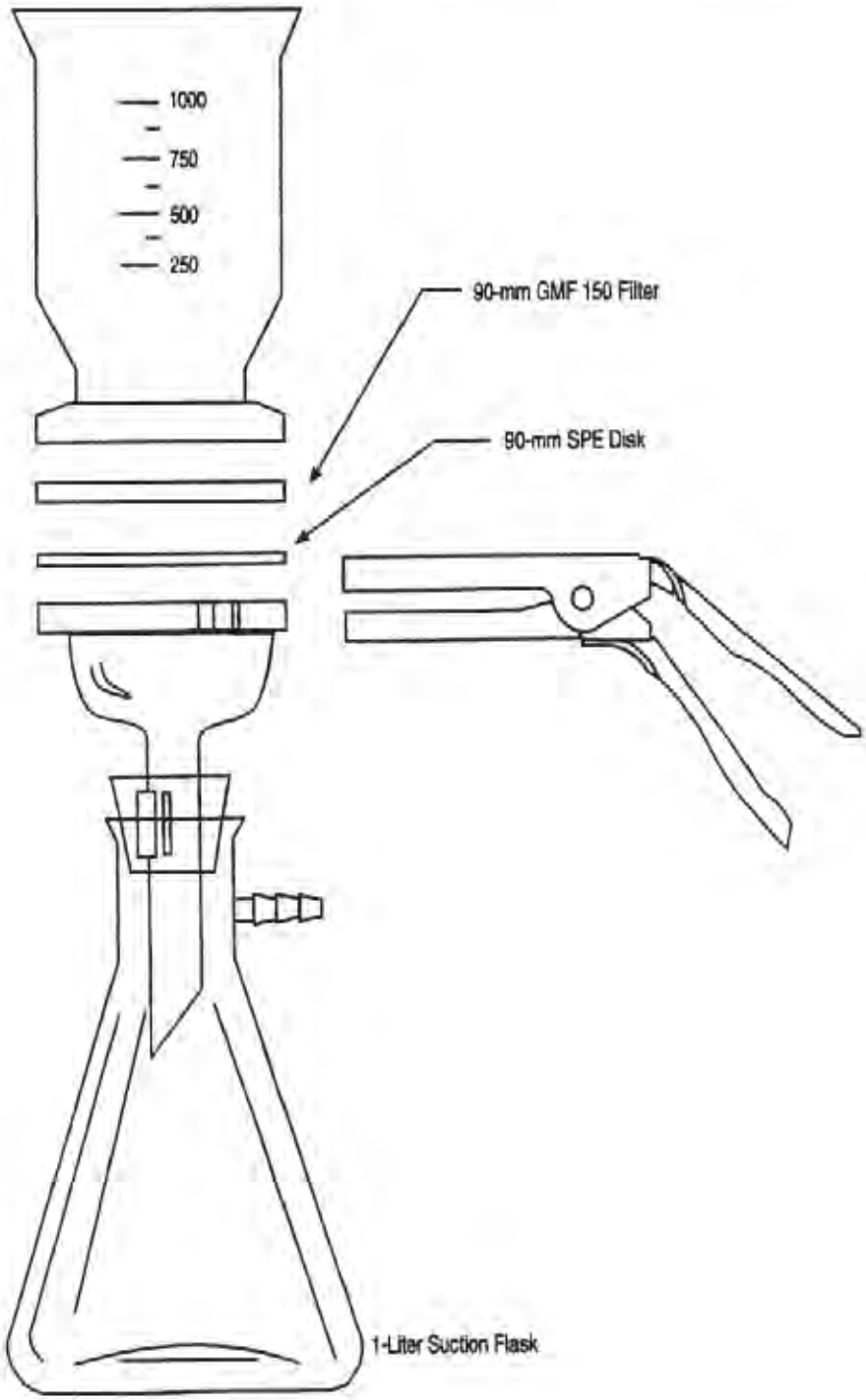
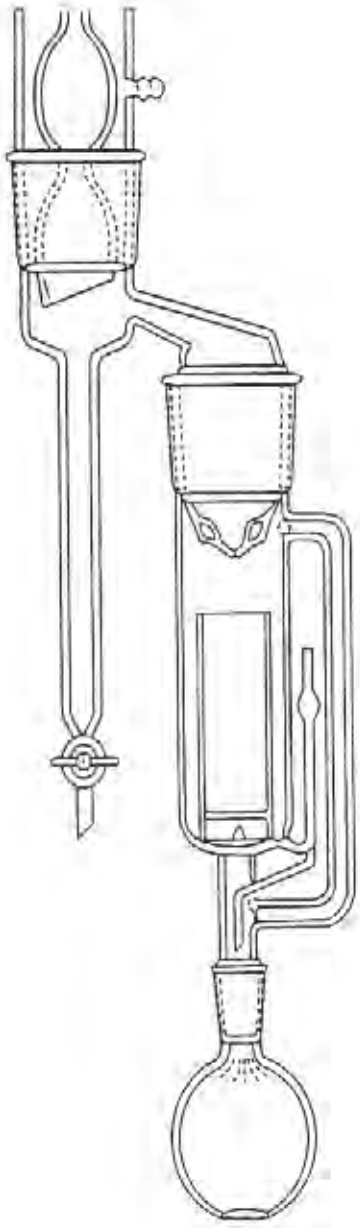


Figure 4. Solid-Phase Extraction Apparatus

82-027-1A



52-0027-9A

Figure 5. Soxhlet/Dean-Stark Extractor

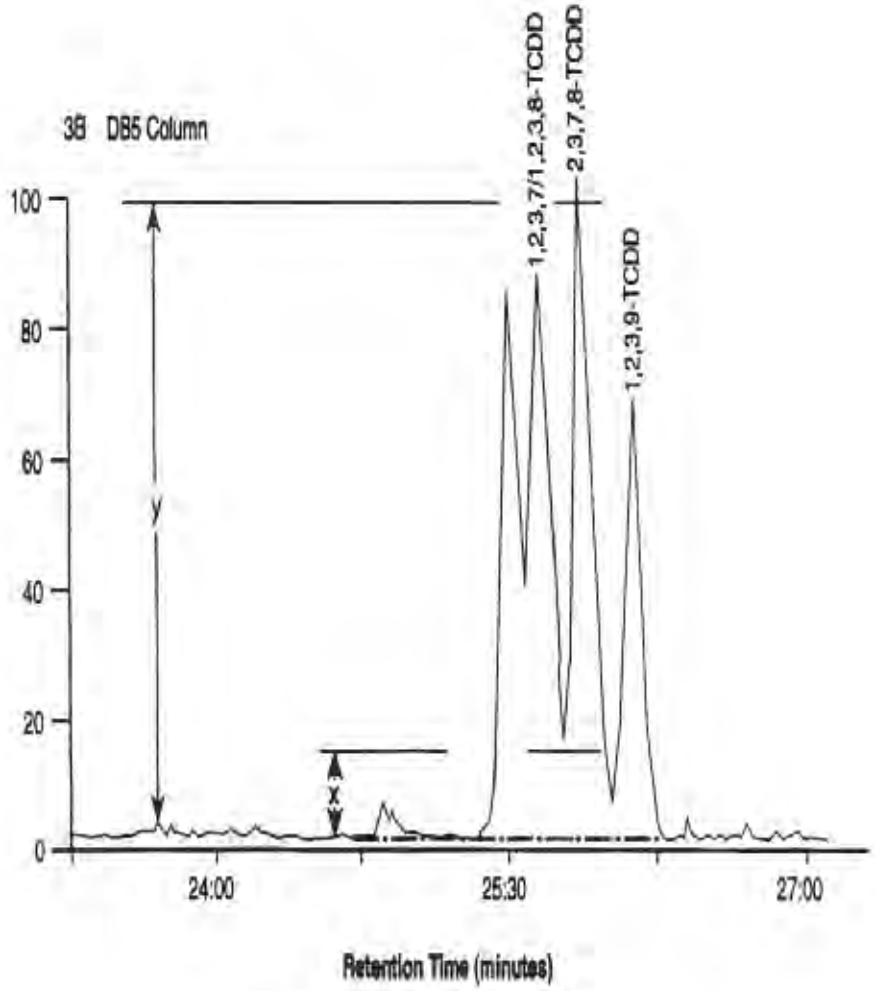


Figure 6. Isomer-Specific Separation of 2,3,7,8-TCDD on DB-5 Column

52-027-03

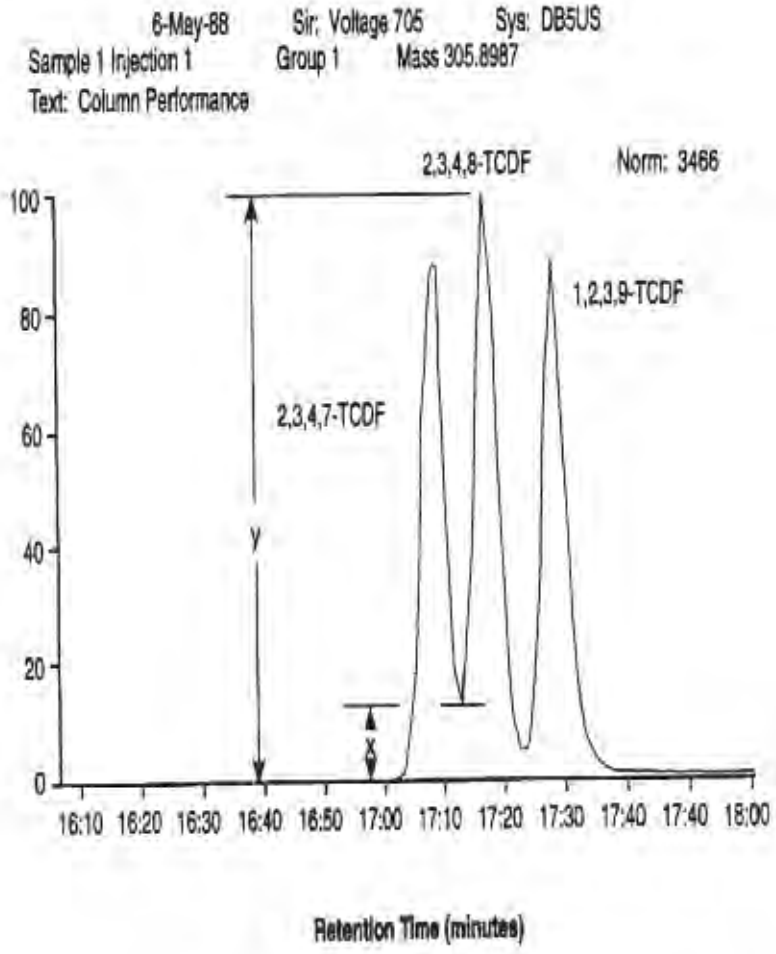


Figure 7. Isomer-Specific Separation of 2,3,7,8-TCDF on DB-5 Column

52-027-4A

24.0 Glossary of Definitions and Purposes

These definitions and purposes are specific to this method but have been conformed to common usage as much as possible.

24.1 Units of weight and Measure and Their Abbreviations

24.1.1 Symbols

°C	degrees Celsius
µL	microliter
µm	micrometer
<	less than
>	greater than
%	percent

24.1.2 Alphabetical abbreviations

amp	ampere
cm	centimeter
g	gram
h	hour
ID	inside diameter
in.	inch
L	liter
M	Molecular ion
m	meter
mg	milligram
min	minute
mL	milliliter
mm	millimeter
m/z	mass-to-charge ratio
N	normal; gram molecular weight of solute divided by hydrogen equivalent of solute, per liter of solution
OD	outside diameter
pg	picogram
ppb	part-per-billion
ppm	part-per-million
ppq	part-per-quadrillion
ppt	part-per-trillion
psig	pounds-per-square inch gauge
v/v	volume per unit volume
w/v	weight per unit volume

24.2 Definitions and Acronyms (in Alphabetical Order)

Analyte—A CDD or CDF tested for by this method. The analytes are listed in Table 1.

Calibration Standard (CAL)—A solution prepared from a secondary standard and/or stock solutions and used to calibrate the response of the instrument with respect to analyte concentration.

Calibration Verification Standard (VER)—The mid-point calibration standard (CS3) that is used in to verify calibration. See Table 4.

CDD—Chlorinated Dibenzo-*p*-ioxin—The isomers and congeners of tetra- through octa-chlorodibenzo-*p*-dioxin.

CDF—Chlorinated Dibenzofuran—The isomers and congeners of tetra- through octa-chlorodibenzofuran.

CS1, CS2, CS3, CS4, CS5—See Calibration standards and Table 4.

Field Blank—An aliquot of reagent water or other reference matrix that is placed in a sample container in the laboratory or the field, and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.

GC—Gas chromatograph or gas chromatography.

GPC—Gel permeation chromatograph or gel permeation chromatography.

HPLC—High performance liquid chromatograph or high performance liquid chromatography.

HRGC—High resolution GC.

HRMS—High resolution MS.

IPR—Initial precision and recovery; four aliquots of the diluted PAR standard analyzed to establish the ability to generate acceptable precision and accuracy. An IPR is performed prior to the first time this method is used and any time the method or instrumentation is modified.

K-D—Kudema-Danish concentrator; a device used to concentrate the analytes in a solvent.

Laboratory Blank—See method blank.

Laboratory Control sample (LCS)—See ongoing precision and recovery standard (OPR).

Laboratory Reagent Blank—See method blank.

May—This action, activity, or procedural step is neither required nor prohibited.

May Not—This action, activity, or procedural step is prohibited.

Method Blank—An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The method blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

Minimum Level (ML)—The level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

MS—Mass spectrometer or mass spectrometry.

Must This action, activity, or procedural step is required.

OPR Ongoing precision and recovery standard (OPR); a laboratory blank spiked with known quantities of analytes. The OPR is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery.

PAR—Precision and recovery standard; secondary standard that is diluted and spiked to form the IPR and OPR.

PFK—Perfluorokerosene; the mixture of compounds used to calibrate the exact m/z scale in the HRMS.

Preparation Blank—See method blank.

Primary Dilution Standard—A solution containing the specified analytes that is purchased or prepared from stock solutions and diluted as needed to prepare calibration solutions and other solutions.

Quality Control Check Sample (QCS)—A sample containing all or a subset of the analytes at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from a source of standards different from the source of calibration standards. It is used to check laboratory performance with test materials prepared external to the normal preparation process.

Reagent Water—Water demonstrated to be free from the analytes of interest and potentially interfering substances at the method detection limit for the analyte.

Relative Standard Deviation (RSD)—The standard deviation times 100 divided by the mean. Also termed "coefficient of variation."

RF—Response factor. See Section 10.6.1.

RR—Relative response. See Section 10.5.2.

RSD—See relative standard deviation.

SDS—Soxhlet/Dean-Stark extractor: an extraction device applied to the extraction of solid and semi-solid materials (Reference 7).

Should—This action, activity, or procedural step is suggested but not required.

SICP—Selected ion current profile: the line described by the signal at an exact m/z.

SPE—Solid-phase extraction: an extraction technique in which an analyte is extracted from an aqueous sample by passage over or through a material capable of reversibly adsorbing the analyte. Also termed liquid-solid extraction.

Stock Solution—A solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

TCDD—Tetrachlorodibenzo-*p*-dioxin.

TCDF—Tetrachlorodibenzofuran.

VER—See calibration verification standard.

Analytical Methods

Grain Size

SOP PTL-10-200

1.0 PURPOSE

1.1. The purpose of this document is to detail the standard operating procedure for the Malvern Mastersizer 2000 laser diffractor on a wet basis.

2.0 SCOPE

2.1. Applies to all laboratory staff who analyzes samples on the Mastersizer 2000.

3.0 RESPONSIBLE PARTIES

3.1. Lab Management
3.2. Laboratory Analysts

4.0 ASSOCIATED MATERIALS

4.1. PV Mastersizer 2000 Form (PTL-10-200A)
4.2. TM Mastersizer 2000 Form (PTL-10-200C)
4.3. PR Mastersizer 2000 Form (PTL-10-200D)
4.4. Instrument Use Log (PTL-12-010A)
4.5. Routine Maintenance Form (PTL-12-011A)
4.6. Non-Routine Maintenance Form (PTL-12-012A)

5.0 INSTRUMENTATION

5.1 The Mastersizer 2000 is a laser diffractor that measures the particle size of liquids and powder in a wet suspension on a volume basis. The system is comprised of the following:

a. Mastersizer 2000
b. Hydro 2000S Sample Dispersion Unit
c. Flow cell
d. Computer
e. Printer
f. Solvent waste container

5.2. The Mastersizer 2000, in conjunction with the computer, measures the particle size of the sample that passes in front of the laser and

in turn produces a volume-weighted histogram and numerical statistics associated with the sample type.

5.3. The flow cell is fitted into the slot of the Mastersizer 2000.

5.4. The flow cell is connected with tubing to the Hydro 2000S sample dispersion unit. The Hydro 2000S recirculates the dispersed sample suspension through the flow cell at a user set speed. The sample suspension circulates through the flow cell as the laser beam passes through the flow cell and diffracts and scatters light.

6.0 PERFORMANCE VERIFICATIONS

6.1. Standards of a known size are analyzed quarterly by a trained operator to ensure that the Mastersizer 2000 is within normal operating parameters.

6.2. The standard is prepared and analyzed according to individual test methods created for each standard. These methods reflect the standard manufacturer's recommendations for sample prep and/or analysis and are stored in the active lab method binder.

6.3. Performance Verification (PV) forms, to be completed by the analyst, describe the standard used, results, pass or fail and analyst and reviewer signature.

6.4. The performance verification passes if the mean/median size is +/- 3% of the known value for all reference materials.

6.5. The data and PV form are in the laboratory maintenance binders.

7.0 USE LOG

7.1. The Use Log form is maintained in the maintenance binder. The log documents all project numbers, the user, date, and company name.

8.0 PROJECT RECORD

8.1 Record all work on PR form

9.0 INSTRUMENT SET-UP

9.1. Turn computer and optical unit on. To turn on the optical unit, press the button on the side of the instrument.

9.2. Fit tubing to recirculator (Hydro2000S) and flow cell.

9.3. Fit the flow cell into the slot and lock it in place by turning the handle.

9.4 To turn on the Hydro 2000S press the button on the back of the recirculator, located right above the power cord.

9.5 Make sure the waste tubing in the back of the instrument is in the solvent waste container.

10.0 SOFTWARE SET-UP

10.1. Open Mastersizer 2000 program. On main windows screen, select
Start
All Programs
Malvern Instruments
Mastersizer 2000 Version 5.1

Instead of this you can also click on the Mastersizer 2000 Icon on the desktop.

10.2 A window comes up asking you to type your user name to log on. The default user name is: Administrator. Press **OK** to go on.

10.3 Another window comes up with four choices
a) Run an existing SOP
b) Edit an existing SOP
c) Use the SOP Creation Wizard
d) Make manual Measurement

Depending on what you want to do select one and press **OK**.

11.0 NEW SOP CREATION WIZARD

11.1 Window opens up – Hit **Next**

11.2 Chose the sample handling unit – Hydro 2000S (A)

11.3 Hit **Next**

11.4 Enter information for Material Name by either choosing:
a) from dropdown menu
or if not already present
b) hitting the material button
1) Now pick from list of assorted materials with known refractive indexes and hit move (that brings it into the dropdown menu on the previous window)
2) Otherwise hit add and fill in the
a) Name of sample
b) Refractive Index of Sample
c) Adsorption
d) Density (Default is 1)

There is a box that gives you a choice of different values for blue light. Our default is to use the same for red and blue light.

11.5. Hit **OK**

11.6 Now info is in the sample materials box which is really the dropdown menu on the other page.

11.7 Hit **OK**

11.8. Enter the dispersant (aka carrier) by choosing from the dropdown menu or if it is not there by hitting the **Dispersant** button and filling in:
a) Name of dispersant
b) Refractive Index of dispersant
c) Adsorption
d) Density (Default is 1)

11.9. Hit **OK**

11.10. Under Result Calculation hit the **Models** button and pick appropriate model:
a) General Purpose (our default)
b) Multiple narrow modes

c) Single mode

11.11. Under Calculation sensitivity choose enhanced normal.

11.12. For particle shape choose:
a) irregular (default)
b) spherical

11.13 Hit **OK**

11.14 Hit **Next**

11.15 Labels window opens fill in appropriate areas
1) Sample name
2) Source – choose supplier from dropdown menu
3) Source name – enter client name
4) Bulk Lot type – choose Lot # from dropdown menu
5) Bulk lot ref. – leave blank (Lot # to be entered at time of analysis for each sample)

11.16 Operator Instructions and comments:
1) check box Display instructions before measurement
2) check box Allow operator to enter comments before measurement
3) uncheck box display instructions after measurement

11.17 Hit **Next**

11.18 Report/Savings Window opens up
a) do not check box always print results (we print them later as needed)
b) under reports page pick Result Analysis PTL –Wet(M).pag (our default) from dropdown menu

11.19 Hit next

11.20 Measurement Window opens up
a) Fill in measurement time (12 Seconds is the default)
b) Fill in background time (12 Seconds is the default) Background time needs to be the same or longer than the measurement time

11.21 Hit **Advanced Options** button and fill in:
- a) Obscuration limits (10-20 is the default) If that needs to be changed uncheck the box and fill in the appropriate limits.
- b) Obscuration filtering – check box enable filtering (this makes sure only measurements in the obscuration limits are made)
- c) For large particles go to Red Only Measurement and check the box enable red only measurement

11.22 Hit **OK**

11.23 Hit **Next**

11.24 Under Sampler Settings set the pump/stir speed to the appropriate RPMs (2000 RPM is our default)

11.25 Under ultrasonics chose from different settings (default is none)

11.26 Under Tank Fill choose manual

11.27 Hit **Next**

11.28 Under check box "create average results" Measurement Cycles pick:
- a) Aliquots per SOP (1 is our default)
- b) Measurements per aliquot (4 is our default)
- c) Delay (60 Seconds is our default)

11.29 Cleaning – choose manual
Make sure to uncheck box "Unable after each aliquot"

11.30 Hit **Next**

11.31 Quantities (default on all choices is either don't specify or none)

11.32 Hit **Next**

11.33 Hit **Finish**

11.34 Save SOP as company name – sample name

Info: If you're ever in doubt about what to choose on any of these hit one of the advice buttons located on every page of the SOP wizard or ask another analyst.

12.0 MANUAL MEASUREMENT

12.1 Open **File**

12.2 Select **New**

12.3. Enter File name (PTL project number; i.e.7731)

12.4. Hit save

12.5 Go to Measure – Manual

12.6 Under Measurement Options Window choose:
a) Materials and fill in as shown in 7.4
b) Measurement fill in everything like 7.19
c) Measurement Cycles fill in number of cycles (measurements) as well as the delay (60 Seconds)

12.7 Hit **OK**

12.8 A screen opens up – when system is clean and ready for measurement

12.9 Hit **Start**

12.10 Once done it goes through the alignment and background measurement screens

12.11 When you get to the documentation screen, enter lot number as well as pre-measurement instructions:
a) Customer name: Sample name:
b) Per Test Method:
c) Analyst:
d) Particle Technology Labs, Ltd. PTL ID: five digit number

12.12 Hit **OK**

12.13 Add sample until appropriate obscuration is reached (in the green range)

12.14 Hit **Start**

13.0 MEASURING USING AN SOP

13.1. Go to File – New

13.2. Enter File name (PTL project number; i.e.7731)

13.3. Hit save

13.4. Go to Measure – start SOP

13.5 Fill the appropriate SOP from list and hit open

13.6 Full recirculator with appropriate solvent

13.7 It goes through the aligning as well as the background measuring screen

13.8 Documentation Screen opens up

13.9 Enter the lot number as well as pre-measurement instructions:

a) Customer name: Sample name:
b) Per Test Method:
c) Analyst:
d) Particle Technology Labs, Ltd. PTL ID: Five digit number

13.10 Hit **OK**

13.11 Add sample until the appropriate obscuration is reached.

13.12 Hit **Start** (that starts the analysis)

13.13 Once done window will open up asking you if you want to run the analysis again

13.14 Hit No after cleaning system follow steps 13.5-13.13.

14.0 CLEANING WINDOWS

14.1. Remove the flow cell from the housing.

14.2. Place flow cell on a paper towel.

14.3. Using the Malvern screwdriver, remove the windows from the flow cell and wipe the surface with cleaning fluid (ex: Acetone, Isopropyl Alcohol, glass cleaner) and a Kimwipe. NEVER wipe the windows when they are dry.

14.4. Check that there are not any fingerprints or smudges on the windows.

14.5. If the windows appear clean, reassemble the flow cell.

14.6. Place flow cell back into the optical unit.

14.7. Perform a background to ensure that the cell is clean and within operating requirements.

14.8 After changing carrier fluids or prior to each new project, a background is performed and printed. The printed background will be placed in the project file.

15.0 PRINTING DATA

15.1. Go to file – open and open the desired project file.

15.2. That opens the record window of the file.

15.3. The average of all runs will be printed and given to the client unless otherwise justified. In addition individual runs can be released at client 's request.

15.4 Select Result Analysis PTL – Wet(M) from toolbar unless otherwise specified.

15.5 That brings up the desired run in the default printout view.

15.6. Hit the printer icon in the toolbar to print out results.

15.7. Select OK.

16.0 PRINTING BACKGROUND

16.1. A background will be printed for the following circumstances:

16.1.1. One background will be printed for each sample or set of samples in a project, which are analyzed without interruption. When a stop in the analysis, break, or end of the day occurs, a new background will be printed to verify that those subsequent samples were analyzed under the same background integrity.

16.1.2. When the carrier fluid is switched. If a project contains samples that need to be analyzed in more than one type of carrier fluid, a background will be printed for each carrier fluid type.

16.1.3. For a performance verification.

16.2 The background is saved with each measurement and can be called back after the analysis.

16.3 Under File, select Open.

16.4 Choose the file that is needed.

16.5 Select the record number or the analysis that you would like to retrieve the background from.

16.6 Click on Data (M) in bar located under the tool menus or go to Configure, View/Report Selection and mark the box next to Data (M). Hit OK.

16.7 Select the print button from the tool bar to print the background.

16.7 Place the background in the project file or with the performance verification.

17.0 CLEAN UP

17.1. Rinse clean carrier fluid through the system until the background is clean.

17.2. If necessary clean the windows and rinse again. (See section 14 Cleaning Windows)

18.0 INSTRUMENT SHUT DOWN

18.1. Exit the Malvern Mastersizer 2000 program

18.2 Turn off the instrument on the side by pressing the button to the off position and pressing the button on the back of the Hydro 2000S to the off position.

18.3 Power the computer down.

19.0 ROUTINE MAINTENANCE

19.1. The connecting tubing and O-rings holding in the windows are checked and/ or replaced quarterly. The documentation concerning the replacement is found in the instrument maintenance binder.

19.2 To change the tubing, first drain the system of all contents. Then remove the tubing from the flow cell by gently pulling the tubing off. The tubing is then removed from the Hydro 2000S by gently pulling. Next, cut two new pieces of tubing the same lengths as the tubing, which was removed. Attach the new tubing to the recirculator and then to the flow cell. Verify that the tubing was placed in the proper locations for circulation.

The tubing will be replaced every quarter.

19.3 To change the O-rings, first drain the system of all contents. Next, remove the cell from the instrument and place on a clean paper towel. Using the Malvern tool, remove the windows from the cell. Very gently, push the windows out of the holder over the paper towel. It is important to keep the windows close to the table top so that they do not fall and break. Once the windows have been removed, use your finger to remove the O-rings. These can be thrown away. Place the new O-rings around the windows and very carefully and gently place them into the window holder. Using as little force as possible, press the O-rings and windows into the window holder.

When O-rings and windows are secure in window holder, replace into cell with the aide of the Malvern tool.

20.0 NON-ROUTINE MAINTENANCE

If the instrument is having any problems, the following steps are taken.

20.1 Ensure that the Performance Verification is current.

20.2 Check the settings on the instrument. Are they the normal set-up?

20.3 If a problem is encountered, notify laboratory management.

20.4 If it is determined that the instrument should be designated as is Out of Service, place a sign on the instrument which clearly states "Out of Service" and the date this occurred.

20.5 Contact the instrument manufacturer service technician.

20.6 If the instrument is repaired in-house, then a Performance Verification will be run to get it back IN SERVICE.

20.7 If the instrument is shipped to the manufacturer for repair, then upon the return of the instrument it will be re-qualified.

21.0 ADDITIONAL INFORMATION

21.1. Consulting the manufacturer's manual is very important for optical theory and operation instructions. This is a procedure guide written to be followed as an adjunct to the PTL SOP.

21.2. Malvern support. Malvern has a technical service department, which is very helpful.

22.0 APPROVALS

Originator _____ Date _____

Director or Laboratory Management _____ Date _____

Quality Assurance _____ Date _____

23.0 CHANGE OF HISTORY

Revision #	Date	Reason for Change	Require Training?
000	02-21-03	Original	
001	05-14-03	Revised section 18.1 and added the last statement into section18.2.	
002	09-24-04	Modified 6.4, 11.11,12.9 and 20.2. Added "Require Training?" into section 22. Added sections 23 and 24, "Documentation Review" and "Impact Assessment" respectively. Added "Effective Date" into heading.	Yes
003	12-13-04	Modified section 14.3.	Yes
004	05-11-05	Added sections 4.2, 4.3, 4.4, and 8.1. Modified- 11.18a from "check box always print results" to "do not check box always print results (we print them later as needed)." Section 11.28- added check box "create average results" Section 11.29- added "Make sure to uncheck box "Unable after each aliquot". Changed 13.14 to "Hit No after cleaning system follow steps 13.5-13.13.	Yes

24.0 DOCUMENTATION REVIEW

Review Date	Comments
05-11-05	See section 23.

25.0 IMPACT ASSESSMENT

SOPs #	Comments
None	
None- 12-13-04	
None- 05-11-05	

Analytical Methods

Inorganics

3010A/3050B/6010B

METHOD 3010A

ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS FOR TOTAL METALS FOR ANALYSIS BY FLAA OR ICP SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 This digestion procedure is used for the preparation of aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for analysis, by flame atomic absorption spectroscopy (FLAA) or inductively coupled argon plasma spectroscopy (ICP). The procedure is used to determine total metals.

1.2 Samples prepared by Method 3010 may be analyzed by FLAA or ICP for the following:

Aluminum	Magnesium
*Arsenic	Manganese
Barium	Molybdenum
Beryllium	Nickel
Cadmium	Potassium
Calcium	*Selenium
Chromium	Sodium
Cobalt	Thallium
Copper	Vanadium
Iron	Zinc
Lead	

* Analysis by ICP

NOTE: See Method 7760 for the digestion and FLAA analysis of Silver.

1.3 This digestion procedure is not suitable for samples which will be analyzed by graphite furnace atomic absorption spectroscopy because hydrochloric acid can cause interferences during furnace atomization. Consult Method 3020A for samples requiring graphite furnace analysis.

2.0 SUMMARY OF METHOD

2.1 A mixture of nitric acid and the material to be analyzed is refluxed in a covered Griffin beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to a low volume, it is refluxed with hydrochloric acid and brought up to volume. If sample should go to dryness, it must be discarded and the sample reprepared.

3.0 INTERFERENCES

3.1 Interferences are discussed in the referring analytical method.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beakers - 150-mL or equivalent.

4.2 Watch glasses - Ribbed and plain or equivalent.

4.3 Qualitative filter paper or centrifugation equipment.

4.4 Graduated cylinder or equivalent - 100mL.

4.5 Funnel or equivalent.

4.6 Hot plate or equivalent heating source - adjustable and capable of maintaining a temperature of 90-95°C.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine levels of impurities. If method blank is < MDL, the acid can be used.

5.4 Hydrochloric acid (1:1), HCl. Prepared from water and hydrochloric acid. Hydrochloric acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable. See Chapter Three, Step 3.1.3, for further information.

6.3 Aqueous wastewaters must be acidified to a pH of < 2 with HNO_3.

7.0 PROCEDURE

7.1 Transfer a 100-mL representative aliquot of the well-mixed sample to a 150-mL Griffin beaker and add 3 mL of concentrated HNO_3. Cover the beaker with a ribbed watch glass or equivalent. Place the beaker on a hot plate or equivalent heating source and cautiously evaporate to a low volume (5 mL), making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 3-mL portion of concentrated HNO_3. Cover the beaker with a nonribbed watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

NOTE: If a sample is allowed to go to dryness, low recoveries will result. Should this occur, discard the sample and reprepare.

7.2 Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, uncover the beaker or use a ribbed watch glass, and evaporate to a low volume (3 mL).

not allowing any portion of the bottom of the beaker to go dry. Cool the beaker. Add a small quantity of 1:1 HCl (10 mL/100 mL of final solution), cover the beaker, and reflux for an additional 15 minutes to dissolve any precipitate or residue resulting from evaporation.

7.3 Wash down the beaker walls and watch glass with water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer. This additional step can cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned. Rinse the filter and filter apparatus with dilute nitric acid and discard the rinsate. Filter the sample and adjust the final volume to 100 mL with reagent water and the final acid concentration to 10%. The sample is now ready for analysis.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each analytical batch of samples processed, blanks should be carried throughout the entire sample-preparation and analytical process. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing blanks.

8.3 Replicate samples should be processed on a routine basis. A replicate sample is a sample brought through the whole sample preparation and analytical process. A replicate sample should be processed with each analytical batch or every 20 samples, whichever is greater. Refer to Chapter One for the proper protocol when analyzing replicates.

8.4 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each batch of samples processed and whenever a new sample matrix is being analyzed. Refer to Chapter One for the proper protocol when analyzing spikes.

8.5 The method of standard addition shall be used for the analysis of all EP extracts and delisting petitions (see Method 7000, Step 8.7). Although not required, use of the method of standard addition is recommended for any sample that is suspected of having an interference.

9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.


Start
7.1 Transfer sample aliquot to beaker add concentrated HNO3
7.1 Heat to evaporate to low volume, cool, and add concentrated HNO3
7.1 Reheat, increase temperature to create gentle reflux action
7.2 Heat to complete digestion, evaporate,add HCl,warm beaker
7.3 Filter if necessary and adjust volume
Use Methods 7000 or 6010

METHOD 3050B

ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS

1.0 SCOPE AND APPLICATION

1.1 This method has been written to provide two separate digestion procedures, one for the preparation of sediments, sludges, and soil samples for analysis by flame atomic absorption spectrometry (FLAA) or inductively coupled plasma atomic emission spectrometry (ICP-AES) and one for the preparation of sediments, sludges, and soil samples for analysis of samples by Graphite Furnace AA (GFAA) or inductively coupled plasma mass spectrometry (ICP-MS). The extracts from these two procedures are not interchangeable and should only be used with the analytical determinations outlined in this section. Samples prepared by this method may be analyzed by ICP-AES or GFAA for all the listed metals as long as the detecion limits are adequate for the required end-use of the data. Alternative determinative techniques may be used if they are scientifically valid and the QC criteria of the method, including those dealing with interferences, can be achieved. Other elements and matrices may be analyzed by this method if performance is demonstrated for the analytes of interest, in the matrices of interest, at the concentration levels of interest (See Section 8.0). The recommended determinative techniques for each element are listed below:

FLAA/ICP-AES		GFAA/ICP-MS
Aluminum	Magnesium	Arsenic
Antimony	Manganese	Beryllium
Barium	Molybdenum	Cadmium
Beryllium	Nickel	Chromium
Cadmium	Potassium	Cobalt
Calcium	Silver	Iron
Chromium	Sodium	Lead
Cobalt	Thallium	Molybdenum
Copper	Vanadium	Selenium
Iron	Zinc	Thallium
Lead		Vanadium

1.2 This method is not a total digestion technique for most samples. It is a very strong acid digestion that will dissolve almost all elements that could become "environmentally available." By design, elements bound in silicate structures are not normally dissolved by this procedure as they are not usually mobile in the environment. If absolute total digestion is required use Method 3052.

2.0 SUMMARY OF METHOD

2.1 For the digestion of samples, a representative 1-2 gram (wet weight) or 1 gram (dry weight) sample is digested with repeated additions of nitric acid (HNO_3) and hydrogen peroxide (H_2O_2).

2.2 For GFAA or ICP-MS analysis, the resultant digestate is reduced in volume while heating and then diluted to a final volume of 100 mL.

2.3 For ICP-AES or FLAA analyses, hydrochloric acid (HCl) is added to the initial digestate and the sample is refluxed. In an optional step to increase the solubility of some metals (see Section 7.3.1: NOTE), this digestate is filtered and the filter paper and residues are rinsed, first with hot HCl and then hot reagent water. Filter paper and residue are returned to the digestion flask, refluxed with additional HCl and then filtered again. The digestate is then diluted to a final volume of 100 mL.

2.4 If required, a separate sample aliquot shall be dried for a total percent solids determination.

3.0 INTERFERENCES

3.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed in accordance with the quality control requirements given in Sec. 8.0 to aid in determining whether Method 3050B is applicable to a given waste.

4.0 APPARATUS AND MATERIALS

4.1 Digestion Vessels - 250-mL.

4.2 Vapor recovery device (e.g., ribbed watch glasses, appropriate refluxing device, appropriate solvent handling system).

4.3 Drying ovens - able to maintain 30°C ± 4°C.

4.4 Temperature measurement device capable of measuring to at least 125°C with suitable precision and accuracy (e.g., thermometer, IR sensor, thermocouple, thermister, etc.)

4.5 Filter paper - Whatman No. 41 or equivalent.

4.6 Centrifuge and centrifuge tubes.

4.7 Analytical balance - capable of accurate weighings to 0.01 g.

4.8 Heating source - Adjustable and able to maintain a temperature of 90-95°C. (e.g., hot plate, block digestor, microwave, etc.)

4.9 Funnel or equivalent.

4.10 Graduated cylinder or equivalent volume measuring device.

4.11 Volumetric Flasks - 100-mL.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades

may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.

5.2 Reagent Water. Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

5.4 Hydrochloric acid (concentrated), HCl. Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

5.5 Hydrogen peroxide (30%), H_2O_2. Oxidant should be analyzed to determine level of impurities. If method blank is < MDL, the peroxide can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be demonstrated to be free of contamination at or below the reporting limit. Plastic and glass containers are both suitable. See Chapter Three, Section 3.1.3, for further information.

6.3 Nonaqueous samples should be refrigerated upon receipt and analyzed as soon as possible.

6.4 It can be difficult to obtain a representative sample with wet or damp materials. Wet samples may be dried, crushed, and ground to reduce subsample variability as long as drying does not affect the extraction of the analytes of interest in the sample.

7.0 PROCEDURE

7.1 Mix the sample thoroughly to achieve homogeneity and sieve, if appropriate and necessary, using a USS #10 sieve. All equipment used for homogenization should be cleaned according to the guidance in Sec. 6.0 to minimize the potential of cross-contamination. For each digestion procedure, weigh to the nearest 0.01 g and transfer a 1-2 g sample (wet weight) or 1 g sample (dry weight) to a digestion vessel. For samples with high liquid content, a larger sample size may be used as long as digestion is completed.

> NOTE: All steps requiring the use of acids should be conducted under a fume hood by properly trained personnel using appropriate laboratory safety equipment. The use of an acid vapor scrubber system for waste minimization is encouraged.

7.2 For the digestion of samples for analysis by GFAA or ICP-MS, add 10 mL of 1:1 HNO_3, mix the slurry, and cover with a watch glass or vapor recovery device. Heat the sample to

95°C ± 5°C and reflux for 10 to 15 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3, replace the cover, and reflux for 30 minutes. If brown fumes are generated, indicating oxidation of the sample by HNO_3, repeat this step (addition of 5 mL of conc. HNO_3) over and over until no brown fumes are given off by the sample indicating the complete reaction with HNO_3. Using a ribbed watch glass or vapor recovery system, either allow the solution to evaporate to approximately 5 mL without boiling or heat at 95°C ± 5°C without boiling for two hours. Maintain a covering of solution over the bottom of the vessel at all times.

NOTE: Alternatively, for direct energy coupling devices, such as a microwave, digest samples for analysis by GFAA or ICP-MS by adding 10 mL of 1:1 HNO_3, mixing the slurry and then covering with a vapor recovery device. Heat the sample to 95°C ± 5°C and reflux for 5 minutes at 95°C ± 5°C without boiling. Allow the sample to cool for 5 minutes, add 5 mL of concentrated HNO_3, heat the sample to 95°C ± 5°C and reflux for 5 minutes at 95°C ± 5°C. If brown fumes are generated, indicating oxidation of the sample by HNO_3, repeat this step (addition of 5 mL concentrated HNO_3) until no brown fumes are given off by the sample indicating the complete reaction with HNO_3. Using a vapor recovery system, heat the sample to 95°C ± 5°C and reflux for 10 minutes at 95°C ± 5°C without boiling.

7.2.1 After the step in Section 7.2 has been completed and the sample has cooled, add 2 mL of water and 3 mL of 30% H_2O_2. Cover the vessel with a watch glass or vapor recovery device and return the covered vessel to the heat source for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the vessel.

NOTE: Alternatively, for direct energy coupled devices: After the Sec. 7.2 "NOTE" step has been completed and the sample has cooled for 5 minutes, add slowly 10 mL of 30% H_2O_2. Care must be taken to ensure that losses do not occur due to excessive vigorous effervesence. Go to Section 7.2.3.

7.2.2 Continue to add 30% H_2O_2 in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

NOTE: Do not add more than a total of 10 mL 30% H_2O_2.

7.2.3 Cover the sample with a ribbed watch glass or vapor recovery device and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL or heat at 95°C ± 5°C without boiling for two hours. Maintain a covering of solution over the bottom of the vessel at all times.

NOTE: Alternatively, for direct energy coupled devices: Heat the acid-peroxide digestate to 95°C ± 5°C in 6 minutes and remain at 95°C ± 5°C without boiling for 10 minutes.

7.2.4 After cooling, dilute to 100 mL with water. Particulates in the digestate should then be removed by filtration, by centrifugation, or by allowing the sample to settle. The sample is now ready for analysis by GFAA or ICP-MS.

7.2.4.1 Filtration - Filter through Whatman No. 41 filter paper (or equivalent).

7.2.4.2 Centrifugation - Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.2.4.3 The diluted digestate solution contains approximately 5% (v/v) HNO_3. For analysis, withdraw aliquots of appropriate volume and add any required reagent or matrix modifier.

7.3 For the analysis of samples for FLAA or ICP-AES, add 10 mL conc. HCl to the sample digest from 7.2.3 and cover with a watch glass or vapor recovery device. Place the sample on/in the heating source and reflux at 95°C ± 5°C for 15 minutes.

NOTE: Alternatively, for direct energy coupling devices, such as a microwave, digest samples for analysis by FLAA and ICP-AES by adding 5 mL HCl and 10 mL H_2O to the sample digest from 7.2.3 and heat the sample to 95°C ± 5°C, Reflux at 95°C ± 5°C without boiling for 5 minutes.

7.4 Filter the digestate through Whatman No. 41 filter paper (or equivalent) and collect filtrate in a 100-mL volumetric flask. Make to volume and analyze by FLAA or ICP-AES.

NOTE: Section 7.5 may be used to improve the solubilities and recoveries of antimony, barium, lead, and silver when necessary. These steps are optional and are not required on a routine basis.

7.5 Add 2.5 mL conc. HNO_3 and 10 mL conc. HCl to a 1-2 g sample (wet weight) or 1 g sample (dry weight) and cover with a watchglass or vapor recovery device. Place the sample on/in the heating source and reflux for 15 minutes.

7.5.1 Filter the digestate through Whatman No. 41 filter paper (or equivalent) and collect filtrate in a 100-mL volumetric flask. Wash the filter paper, while still in the funnel, with no more than 5 mL of hot (~95°C) HCl, then with 20 mL of hot (~95°C) reagent water. Collect washings in the same 100-mL volumetric flask.

7.5.2 Remove the filter and residue from the funnel, and place them back in the vessel. Add 5 mL of conc. HCl, place the vessel back on the heating source, and heat at 95°C ± 5°C until the filter paper dissolves. Remove the vessel from the heating source and wash the cover and sides with reagent water. Filter the residue and collect the filtrate in the same 100-mL volumetric flask. Allow filtrate to cool, then dilute to volume.

NOTE: High concentrations of metal salts with temperature-sensitive solubilities can result in the formation of precipitates upon cooling of primary and/or secondary filtrates. If precipitation occurs in the flask upon cooling, do not dilute to volume.

7.5.3 If a precipitate forms on the bottom of a flask, add up to 10 mL of concentrated HCl to dissolve the precipitate. After precipitate is dissolved, dilute to volume with reagent water. Analyze by FLAA or ICP-AES.

7.6 Calculations

7.6.1 The concentrations determined are to be reported on the basis of the actual weight of the sample. If a dry weight analysis is desired, then the percent solids of the sample must also be provided.

7.6.2 If percent solids is desired, a separate determination of percent solids must be performed on a homogeneous aliquot of the sample.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each batch of samples processed, a method blank should be carried throughout the entire sample preparation and analytical process according to the frequency described in Chapter One. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing method blanks.

8.3 Spiked duplicate samples should be processed on a routine basis and whenever a new sample matrix is being analyzed. Spiked duplicate samples will be used to determine precision and bias. The criteria of the determinative method will dictate frequency, but 5% (one per batch) is recommended or whenever a new sample matrix is being analyzed. Refer to Chapter One for the proper protocol when analyzing spiked replicates.

8.4 Limitations for the FLAA and ICP-AES optional digestion procedure. Analysts should be aware that the upper linear range for silver, barium, lead, and antimony may be exceeded with some samples. If there is a reasonable possibility that this range may be exceeded, or if a sample's analytical result exceeds this upper limit, a smaller sample size should be taken through the entire procedure and re-analyzed to determine if the linear range has been exceeded. The approximate linear upper ranges for a 2 gram sample size:

Ag	2,000 mg/kg
As	1,000,000 mg/kg
Ba	2,500 mg/kg
Be	1,000,000 mg/kg
Cd	1,000,000 mg/kg
Co	1,000,000 mg/kg
Cr	1,000,000 mg/kg
Cu	1,000,000 mg/kg
Mo	1,000,000 mg/kg
Ni	1,000,000 mg/kg
Pb	200,000 mg/kg
Sb	200,000 mg/kg
Se	1,000,000 mg/kg
Tl	1,000,000 mg/kg
V	1,000,000 mg/kg
Zn	1,000,000 mg/kg

NOTE: These ranges will vary with sample matrix, molecular form, and size.

9.0 METHOD PERFORMANCE

9.1 In a single laboratory, the recoveries of the three matrices presented in Table 2 were obtained using the digestion procedure outlined for samples prior to analysis by FLAA and ICP-AES. The spiked samples were analyzed in duplicate. Tables 3-5 represents results of analysis of NIST Standard Reference Materials that were obtained using both atmospheric pressure microwave digestion techniques and hot-plate digestion procedures.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

3. Edgell, K.; USEPA Method Study 37 - SW-846 Method 3050 Acid Digestion of Sediments, Sludges, and Soils. EPA Contract No. 68-03-3254, November 1988.

4. Kimbrough, David E., and Wakakuwa, Janice R. Acid Digestion for Sediments, Sludges, Soils, and Solid Wastes. A Proposed Alternative to EPA SW 846 Method 3050. Environmental Science and Technology, Vol. 23, Page 898, July 1989.

5. Kimbrough, David E., and Wakakuwa, Janice R. Report of an Interlaboratory Study Comparing EPA SW 846 Method 3050 and an Alternative Method from the California Department of Health Services, Fifth Annual Waste Testing and Quality Assurance Symposium, Volume I, July 1989. Reprinted in Solid Waste Testing and Quality Assurance: Third Volume, ASTM STP 1075, Page 231, C.E. Tatsch, Ed., American Society for Testing and Materials, Philadelphia, 1991.

6. Kimbrough, David E., and Wakakuwa, Janice R. A Study of the Linear Ranges of Several Acid Digestion Procedures, Environmental Science and Technology, Vol. 26, Page 173, January 1992. Presented Sixth Annual Waste Testing and Quality Assurance Symposium, July 1990.

7. Kimbrough, David E., and Wakakuwa, Janice R. A Study of the Linear Ranges of Several Acid Digestion Procedures, Sixth Annual Waste Testing and Quality Assurance Symposium, Reprinted in Solid Waste Testing and Quality Assurance: Fourth Volume, ASTM STP 1076, Ed., American Society for Testing and Materials, Philadelphia, 1992.

8. NIST published leachable concentrations. Found in addendum to certificate of analysis for SRMs 2709, 2710, 2711 - August 23, 1993.

9. Kingston, H.M. Haswell, S.J. ed., Microwave Enhanced Chemistry, Professional Reference Book Series, American Chemical Society, Washington, D.C., Chapter 3, 1997.

TABLE 1

STANDARD RECOVERY (%) COMPARISON FOR METHODS 3050A AND 3050B[a]

Analyte	METHOD 3050A[a]	METHOD 3050B w/option[a]
Ag	9.5	98
As	86	102
Ba	97	103
Be	96	102
Cd	101	99
Co	99	105
Cr	98	94
Cu	87	94
Mo	97	96
Ni	98	92
Pb	97	95
Sb	87	88
Se	94	91
Tl	96	96
V	93	103
Zn	99	95

[a] All values are percent recovery. Samples: 4 mL of 100 mg/mL multistandard; n = 3.

TABLE 2

PERCENT RECOVERY COMPARISON FOR METHODS 3050A AND 3050B

Analyte	Percent Recovery[a,c]							
	Sample 4435		Sample 4766		Sample HJ		Average	
	3050A	3050B	3050A	3050B	3050A	3050B	3050A	3050B
Ag	9.8	103	15	89	56	93	27	95
As	70	102	80	95	83	102	77	100
Ba	85	94	78	95	b	b	81	94
Be	94	102	108	98	99	94	99	97
Cd	92	88	91	95	95	97	93	94
Co	90	94	87	95	89	93	89	94
Cr	90	95	89	94	72	101	83	97
Cu	81	88	85	87	70	106	77	94
Mo	79	92	83	98	87	103	83	98
Ni	88	93	93	100	87	101	92	98
Pb	82	92	80	91	77	91	81	91
Sb	28	84	23	77	46	76	32	79
Se	84	89	81	96	99	96	85	94
Tl	88	87	69	95	66	67	74	83
V	84	97	86	96	90	88	87	93
Zn	96	106	78	75	b	b	87	99

a - Samples: 4 mL of 100 mg/mL multi-standard in 2 g of sample. Each value is percent recovery and is the average of duplicate spikes.

b - Unable to accurately quantitate due to high background values.

c - Method 3050B using optional section.

Table 3
Results of Analysis of Nist Standard Reference Material 2704
"River Sediment" Using Method 3050B (µg/g ± SD)

Element	Atm. Pressure Microwave Assisted Method with Power Control	Atm. Pressure Microwave Assisted Method with Temperature Control (gas-bulb)	Atm. Pressure Microwave Assisted Method with Temperature Control (IR-sensor)	Hot-Plate	NIST Certified Values for Total Digestion (µg/g ±95% CI)
Cu	101 ± 7	89 ± 1	98 ± 1.4	100 ± 2	98.6 ± 5.0
Pb	160 ± 2	145 ± 6	145 ± 7	146 ± 1	161 ± 17
Zn	427 ± 2	411 ± 3	405 ± 14	427 ± 5	438 ± 12
Cd	NA	3.5 ± 0.66	3.7 ± 0.9	NA	3.45 ± 0.22
Cr	82 ± 3	79 ± 2	85 ± 4	89 ± 1	135 ± 5
Ni	42 ± 1	36 ± 1	38 ± 4	44 ± 2	44.1 ± 3.0

NA - Not Available

Table 4
Results of Analysis of NIST Standard Reference Material 2710
"Montana Soil (Highly Elevated Trace Element Concentrations)" Using Method 3050B
(µg/g ± SD)

Element	Atm. Pressure Microwave Assisted Method with Power Control	Atm. Pressure Microwave Assisted Method with Temperature Control (gas-bulb)	Atm. Pressure Microwave Assisted Method with Temperature Control (IR-sensor)	Hot-Plate	NIST Leachable Concentrations Using Method 3050	NIST Certified Values for Total Digestion (µg/g ±95% CI)
Cu	2640 ± 60	2790 ± 41	2480 ± 33	2910 ± 59	2700	2950 ± 130
Pb	5640 ± 117	5430 ± 72	5170 ± 34	5720 ± 280	5100	5532 ± 80
Zn	6410 ± 74	5810 ± 34	6130 ± 27	6230 ± 115	5900	6952 ± 91
Cd	NA	20.3 ± 1.4	20.2 ± 0.4	NA	20	21.8 ± 0.2
Cr	20 ± 1.6	19 ± 2	18 ± 2.4	23 ± 0.5	19	39*

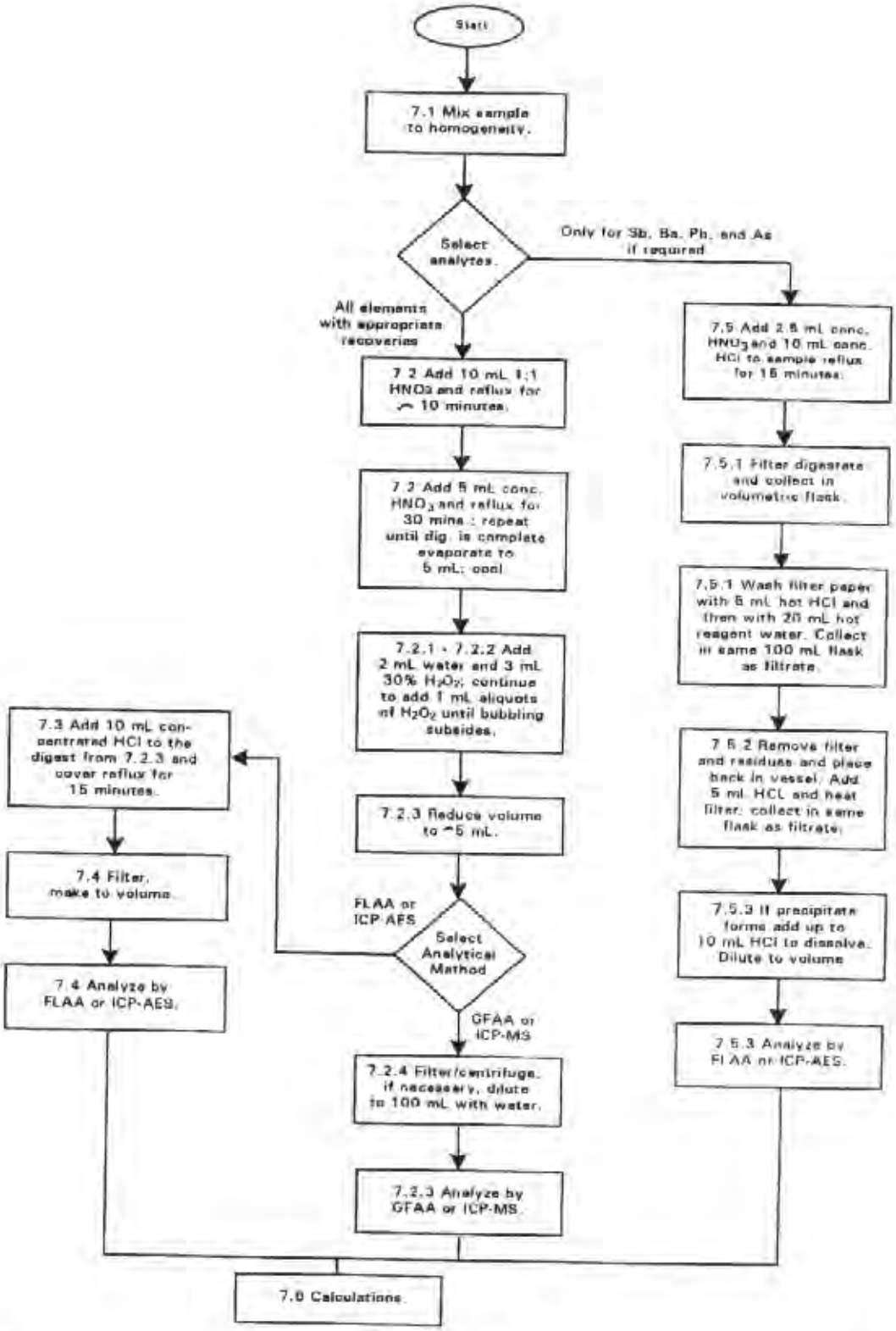
Ni	7.8 ± 0.28	10 ± 1	9.1 ± 1.1	7 ± 0.44	10.1	14.3 ± 1.0

NA - Not Available * Non-certified values, for information only

Table 5
Results of Analysis of NIST Standard Reference Material 2711
"Montana Soil (Moderately Elevated Trace Element Concentrations)" Using Method 3050B
(µg/g ± SD)

Element	Atm. Pressure Microwave Assisted Method with Power Control	Atm. Pressure Microwave Assisted Method with Temperature Control (gas-bulb)	Atm. Pressure Microwave Assisted Method with Temperature Control (IR-sensor)	Hot-Plate	NIST Leachable Concentrations Using Method 3050	NIST Certified Values for Total Digestion (µg/g ±95% CI)
Cu	107 ± 4.6	98 ± 5	98 ± 3.8	111 ± 6.4	100	114 ± 2
Pb	1240 ± 68	1130 ± 20	1120 ± 29	1240 ± 38	1100	1162 ± 31
Zn	330 ± 17	312 ± 2	307 ± 12	340 ± 13	310	350.4 ± 4.8
Cd	NA	39.6 ± 3.9	40.9 ± 1.9	NA	40	41.7 ± 0.25
Cr	22 ± 0.35	21 ± 1	15 ± 1.1	23 ± 0.9	20	47*
Ni	15 ± 0.2	17 ± 2	15 ± 1.6	16 ± 0.4	16	20.6 ± 1.1

NA - Not Available
* Non-certified values, for information only.


Start
7.1 Mix sample to homogeneity.
Select analytes.
Only for Sb, Ba, Pb, and As if required
All elements with appropriate recoveries
7.2 Add 10 mL 1:1 HNO3 and reflux for ~ 10 minutes.
7.2 Add 5 mL conc. HNO3 and reflux for 30 mins.; repeat until dig. is complete evaporate to 5 mL; cool
7.2.1 - 7.2.2 Add 2 mL water and 3 mL 30% H2O2; continue to add 1 mL aliquots of H2O2 until bubbling subsides.
7.2.3 Reduce volume to ~5 mL.
FLAA or ICP-AES
Select Analytical Method
GFAA or ICP-MS
7.2.4 Filter/centrifuge, if necessary, dilute to 100 mL with water.
7.2.5 Analyze by GFAA or ICP-MS.
7.3 Add 10 mL concentrated HCl to the digest from 7.2.3 and cover reflux for 15 minutes.
7.4 Filter, make to volume.
7.4 Analyze by FLAA or ICP-AES.
7.5 Add 2.5 mL conc. HNO3 and 10 mL conc. HCl to sample reflux for 15 minutes.
7.5.1 Filter digestate and collect in volumetric flask.
7.5.1 Wash filter paper with 5 mL hot HCl and then with 20 mL hot reagent water. Collect in same 100 mL flask as filtrate.
7.5.2 Remove filter and residues and place back in vessel. Add 5 mL HCL and heat filter; collect in same flask as filtrate.
7.5.3 If precipitate forms add up to 10 mL HCl to dissolve. Dilute to volume
7.5.3 Analyze by FLAA or ICP-AES.
7.6 Calculations

METHOD 6010B

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-atomic emission spectrometry (ICP-AES) determines trace elements, including metals, in solution. The method is applicable to all of the elements listed in Table 1. All matrices, excluding filtered groundwater samples but including ground water, aqueous samples, TCLP and EP extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis. Groundwater samples that have been prefiltered and acidified will not need acid digestion. Samples which are not digested must either use an internal standard or be matrix matched with the standards. Refer to Chapter Three for the appropriate digestion procedures.

1.2 Table 1 lists the elements for which this method is applicable. Detection limits, sensitivity, and the optimum and linear concentration ranges of the elements can vary with the wavelength, spectrometer, matrix and operating conditions. Table 1 lists the recommended analytical wavelengths and estimated instrumental detection limits for the elements in clean aqueous matrices. The instrument detection limit data may be used to estimate instrument and method performance for other sample matrices. Elements and matrices other than those listed in Table 1 may be analyzed by this method if performance at the concentration levels of interest (see Section 8.0) is demonstrated.

1.3 Users of the method should state the data quality objectives prior to analysis and must document and have on file the required initial demonstration performance data described in the following sections prior to using the method for analysis.

1.4 Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences described in this method.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods (e.g. Chapter Three). When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

2.2 This method describes multielemental determinations by ICP-AES using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. In one mode of analysis the position used should be as free as possible from spectral interference and should reflect the same change in background

intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in Section 3.0 should also be recognized and appropriate corrections made; tests for their presence are described in Section 8.5. Alternatively, users may choose multivariate calibration methods. In this case, point selections for background correction are superfluous since whole spectral regions are processed.

3.0 INTERFERENCES

3.1 Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

3.1.1 Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate when alternate wavelengths are desirable because of severe spectral interference. These scans will also show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by measured emission on only one side. The locations selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The locations used for routine measurement must be free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak. For multivariate methods using whole spectral regions, background scans should be included in the correction algorithm. Off-line spectral interferences are handled by including spectra on interfering species in the algorithm.

3.1.2 To determine the appropriate location for off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the analyst must determine and document both the overlapping and nearby spectral interference effects from all method analytes and common elements and provide for their automatic correction on all analyses. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Normally, 100 mg/L single element solutions are sufficient; however, for analytes such as iron that may be found at high concentration, a more appropriate test would be to use a concentration near the upper analytical range limit.

3.1.3 Spectral overlaps may be avoided by using an alternate wavelength or can be compensated by equations that correct for interelement contributions. Instruments that use equations for interelement correction **require** the interfering elements be analyzed at the same time as the element of interest. When operative and uncorrected, interferences will produce false positive determinations and be reported as analyte concentrations. More extensive information on interferant effects at various wavelengths and resolutions is available in reference wavelength tables and books. Users may apply interelement

correction equations determined on their instruments with tested concentration ranges to compensate (off line or on line) for the effects of interfering elements. Some potential spectral interferences observed for the recommended wavelengths are given in Table 2. For multivariate methods using whole spectral regions, spectral interferences are handled by including spectra of the interfering elements in the algorithm. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature are listed. These overlaps were observed with a single instrument having a working resolution of 0.035 nm.

3.1.4 When using interelement correction equations, the interference may be expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that As is to be determined (at 193.696 nm) in a sample containing approximately 10 mg/L of Al. According to Table 2, 100 mg/L of Al would yield a false signal for As equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of Al would result in a false signal for As equivalent to approximately 0.13 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary.

3.1.5 Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating, the entrance and exit slit widths, and by the order of dispersion. Interelement corrections will also vary depending upon the choice of background correction points. Selecting a background correction point where an interfering emission line may appear should be avoided when practical. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. Users should not forget that some samples may contain uncommon elements that could contribute spectral interferences.

3.1.6 The interference effects must be evaluated for each individual instrument whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). When using the recommended wavelengths, the analyst is required to determine and document for each wavelength the effect from referenced interferences (Table 2) as well as any other suspected interferences that may be specific to the instrument or matrix. The analyst is encouraged to utilize a computer routine for automatic correction on all analyses.

3.1.7 Users of sequential instruments must verify the absence of spectral interference by scanning over a range of 0.5 nm centered on the wavelength of interest for several samples. The range for lead, for example, would be from 220.6 to 220.1 nm. This procedure must be repeated whenever a new matrix is to be analyzed and when a new calibration curve using different instrumental conditions is to be prepared. Samples that show an elevated background emission across the range may be background corrected by applying a correction factor equal to the emission adjacent to the line or at two points on either side of the line and interpolating between them. An alternate wavelength that does not exhibit a background shift or spectral overlap may also be used.

3.1.8 If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. The concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and divided by 10. If after the subtraction of the calibration blank the apparent analyte concentration falls outside of this range in either a positive or negative direction, a change in the correction factor of more than 10% should be suspected. The cause of the change should be determined and corrected and the correction factor updated. The interference check solutions should be analyzed more than once to confirm a change has occurred. Adequate rinse time between solutions and before analysis of the calibration blank will assist in the confirmation.

3.1.9 When interelement corrections are applied, their accuracy should be verified, daily, by analyzing spectral interference check solutions. If the correction factors or multivariate correction matrices tested on a daily basis are found to be within the 20% criteria for 5 consecutive days, the required verification frequency of those factors in compliance may be extended to a weekly basis. Also, if the nature of the samples analyzed is such they do not contain concentrations of the interfering elements at ± one reporting limit from zero, daily verification is not required. All interelement spectral correction factors or multivariate correction matrices must be verified and updated every six months or when an instrumentation change, such as in the torch, nebulizer, injector, or plasma conditions occurs. Standard solution should be inspected to ensure that there is no contamination that may be perceived as a spectral interference.

3.1.10 When interelement corrections are <u>not</u> used, verification of absence of interferences is required.

3.1.10.1 One method is to use a computer software routine for comparing the determinative data to limits files for notifying the analyst when an interfering element is detected in the sample at a concentration that will produce either an apparent false positive concentration, (i.e., greater than) the analyte instrument detection limit, or false negative analyte concentration, (i.e., less than the lower control limit of the calibration blank defined for a 99% confidence interval).

3.1.10.2 Another method is to analyze an Interference Check Solution(s) which contains similar concentrations of the major components of the samples (>10 mg/L) on a continuing basis to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data. If the check solution confirms an operative interference that is $\geq$ 20% of the analyte concentration, the analyte must be determined using (1) analytical and background correction wavelengths (or spectral regions) free of the interference, (2) by an alternative wavelength, or (3) by another documented test procedure.

3.2 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample or by using a peristaltic pump, by using an internal standard or by using a high solids nebulizer. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, affecting aerosol flow rate

and causing instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, using a high solids nebulizer or diluting the sample. Also, it has been reported that better control of the argon flow rate, especially to the nebulizer, improves instrument performance; this may be accomplished with the use of mass flow controllers. The test described in Section 8.5.1 will help determine if a physical interference is present.

3.3 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique, but if observed, can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

3.4 Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer and from the build up of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements at a concentration ten times the usual amount or at the top of the linear dynamic range. The aspiration time for this sample should be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of two of the method detection limit should be noted. Until the required rinse time is established, this method suggests a rinse period of at least 60 seconds between samples and standards. If a memory interference is suspected, the sample must be reanalyzed after a rinse period of sufficient length. Alternate rinse times may be established by the analyst based upon their DQOs.

3.5 Users are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests. If the instrument does not display negative values, fortify the interference check solution with the elements of interest at 0.5 to 1 mg/L and measure the added standard concentration accordingly. Concentrations should be within 20% of the true spiked concentration or dilution of the samples will be necessary. In the absence of measurable analyte, overcorrection could go undetected if a negative value is reported as zero.

3.6 The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferant concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

4.0 APPARATUS AND MATERIALS

4.1 Inductively coupled argon plasma emission spectrometer:

4.1.1 Computer-controlled emission spectrometer with background correction.

4.1.2 Radio-frequency generator compliant with FCC regulations.

4.1.3 Optional mass flow controller for argon nebulizer gas supply.

4.1.4 Optional peristaltic pump.

4.1.5 Optional Autosampler.

4.1.6 Argon gas supply - high purity.

4.2 Volumetric flasks of suitable precision and accuracy.

4.3 Volumetric pipets of suitable precision and accuracy.

5.0 REAGENTS

5.1 Reagent or trace metals grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is in question analyze for contamination. If the concentration of the contamination is less than the MDL then the reagent is acceptable.

5.1.1 Hydrochloric acid (conc), HCl.

5.1.2 Hydrochloric acid (1:1), HCl. Add 500 mL concentrated HCl to 400 mL water and dilute to 1 liter in an appropriately sized beaker.

5.1.3 Nitric acid (conc), HNO_3.

5.1.4 Nitric acid (1:1), HNO_3. Add 500 mL concentrated HNO_3 to 400 mL water and dilute to 1 liter in an appropriately sized beaker.

5.2 Reagent Water. All references to water in the method refer to reagent water unless otherwise specified. Reagent water will be interference free. Refer to Chapter One for a definition of reagent water.

5.3 Standard stock solutions may be purchased or prepared from ultra- high purity grade chemicals or metals (99.99% pure or greater). All salts must be dried for 1 hour at 105°C, unless otherwise specified.

Note: This section does not apply when analyzing samples that have been prepared by Method 3040.

CAUTION: Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

Typical stock solution preparation procedures follow. Concentrations are calculated based upon the weight of pure metal added, or with the use of the element fraction and the weight of the metal salt added.

For metals:

$$\text{Concentration (ppm)} = \frac{\text{weight (mg)}}{\text{volume (L)}}$$

For metal salts:

$$\text{Concentration (ppm)} = \frac{\text{weight (mg)} \times \text{mole fraction}}{\text{volume (L)}}$$

5.3.1 Aluminum solution, stock, 1 mL = 1000 µg Al: Dissolve 1.000 g of aluminum metal, weighed accurately to at least four significant figures, in an acid mixture of 4.0 mL of (1:1) HCl and 1.0 mL of concentrated $HN0_3$ in a beaker. Warm beaker slowly to effect solution. When dissolution is complete, transfer solution quantitatively to a 1-liter flask, add an additional 10.0 mL of (1:1) HCl and dilute to volume with reagent water.

NOTE: Weight of analyte is expressed to four significant figures for consistency with the weights below because rounding to two decimal places can contribute up to 4 % error for some of the compounds.

5.3.2 Antimony solution, stock, 1 mL = 1000 µg Sb: Dissolve 2.6673 g $K(SbO)C_4H_4O_6$ (element fraction Sb = 0.3749), weighed accurately to at least four significant figures, in water, add 10 mL (1:1) HCl, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.3 Arsenic solution, stock, 1 mL = 1000 µg As: Dissolve 1.3203 g of As_2O_3 (element fraction As = 0.7574), weighed accurately to at least four significant figures, in 100 mL of water containing 0.4 g NaOH. Acidify the solution with 2 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.4 Barium solution, stock, 1 mL = 1000 µg Ba: Dissolve 1.5163 g $BaCl_2$ (element fraction Ba = 0.6595), dried at 250°C for 2 hours, weighed accurately to at least four significant figures, in 10 mL water with 1 mL (1:1) HCl. Add 10.0 mL (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.5 Beryllium solution, stock, 1 mL = 1000 µg Be: Do not dry. Dissolve 19.6463 g $BeSO_4 4H_2O$ (element fraction Be = 0.0509), weighed accurately to at least four significant figures, in water, add 10.0 mL concentrated HNO_3, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.6 Boron solution, stock, 1 mL = 1000 µg B: Do not dry. Dissolve 5.716 g anhydrous H_3BO_3 (B fraction = 0.1749), weighed accurately to at least four significant figures, in reagent water and dilute in a 1-L volumetric flask with reagent water. Transfer immediately after mixing in a clean polytetrafluoroethylene (PTFE) bottle to minimize any leaching of boron from the glass volumetric container. Use of a non-glass volumetric flask is recommended to avoid boron contamination from glassware.

5.3.7 Cadmium solution, stock, 1 mL = 1000 µg Cd: Dissolve 1.1423 g CdO (element fraction Cd = 0.8754), weighed accurately to at least four significant figures, in a

minimum amount of (1:1) HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.8 Calcium solution, stock, 1 mL = 1000 µg Ca: Suspend 2.4969 g $CaCO_3$ (element Ca fraction = 0.4005), dried at 180°C for 1 hour before weighing, weighed accurately to at least four significant figures, in water and dissolve cautiously with a minimum amount of (1:1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.9 Chromium solution, stock, 1 mL = 1000 µg Cr: Dissolve 1.9231 g CrO_3 (element fraction Cr = 0.5200), weighed accurately to at least four significant figures, in water. When solution is complete, acidify with 10 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.10 Cobalt solution, stock, 1 mL = 1000 µg Co: Dissolve 1.00 g of cobalt metal, weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.11 Copper solution, stock, 1 mL = 1000 µg Cu: Dissolve 1.2564 g CuO (element fraction Cu = 0.7989), weighed accurately to at least four significant figures), in a minimum amount of (1:1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.12 Iron solution, stock, 1 mL = 1000 µg Fe: Dissolve 1.4298 g Fe_2O_3 (element fraction Fe = 0.6994), weighed accurately to at least four significant figures, in a warm mixture of 20 mL (1:1) HCl and 2 mL of concentrated HNO_3. Cool, add an additional 5.0 mL of concentrated HNO_3, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.13 Lead solution, stock, 1 mL = 1000 µg Pb: Dissolve 1.5985 g $Pb(NO_3)_2$ (element fraction Pb = 0.6256), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10 mL (1:1) HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.14 Lithium solution, stock, 1 mL = 1000 µg Li: Dissolve 5.3248 g lithium carbonate (element fraction Li = 0.1878), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.15 Magnesium solution, stock, 1 mL = 1000 µg Mg: Dissolve 1.6584 g MgO (element fraction Mg = 0.6030), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL (1:1) concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.16 Manganese solution, stock, 1 mL = 1000 µg Mn: Dissolve 1.00 g of manganese metal, weighed accurately to at least four significant figures, in acid mixture (10 mL concentrated HCl and 1 mL concentrated HNO_3) and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.17 Mercury solution, stock, 1 mL = 1000 µg Hg: Do not dry, highly toxic element. Dissolve 1.354 g $HgCl_2$ (Hg fraction = 0.7388) in reagent water. Add 50.0 mL concentrated HNO_3 and dilute to volume in 1-L volumetric flask with reagent water.

5.3.18 Molybdenum solution, stock, 1 mL = 1000 µg Mo: Dissolve 1.7325 g $(NH_4)_6Mo_7O_{24}.4H_2O$ (element fraction Mo = 0.5772), weighed accurately to at least four significant figures, in water and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.19 Nickel solution, stock, 1 mL = 1000 µg Ni: Dissolve 1.00 g of nickel metal, weighed accurately to at least four significant figures, in 10.0 mL hot concentrated HNO_3, cool, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.20 Phosphate solution, stock, 1 mL = 1000 µg P: Dissolve 4.3937 g anhydrous KH_2PO_4 (element fraction P = 0.2276), weighed accurately to at least four significant figures, in water. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.21 Potassium solution, stock, 1 mL = 1000 µg K: Dissolve 1.9069 g KCl (element fraction K = 0.5244) dried at 110°C, weighed accurately to at least four significant figures, in water, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.22 Selenium solution, stock, 1 mL = 1000 µg Se: Do not dry. Dissolve 1.6332 g H_2SeO_3 (element fraction Se = 0.6123), weighed accurately to at least four significant figures, in water and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.23 Silica solution, stock, 1 mL = 1000 µg SiO_2: Do not dry. Dissolve 2.964 g NH_4SiF_6, weighed accurately to at least four significant figures, in 200 mL (1:20) HCl with heating at 85°C to effect dissolution. Let solution cool and dilute to volume in a 1-L volumetric flask with reagent water.

5.3.24 Silver solution, stock, 1 mL = 1000 µg Ag: Dissolve 1.5748 g $AgNO_3$ (element fraction Ag = 0.6350), weighed accurately to at least four significant figures, in water and 10 mL concentrated HNO_3. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.25 Sodium solution, stock, 1 mL = 1000 µg Na: Dissolve 2.5419 g NaCl (element fraction Na = 0.3934), weighed accurately to at least four significant figures, in water. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.26 Strontium solution, stock, 1 mL = 1000 µg Sr: Dissolve 2.4154 g of strontium nitrate ($Sr(NO_3)_2$) (element fraction Sr = 0.4140), weighed accurately to at least four significant figures, in a 1-liter flask containing 10 mL of concentrated HCl and 700 mL of water. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.27 Thallium solution, stock, 1 mL = 1000 µg Tl: Dissolve 1.3034 g $TlNO_3$ (element fraction Tl = 0.7672), weighed accurately to at least four significant figures, in water. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.28 Tin solution, stock, 1 mL = 1000 µg Sn: Dissolve 1.000 g Sn shot, weighed accurately to at least 4 significant figures, in 200 mL (1:1) HCl with heating to effect dissolution. Let solution cool and dilute with (1:1) HCl in a 1-L volumetric flask.

5.3.29 Vanadium solution, stock, 1 mL = 1000 µg V: Dissolve 2.2957 g NH_4VO_3 (element fraction V = 0.4356), weighed accurately to at least four significant figures, in a minimum amount of concentrated HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.30 Zinc solution, stock, 1 mL = 1000 µg Zn: Dissolve 1.2447 g ZnO (element fraction Zn = 0.8034), weighed accurately to at least four significant figures, in a minimum amount of dilute HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.4 Mixed calibration standard solutions - Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks (see Table 3). Add the appropriate types and volumes of acids so that the standards are matrix matched with the sample digestates. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Some typical calibration standard combinations are listed in Table 3.

NOTE: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of water and warm the flask until the solution clears. Cool and dilute to 100 mL with water. For this acid combination, the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap-water matrix for 30 days. Higher concentrations of silver require additional HCl.

5.5 Two types of blanks are required for the analysis for samples prepared by any method other than 3040. The calibration blank is used in establishing the analytical curve, and the method blank is used to identify possible contamination resulting from varying amounts of the acids used in the sample processing.

5.5.1 The calibration blank is prepared by acidifying reagent water to the same concentrations of the acids found in the standards and samples. Prepare a sufficient quantity to flush the system between standards and samples. The calibration blank will also be used for all initial and continuing calibration blank determinations (see Sections 7.3 and 7.4).

5.5.2 The method blank must contain all of the reagents in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

5.6 The Initial Calibration Verification (ICV) is prepared by the analyst by combining compatible elements from a standard source different than that of the calibration standard and at concentrations within the linear working range of the instrument (see Section 8.6.1 for use).

5.7 The Continuing Calibration Verification (CCV)) should be prepared in the same acid matrix using the same standards used for calibration at a concentration near the mid-point of the calibration curve (see Section 8.6.1 for use).

5.8 The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest, particularly those with known interferences at 0.5 to 1 mg/L. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material in Chapter Three, Inorganic Analytes, Sections 3.1 through 3.3.

7.0 PROCEDURE

7.1 Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Groundwater samples which have been prefiltered and acidified will not need acid digestion. Samples which are not digested must either use an internal standard or be matrix matched with the standards. Solubilization and digestion procedures are presented in Sample Preparation Methods (Chapter Three, Inorganic Analytes).

7.2 Set up the instrument with proper operating parameters established as detailed below. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 minutes of operation prior to calibration). Operating conditions - The analyst should follow the instructions provided by the instrument manufacturer.

7.2.1 Before using this procedure to analyze samples, there must be data available documenting initial demonstration of performance. The required data document the selection criteria of background correction points; analytical dynamic ranges, the applicable equations, and the upper limits of those ranges; the method and instrument detection limits; and the determination and verification of interelement correction equations or other routines for correcting spectral interferences. This data must be generated using the same instrument, operating conditions and calibration routine to be used for sample analysis. These documented data must be kept on file and be available for review by the data user or auditor.

7.2.2 Specific wavelengths are listed in Table 1. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. Because of differences among various makes and models of spectrometers, specific instrument operating conditions cannot be provided. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality to the program and data user. The analyst should follow the instructions provided by the instrument manufacturer unless other conditions provide similar or better performance for

a task. Operating conditions for aqueous solutions usually vary from 1100 to 1200 watts forward power, 14 to 18 mm viewing height, 15 to 19 liters/min argon coolant flow, 0.6 to 1.5 L/min argon nebulizer flow, 1 to 1.8 mL/min sample pumping rate with a 1 minute preflush time and measurement time near 1 second per wavelength peak for sequential instruments and 10 seconds per sample for simultaneous instruments. For an axial plasma, the conditions will usually vary from 1100-1500 watts forward power, 15-19 liters/min argon coolant flow, 0.6-1.5 L/min argon nebulizer flow, 1-1.8 mL/min sample pumping rate with a 1 minute preflush time and measurement time near 1 second per wavelength peak for sequential instruments and 10 seconds per sample for simultaneous instruments. Reproduction of the Cu/Mn intensity ratio at 324.754 nm and 257.610 nm respectively, by adjusting the argon aerosol flow has been recommended as a way to achieve repeatable interference correction factors.

7.2.3 The plasma operating conditions need to be optimized prior to use of the instrument. This routine is not required on a daily basis, but only when first setting up a new instrument or following a change in operating conditions. The following procedure is recommended or follow manufacturer's recommendations. The purpose of plasma optimization is to provide a maximum signal to background ratio for some of the least sensitive elements in the analytical array. The use of a mass flow controller to regulate the nebulizer gas flow or source optimization software greatly facilitates the procedure.

7.2.3.1 Ignite the radial plasma and select an appropriate incident RF power. Allow the instrument to become thermally stable before beginning, about 30 to 60 minutes of operation. While aspirating a 1000 ug/L solution of yttrium, follow the instrument manufacturer's instructions and adjust the aerosol carrier gas flow rate through the nebulizer so a definitive blue emission region of the plasma extends approximately from 5 to 20 mm above the top of the load coil. Record the nebulizer gas flow rate or pressure setting for future reference. The yttrium solution can also be used for coarse optical alignment of the torch by observing the overlay of the blue light over the entrance slit to the optical system.

7.2.3.2 After establishing the nebulizer gas flow rate, determine the solution uptake rate of the nebulizer in mL/min by aspirating a known volume of calibration blank for a period of at least three minutes. Divide the volume aspirated by the time in minutes and record the uptake rate; set the peristaltic pump to deliver the rate in a steady even flow.

7.2.3.3 Profile the instrument to align it optically as it will be used during analysis. The following procedure can be used for both horizontal and vertical optimization in the radial mode, but is written for vertical. Aspirate a solution containing 10 ug/L of several selected elements. These elements can be As, Se, Tl or Pb as the least sensitive of the elements and most needing to be optimize or others representing analytical judgement (V, Cr, Cu, Li and Mn are also used with success). Collect intensity data at the wavelength peak for each analyte at 1 mm intervals from 14 to 18 mm above the load coil. (This region of the plasma is referred to as the analytical zone.) Repeat the process using the calibration blank. Determine the net signal to blank intensity ratio for each analyte for each viewing height setting. Choose the height for viewing the plasma that provides the best net intensity ratios for the elements analyzed or the highest intensity ratio for the least

sensitive element. For optimization in the axial mode, follow the instrument manufacturer's instructions.

7.2.3.4 The instrument operating condition finally selected as being optimum should provide the lowest reliable instrument detection limits and method detection limits.

7.2.3.5 If either the instrument operating conditions, such as incident power or nebulizer gas flow rate are changed, or a new torch injector tube with a different orifice internal diameter is installed, the plasma and viewing height should be re-optimized.

7.2.3.6 After completing the initial optimization of operating conditions, but before analyzing samples, the laboratory must establish and initially verify an interelement spectral interference correction routine to be used during sample analysis. A general description concerning spectral interference and the analytical requirements for background correction in particular are discussed in the section on interferences. Criteria for determining an interelement spectral interference is an apparent positive or negative concentration for the analyte that falls within ± one reporting limit from zero. The upper control limit is the analyte instrument detection limit. Once established the entire routine must be periodically verified every six months. Only a portion of the correction routine must be verified more frequently or on a daily basis. Initial and periodic verification of the routine should be kept on file. Special cases where continual verification is required are described elsewhere.

7.2.3.7 Before daily calibration and after the instrument warmup period, the nebulizer gas flow rate must be reset to the determined optimized flow. If a mass flow controller is being used, it should be set to the recorded optimized flow rate. In order to maintain valid spectral interelement correction routines the nebulizer gas flow rate should be the same (< 2% change) from day to day.

7.2.4 For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements.

7.2.5 Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on each particular instrument. All measurements must be within the instrument linear range where the correction equations are valid.

7.2.5.1 Method detection limits must be established for all wavelengths utilized for each type of matrix commonly analyzed. The matrix used for the MDL calculation must contain analytes of known concentrations within 3-5 times the anticipated detection limit. Refer to Chapter One for additional guidance on the performance of MDL studies.

7.2.5.2 Determination of limits using reagent water represent a best case situation and do not represent possible matrix effects of real world samples.

7.2.5.3 If additional confirmation is desired, reanalyze the seven replicate aliquots on two more non consecutive days and again calculate the method detection limit values for each day. An average of the three values for each analyte may provide for a more appropriate estimate. Successful analysis of samples with added analytes or using method of standard additions can give confidence in the method detection limit values determined in reagent water.

7.2.5.4 The upper limit of the linear dynamic range must be established for each wavelength utilized by determining the signal responses from a minimum for three, preferably five, different concentration standards across the range. One of these should be near the upper limit of the range. The ranges which may be used for the analysis of samples should be judged by the analyst from the resulting data. The data, calculations and rationale for the choice of range made should be documented and kept on file. The upper range limit should be an observed signal no more than 10% below the level extrapolated from lower standards. Determined analyte concentrations that are above the upper range limit must be diluted and reanalyzed. The analyst should also be aware that if an interelement correction from an analyte above the linear range exists, a second analyte where the interelement correction has been applied may be inaccurately reported. New dynamic ranges should be determined whenever there is a significant change in instrument response. For those analytes that periodically approach the upper limit, the range should be checked every six months. For those analytes that are known interferences, and are present at above the linear range, the analyst should ensure that the interelement correction has not been inaccurately applied.

NOTE: Many of the alkali and alkaline earth metals have non-linear response curves due to ionization and self absorption effects. These curves may be used if the instrument allows; however the effective range must be checked and the second order curve fit should have a correlation coefficient of 0.995 or better. Third order fits are not acceptable. These non-linear response curves should be revalidated and recalculated every six months. These curves are much more sensitive to changes in operating conditions than the linear lines and should be checked whenever there have been moderate equipment changes.

7.2.6 The analyst must (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.

7.3 Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Section 5.4. Flush the system with the calibration blank (Section 5.5.1) between each standard or as the manufacturer recommends. (Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.) The calibration curve must consist of a minimum of a blank and a standard.

7.4 For all analytes and determinations, the laboratory must analyze an ICV (Section 5.6), a calibration blank (Section 5.5.1), and a continuing calibration verification (CCV) (Section 5.7) immediately following daily calibration. A calibration blank and either a calibration verification (CCV) or an ICV must be analyzed after every tenth sample and at the end of the sample run. Analysis of

the check standard and calibration verification must verify that the instrument is within ± 10% of calibration with relative standard deviation < 5% from replicate (minimum of two) integrations. If the calibration cannot be verified within the specified limits, the sample analysis must be discontinued, the cause determined and the instrument recalibrated. All samples following the last acceptable ICV, CCV or check standard must be reanalyzed. The analysis data of the calibration blank, check standard, and ICV or CCV must be kept on file with the sample analysis data.

7.5 Rinse the system with the calibration blank solution (Section 5.5.1) before the analysis of each sample. The rinse time will be one minute. Each laboratory may establish a reduction in this rinse time through a suitable demonstration.

7.6 Calculations: If dilutions were performed, the appropriate factors must be applied to sample values. All results should be reported with up to three significant figures.

7.7 The MSA should be used if an interference is suspected or a new matrix is encountered. When the method of standard additions is used, standards are added at one or more levels to portions of a prepared sample. This technique compensates for enhancement or depression of an analyte signal by a matrix. It will not correct for additive interferences, such as contamination, interelement interferences, or baseline shifts. This technique is valid in the linear range when the interference effect is constant over the range, the added analyte responds the same as the endogenous analyte, and the signal is corrected for additive interferences. The simplest version of this technique is the single addition method. This procedure calls for two identical aliquots of the sample solution to be taken. To the first aliquot, a small volume of standard is added, while to the second aliquot, a volume of acid blank is added equal to the standard addition. The sample concentration is calculated by: multiplying the intensity value for the unfortified aliquot by the volume (Liters) and concentration (mg/L or mg/kg) of the standard addition to make the numerator; the difference in intensities for the fortified sample and unfortified sample is multiplied by the volume (Liters) of the sample aliquot for the denominator. The quotient is the sample concentration.

For more than one fortified portion of the prepared sample, linear regression analysis can be applied using a computer or calculator program to obtain the concentration of the sample solution.

NOTE: Refer to Method 7000 for a more detailed discussion of the MSA.

7.8 An alternative to using the method of standard additions is the internal standard technique. Add one or more elements not in the samples and verified not to cause an interelement spectral interference to the samples, standards and blanks; yttrium or scandium are often used. The concentration should be sufficient for optimum precision but not so high as to alter the salt concentration of the matrix. The element intensity is used by the instrument as an internal standard to ratio the analyte intensity signals for both calibration and quantitation. This technique is very useful in overcoming matrix interferences especially in high solids matrices.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection. All quality control measures described in Chapter One should be followed.

8.2 Dilute and reanalyze samples that exceed the linear calibration range or use an alternate, less sensitive line for which quality control data is already established.

8.3 Employ a minimum of one method blank per sample batch to determine if contamination or any memory effects are occurring. A method blank is a volume of reagent water carried through the same preparation process as a sample (refer to Chapter One).

8.4 Analyze matrix spiked duplicate samples at a frequency of one per matrix batch. A matrix duplicate sample is a sample brought through the entire sample preparation and analytical process in duplicate.

8.4.1.1 The relative percent difference between spiked matrix duplicate determinations is to be calculated as follows:

$$RPD = \frac{|D_1 - D_2|}{(|D_1 + D_2|)/2} \times 100$$

where:

RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (replicate).

(A control limit of ± 20% RPD or within the documented historical acceptance limits for each matrix shall be used for sample values greater than ten times the instrument detection limit.)

8.4.1.2 The spiked sample or spiked duplicate sample recovery is to be within ± 25% of the actual value or within the documented historical acceptance limits for each matrix.

8.5 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in Sections 8.5.1 and 8.5.2, will ensure that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

8.5.1 Dilution Test: If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrumental detection limit after dilution), an analysis of a 1:5 dilution should agree within ± 10% of the original determination. If not, a chemical or physical interference effect should be suspected.

8.5.2 Post Digestion Spike Addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75% to 125% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected.

CAUTION: If spectral overlap is suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

8.6 Check the instrument standardization by analyzing appropriate QC samples as follows.

8.6.1 Verify calibration with the Continuing Calibration Verification (CCV) Standard immediately following daily calibration, after every ten samples, and at the end of an analytical run. Check calibration with an ICV following the initial calibration (Section 5.6). At the laboratory's discretion, an ICV may be used in lieu of the continuing calibration verifications. If used in this manner, the ICV should be at a concentration near the mid-point of the calibration curve. Use a calibration blank (Section 5.5.1) immediately following daily calibration, after every 10 samples and at the end of the analytical run.

8.6.1.1 The results of the ICV and CCVs are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and recalibrate the instrument.

8.6.1.2 The results of the check standard are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and recalibrate the instrument.

8.6.1.3 The results of the calibration blank are to agree within three times the IDL. If not, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples. If the blank is less than 1/10 the concentration of the action level of interest, and no sample is within ten percent of the action limit, analyses need not be rerun and recalibration need not be performed before continuation of the run.

8.6.2 Verify the interelement and background correction factors at the beginning of each analytical run. Do this by analyzing the interference check sample (Section 5.8). Results should be within ± 20% of the true value.

9.0 METHOD PERFORMANCE

9.1 In an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations.

9.2 Performance data for aqueous solutions and solid samples from a multilaboratory study (9) are provided in Tables 5 and 6.

10.0 REFERENCES

1. Boumans, P.W.J.M. Line Coincidence Tables for Inductively Coupled Plasma Atomic Emission Spectrometry, 2nd Edition. Pergamon Press, Oxford, United Kingdom, 1984.

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3. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

4. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

5. Jones, C.L. et al. An Interlaboratory Study of Inductively Coupled Plasma Atomic Emission Spectroscopy Method 6010 and Digestion Method 3050. EPA-600/4-87-032, U.S. Environmental Protection Agency, Las Vegas, Nevada, 1987.

TABLE 1
RECOMMENDED WAVELENGTHS AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Detection Element	Wavelength[a] (nm)	Estimated IDL[b] (µg/L)
Aluminum	308.215	30
Antimony	206.833	21
Arsenic	193.696	35
Barium	455.403	0.87
Beryllium	313.042	0.18
Boron	249.678x2	3.8
Cadmium	226.502	2.3
Calcium	317.933	6.7
Chromium	267.716	4.7
Cobalt	228.616	4.7
Copper	324.754	3.6
Iron	259.940	4.1
Lead	220.353	28
Lithium	670.784	2.8
Magnesium	279.079	20
Manganese	257.610	0.93
Mercury	194.227x2	17
Molybdenum	202.030	5.3
Nickel	231.604x2	10
Phosphorus	213.618	51
Potassium	766.491	See note c
Selenium	196.026	50
Silica (SiO_2)	251.611	17
Silver	328.068	4.7
Sodium	588.995	19
Strontium	407.771	0.28
Thallium	190.864	27
Tin	189.980x2	17
Titanium	334.941	5.0
Vanadium	292.402	5.0
Zinc	213.856x2	1.2

[a]The wavelengths listed (where x2 indicates second order) are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted (e.g., in the case of an interference) if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see Section 3.1). In time, other elements may be added as more information becomes available and as required.

[b]The estimated instrumental detection limits shown are provided as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

[c]Highly dependent on operating conditions and plasma position.

TABLE 2
POTENTIAL INTERFERENCES
ANALYTE CONCENTRATION EQUIVALENTS ARISING FROM
INTERFERENCE AT THE 100-mg/L LEVEL[c]

Analyte	Wavelength (nm)	Interferant[a,b] Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Tl	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	0.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

[a] Dashes indicate that no interference was observed even when interferents were introduced at the following levels:

Al -	1000 mg/L	Mg -	1000 mg/L
Ca -	1000 mg/L	Mn -	200 mg/L
Cr -	200 mg/L	Tl -	200 mg/L
Cu -	200 mg/L	V -	200 mg/L
Fe -	1000 mg/L		

[b] The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferant figure.

[c] Interferences will be affected by background choice and other interferences may be present.

TABLE 3
MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As, Mo
IV	Al, Ca, Cr, K, Na, Ni,Li, and Sr
V	Ag (see "NOTE" to Section 5.4), Mg, Sb, and Tl
VI	P

TABLE 4. ICP PRECISION AND ACCURACY DATA[a]

Element	Sample No. 1				Sample No. 2				Sample No. 3			
	True Conc. (ug/L)	Mean Conc. (ug/L)	RSD[b] (%)	Accuracy[d] (%)	True Conc. (ug/L)	Mean Conc. (ug/L)	RSD[b]	Accuracy[d] (%)	True Conc. (ug/L)	Mean Conc. (ug/L)	RSD[b] (%)	Accuracy[d] (%)
Be	750	733	6.2	98	20	20	9.8	100	180	176	5.2	98
Mn	350	345	2.7	99	15	15	6.7	100	100	99	3.3	99
V	750	749	1.8	100	70	69	2.9	99	170	169	1.1	99
As	200	208	7.5	104	22	19	23	86	60	63	17	105
Cr	150	149	3.8	99	10	10	18	100	50	50	3.3	100
Cu	250	235	5.1	94	11	11	40	100	70	67	7.9	96
Fe	600	594	3.0	99	20	19	15	95	180	178	6.0	99
Al	700	696	5.6	99	60	62	33	103	160	161	13	101
Cd	50	48	12	96	2.5	2.9	16	116	14	13	16	93
Co	700	512	10	73	20	20	4.1	100	120	108	21	90
Ni	250	245	5.8	98	30	28	11	93	60	55	14	92
Pb	250	236	16	94	24	30	32	125	80	80	14	100
Zn	200	201	5.6	100	16	19	45	119	80	82	9.4	102
Se[c]	40	32	21.9	80	6	8.5	42	142	10	8.5	8.3	85

[a] Not all elements were analyzed by all laboratories.
[b] RSD = relative standard deviation.
[c] Results for Se are from two laboratories.
[d] Accuracy is expressed as the mean concentration divided by the true concentration times 100.

TABLE 5

ICP-AES PRECISION AND ACCURACY FOR AQUEOUS SOLUTIONS[a]

Element	Mean Conc. (mg/L)	N[b]	RSD[b] (%)	Accuracy[c] (%)
Al	14.8	8	6.3	100
Sb	15.1	8	7.7	102
As	14.7	7	6.4	99
Ba	3.66	7	3.1	99
Be	3.78	8	5.8	102
Cd	3.61	8	7.0	97
Ca	15.0	8	7.4	101
Cr	3.75	8	8.2	101
Co	3.52	8	5.9	95
Cu	3.58	8	5.6	97
Fe	14.8	8	5.9	100
Pb	14.4	7	5.9	97
Mg	14.1	8	6.5	96
Mn	3.70	8	4.3	100
Mo	3.70	8	6.9	100
Ni	3.70	7	5.7	100
K	14.1	8	6.6	95
Se	15.3	8	7.5	104
Ag	3.69	8	9.1	100
Na	14.0	8	4.2	95
Tl	15.1	7	8.5	102
V	3.51	8	6.6	95
Zn	3.57	8	8.3	96

[a]these performance values are independent of sample preparation because the labs analyzed portions of the same solutions

[b]N = Number of measurements for mean and relative standard deviation (RSD).

[c]Accuracy is expressed as a percentage of the nominal value for each analyte in acidified, multi-element solutions.

TABLE 6

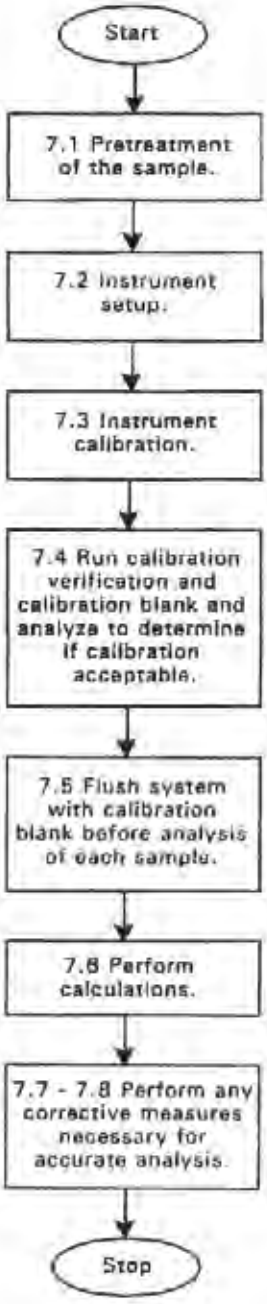
ICP-AES PRECISION AND BIAS FOR SOLID WASTE DIGESTS[a]

Element	Spiked Coal Fly Ash (NIST-SRM 1633a) Mean Conc. (mg/L)	N[b]	RSD[b] (%)	Bias[c] (%AAS)	Spiked Electroplating Sludge Mean Conc. (mg/L)	N[b]	RSD[b] (%)	Bias[c] (%AAS)
Al	330	8	16	104	127	8	13	110
Sb	3.4	6	73	96	5.3	7	24	120
As	21	8	83	270	5.2	7	8.6	87
Ba	133	8	8.7	101	1.6	8	20	58
Be	4.0	8	57	460	0.9	7	9.9	110
Cd	0.97	6	5.7	101	2.9	7	9.9	90
Ca	87	6	5.6	208	954	7	7.0	97
Cr	2.1	7	36	106	154	7	7.8	93
Co	1.2	6	21	94	1.0	7	11	85
Cu	1.9	6	9.7	118	156	8	7.8	97
Fe	602	8	8.8	102	603	7	5.6	98
Pb	4.6	7	22	94	25	7	5.6	98
Mg	15	8	15	110	35	8	20	84
Mn	1.8	7	14	104	5.9	7	9.6	95
Mo	891	8	19	105	1.4	7	36	110
Ni	1.6	6	8.1	91	9.5	7	9.6	90
K	46	8	4.2	98	51	8	5.8	82
Se	6.4	5	16	73	8.7	7	13	101
Ag	1.4	3	17	140	0.75	7	19	270
Na	20	8	49	130	1380	8	9.8	95
Tl	6.7	4	22	260	5.0	7	20	180
V	1010	5	7.5	100	1.2	6	11	80
Zn	2.2	6	7.6	93	266	7	2.5	101

[a]These performance values are independent of sample preparation because the labs analyzed portions of the same digests.

[b]N = Number of measurements for mean and relative standard deviation (RSD).

[c]Bias for the ICP-AES data is expressed as a percentage of atomic absorption spectroscopy (AA) data for the same digests.


Start
7.1 Pretreatment of the sample.
7.2 Instrument setup.
7.3 Instrument calibration.
7.4 Run calibration verification and calibration blank and analyze to determine if calibration acceptable.
7.5 Flush system with calibration blank before analysis of each sample.
7.6 Perform calculations.
7.7 - 7.8 Perform any corrective measures necessary for accurate analysis.
Stop

Analytical Methods

Mercury

7470A/7471A

METHOD 7470A

MERCURY IN LIQUID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7470 is a cold-vapor atomic absorption procedure approved for determining the concentration of mercury in mobility-procedure extracts, aqueous wastes, and ground waters. (Method 7470 can also be used for analyzing certain solid and sludge-type wastes; however, Method 7471 is usually the method of choice for these waste types.) All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the liquid samples must be prepared according to the procedure discussed in this method.

2.2 Method 7470, a cold vapor atomic absorption technique, is based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical detection limit for this method is 0.0002 mg/L.

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

3.3 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit with an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable-speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis, and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 liter air/min may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 liter/min.

4.7 Aeration tubing: A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10°C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1 of reference 1 or according to the instrument manufacturers instructions. The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system. Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. Equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_3; or

2. 0.25% Iodine in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580 13 or #580 22.

4.10 Hot plate or equivalent - Adjustable and capable of maintaining a temperature of 90-95°C.

4.11 Graduated cylinder or equivalent.

5.0 REAGENTS

5.1 Reagent Water: Reagent water will be interference free. All references to water in this method will refer to reagent water unless otherwise specified.

5.2 Sulfuric acid (H_2SO_4), concentrated: Reagent grade.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1.0 liter.

5.4 Nitric acid (HNO_3), concentrated: Reagent grade of low mercury content. If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

5.5 Stannous sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N H_2SO_4. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

5.6 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in reagent water and dilute to 100 mL. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

5.7 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of reagent water.

5.8 Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate in 100 mL of reagent water.

5.9 Stock mercury solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of reagent water. Add 10 mL of concentrated HNO_3 and adjust the volume to 100.0 mL (1 mL = 1 mg Hg). Stock solutions may also be purchased.

5.10 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at

0.15% nitric acid. This acid should be added to the flask, as needed, before addition of the aliquot.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH <2 with HNO_3. The suggested maximum holding times for mercury is 28 days.

6.4 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation: Transfer 100 mL, or an aliquot diluted to 100 mL, containing <1.0 µg of mercury, to a 300-mL BOD bottle or equivalent. Add 5 mL of H_2SO_4 and 2.5 mL of concentrated HNO_3, mixing after each addition. Add 15 mL of potassium permanganate solution to each sample bottle. Sewage samples may require additional permanganate. Ensure that equal amounts of permanganate are added to standards and blanks. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 min. Add 8 mL of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate. After a delay of at least 30 sec, add 5 mL of stannous sulfate, immediately attach the bottle to the aeration apparatus, and continue as described in Paragraph 7.3.

7.2 Standard preparation: Transfer 0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10.0-mL aliquots of the mercury working standard, containing 0-1.0 µg of mercury, to a series of 300-mL BOD bottles. Add enough reagent water to each bottle to make a total volume of 100 mL. Mix thoroughly and add 5 mL of concentrated H_2SO_4 and 2.5 mL of concentrated HNO_3 to each bottle. Add 15 mL of $KMnO_4$ solution to each bottle and allow to stand at least 15 min. Add 8 mL of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. When the solution has been decolorized, wait 30 sec, add 5 mL of the stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Paragraph 7.3.

7.3 Analysis: At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter/min, is allowed to run continuously. The absorbance will increase and reach a maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass

valve, remove the stopper and frit from the BOD bottle, and continue the aeration. Because of instrument variation refer to the manufacturers recommended operating conditions when using this method.

7.4 Construct a calibration curve by plotting the absorbances of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve. Duplicates, spiked samples, and check standards should be routinely analyzed.

7.5 Calculate metal concentrations (1) by the method of standard additions, or (2) from a calibration curve. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 ug/g dry weight).

8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

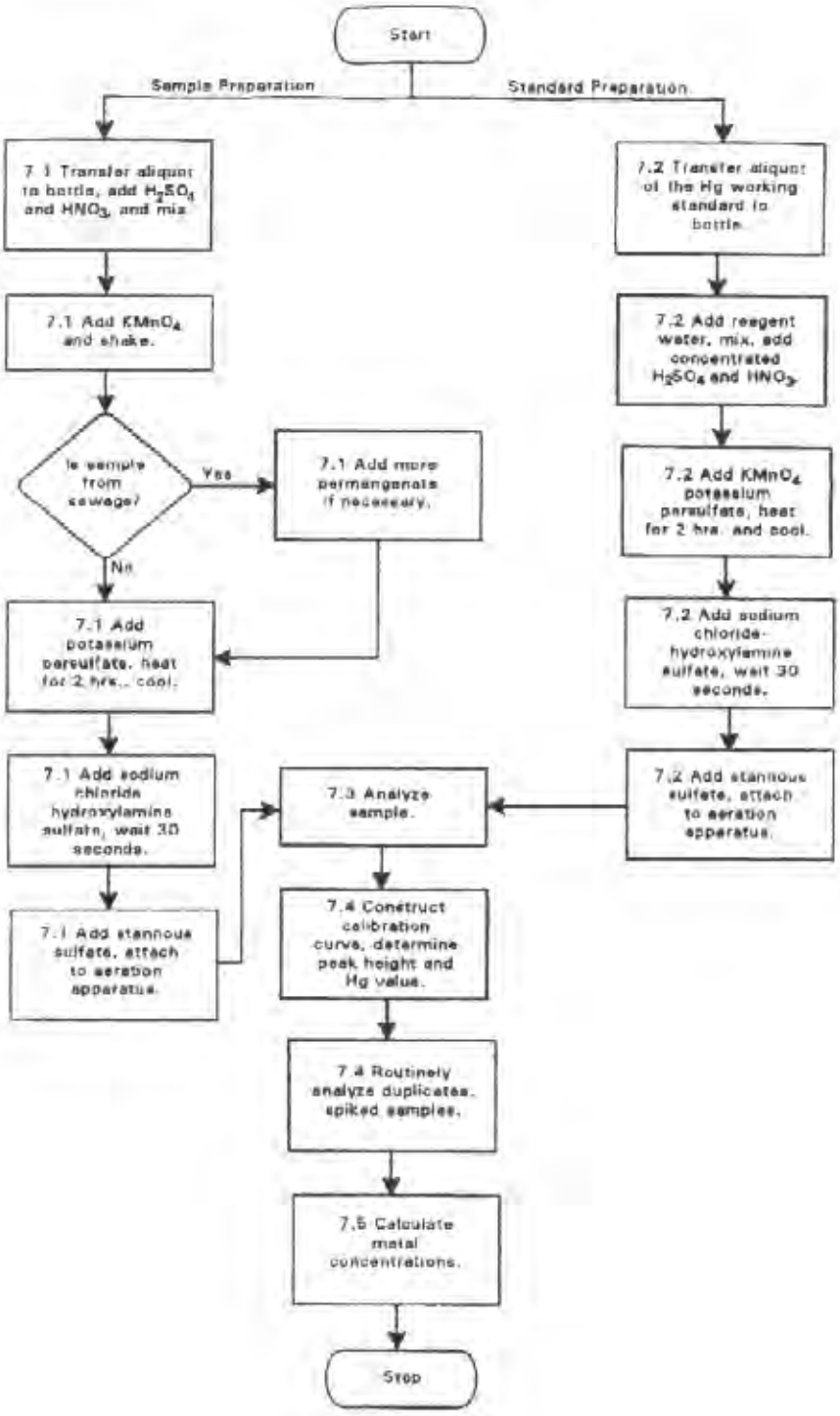
9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 245.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 245.1.

METHOD 7470A
MERCURY IN LIQUID WASTE (MANUAL COLD-VAPOR TECHNIQUE)



METHOD 7471A

MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7471 is approved for measuring total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials. All samples must be subjected to an appropriate dissolution step prior to analysis. If this dissolution procedure is not sufficient to dissolve a specific matrix type or sample, then this method is not applicable for that matrix.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the solid or semi-solid samples must be prepared according to the procedures discussed in this method.

2.2 Method 7471, a cold vapor atomic absorption method, is based on the absorption of radiation at the 253.7 nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical instrument detection limit (IDL) for this method is 0.0002 mg/L.

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/Kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/Kg had no effect on recovery of mercury from spiked samples.

3.3 Samples high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit with an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable-speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis, and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 L/min air may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 L/min.

4.7 Aeration tubing: A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10°C above ambient.

4.9 The cold vapor generator is assembled as shown in Figure 1 of reference 1 or according to the instrument manufacturers instructions. The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system. Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or
2. 0.25% iodine in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barneby and Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580-13 or #580-22.

4.10 Hot plate or equivalent - Adjustable and capable of maintaining a temperature of 90-95°C.

4.11 Graduated cylinder or equivalent.

5.0 REAGENTS

5.1 Reagent Water: Reagent water will be interference free. All references to water in this method refer to reagent water unless otherwise specified.

5.2 Aqua regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1 liter.

5.4 Stannous sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. A 10% solution of stannous chloride can be substituted for stannous sulfate.

5.5 Sodium chloride hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in reagent water and dilute to 100 mL. Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

5.6 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of reagent water.

5.7 Mercury stock solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of reagent water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL (1.0 mL = 1.0 mg Hg).

5.8 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug/mL. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask, as needed, before adding the aliquot.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Non aqueous samples shall be refrigerated, when possible, and analyzed as soon as possible."

7.0 PROCEDURE

7.1 Sample preparation: Weigh triplicate 0.2-g portions of untreated sample and place in the bottom of a BOD bottle. Add 5 mL of reagent water and 5 mL of aqua regia. Heat 2 min in a water bath at 95°C. Cool; then add 50 mL reagent water and 15 mL potassium permanganate solution to each sample bottle. Mix thoroughly and place in the water bath for 30 min at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate.

> CAUTION: Do this addition under a hood, as Cl_2 could be evolved. Add 55 mL of reagent water. Treating each bottle individually, add 5 mL of stannous sulfate and immediately attach the bottle to the aeration apparatus. Continue as described under step 7.4.

7.2 An alternate digestion procedure employing an autoclave may also be used. In this method, 5 mL of concentrated H_2SO_4 and 2 mL of concentrated HNO_3 are added to the 0.2 g of sample. Add 5 mL of saturated $KMnO_4$ solution and cover the bottle with a piece of aluminum foil. The samples are autoclaved at 121°C and 15 lb for 15 min. Cool, dilute to a volume of 100 mL with reagent water, and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Purge the dead air space and continue as described under step 7.4. Refer to the caution statement in section 7.1 for the proper protocol in reducing the excess permanganate solution and adding stannous sulfate.

7.3 Standard preparation: Transfer 0.0 , 0.5 , 1.0 , 2.0 , 5.0-, and 10-mL aliquots of the mercury working standard, containing 0 1.0 ug of mercury, to a series of 300-ml BOD bottles or equivalent. Add enough reagent water to each bottle to make a total volume of 10 mL. Add 5 mL of aqua regia and heat 2 min in a water bath at 95°C. Allow the sample to cool; add 50 mL reagent water and 15 mL of $KMnO_4$ solution to each bottle and return to the water bath for 30 min. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Add 50 mL of reagent water. Treating each bottle individually, add 5 mL of stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Step 7.4.

7.4 Analysis: At this point, the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 L/min, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the fritted tubing from the BOD bottle, and continue the aeration.

7.5 Construct a calibration curve by plotting the absorbances of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve. Duplicates, spiked samples, and check standards should be routinely analyzed.

7.6 Calculate metal concentrations: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 ug/g dry weight).

8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 245.5 of Methods for Chemical Analysis of Water and Wastes.

9.2 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

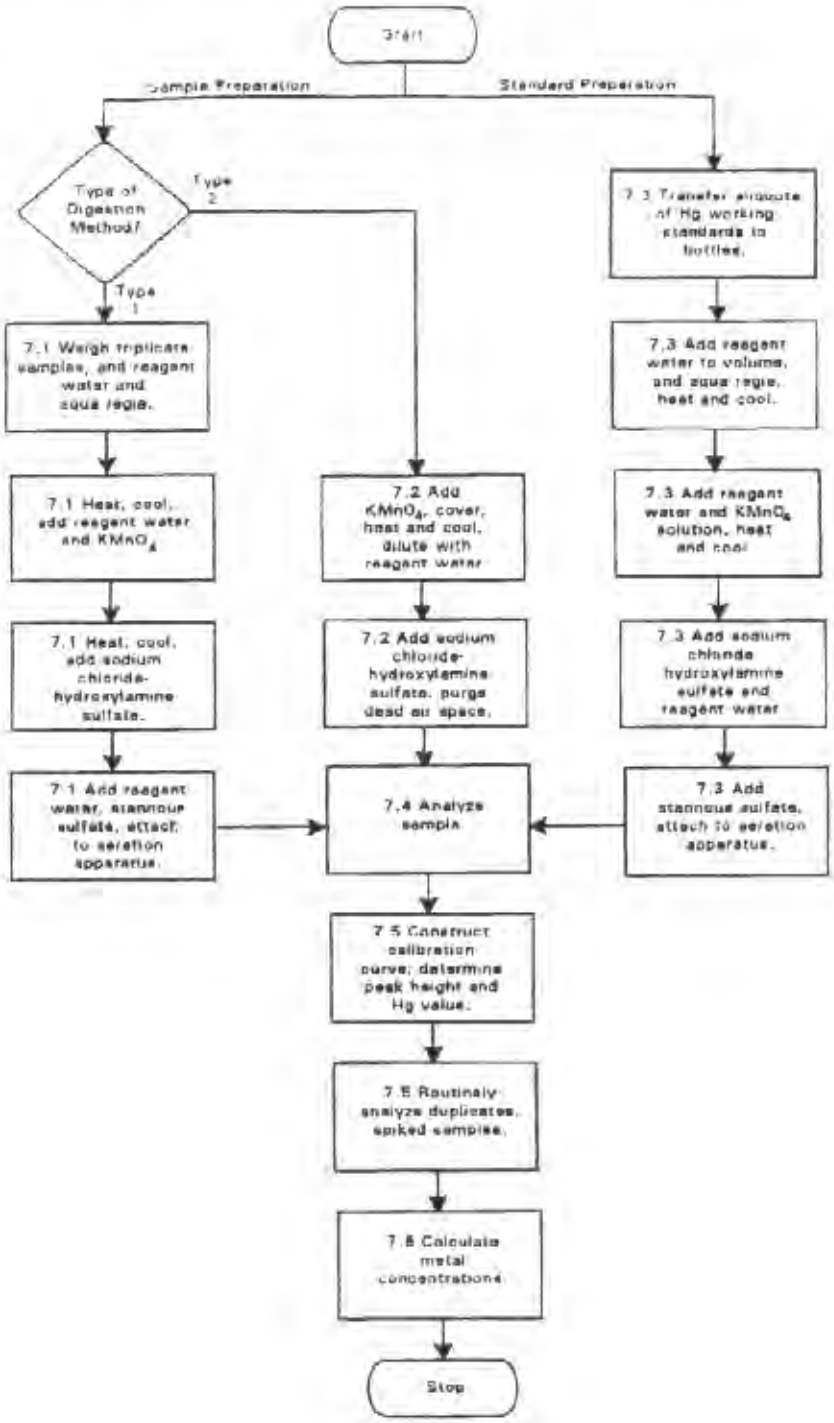
10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 245.5.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Emission control dust	Not known	12, 12 ug/g
Wastewater treatment sludge	Not known	0.4, 0.28 ug/g


Start
Sample Preparation
Standard Preparation
Type of Digestion Method?
Type 2
Type 1
7.1 Weigh triplicate samples, and reagent water and aqua regia.
7.1 Heat, cool, add reagent water and KMnO4
7.1 Heat, cool, add sodium chloride-hydroxylamine sulfate.
7.1 Add reagent water, stannous sulfate, attach to aeration apparatus.
7.2 Add KMnO4, cover, heat and cool, dilute with reagent water
7.2 Add sodium chloride-hydroxylamine sulfate, purge dead air space.
7.3 Transfer aliquots of Hg working standards to bottles.
7.3 Add reagent water to volume, and aqua regia, heat and cool.
7.3 Add reagent water and KMnO4 solution, heat and cool
7.3 Add sodium chloride hydroxylamine sulfate and reagent water
7.3 Add stannous sulfate, attach to aeration apparatus.
7.4 Analyze sample
7.5 Construct calibration curve; determine peak height and Hg value.
7.6 Routinely analyze duplicates, spiked samples.
7.8 Calculate metal concentrations
Stop

Analytical Methods

Moisture Content

ASTM D2974

Designation: D 2974 – 00

Standard Test Methods for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils[1]

This standard is issued under the fixed designation D 2974; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These test methods cover the measurement of moisture content, ash content, and organic matter in peats and other organic soils, such as organic clays, silts, and mucks.

1.2 The values stated in SI units are to be regarded as the standard. No other units of measurement are included in this standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 653 Terminology Relating to Rock, Soil, and Contained Fluids[2]

D 3740 Practice for the Evaluation of Agencies Engaged in the Testing and/or Inspection of Soil and Rock as Used in Engineering Design and Construction[2]

D 4753 Standard Specifications for Evaluating, Selecting, and Specifying Balances and Scales for Use in Soil and Rock Testing[2]

E 145 Specification for Gravity Convection and Forced Ventilation Ovens[3]

3. Terminology

3.1 *Definitions*:

3.1.1 For common definitions of terms in this standard, refer to Terminology D 653.

4. Summary of Test Methods

4.1 *Test Method A*—Moisture is determined by drying a peat or organic soil sample at 105°C. The moisture content is expressed either as a percent of the oven dry mass or of the as-received mass.

4.2 *Test Method B*—This is an alternative moisture method which removes the total moisture in two steps: (*1*) evaporation of moisture in air at room temperature (air-drying), and (2) the subsequent oven drying of the air-dried sample at 105°C. This method provides a more stable sample, the air-dried sample, when tests for nitrogen, pH, cation exchange, and the like are to be made.

4.3 *Test Methods C and D*—Ash content of a peat or organic soil sample is determined by igniting the oven-dried sample from the moisture content determination in a muffle furnace at 440°C (Method C) or 750°C (Method D). The substance remaining after ignition is the ash. The ash content is expressed as a percentage of the mass of the oven-dried sample.

4.4 Organic matter is determined by subtracting percent ash content from one hundred.

5. Significance and Use

5.1 This test method can be used to determine the moisture content, ash content, and percent organic matter in soil.

5.2 The percent organic matter is important in classifying a peat or other organic soil.

NOTE 1—The quality of the result produced by this standard is dependent on the competence of the personnel performing it, and the suitability of the equipment and facilities used. Agencies that meet the criteria of Practice D 3740 are generally considered capable of competent and objective testing/sampling/inspection/etc. Users of this standard are cautioned that compliance with Practice D 3740 does not in itself assure reliable results. Reliable results depend on many factors; Practice D 3740 provides a means of evaluating some of those factors.

6. Apparatus

6.1 *Oven*, meeting the requirements of E 145 and capable of being regulated to a constant temperature of 105 ± 5°C.

NOTE 2—The temperature of 105°C is quite critical for organic soils. The oven should be checked for "hot spots" to avoid possible ignition of the specimen.

6.2 *Muffle Furnace*, capable of producing constant temperatures of 440°C and 750°C.

6.3 *Balance or Scale*, a balance or scale for determining the mass of the soil having a minimum capacity of 500 g and

[1] These test methods are under the jurisdiction of ASTM Committee D18 on Soil and Rock and are the direct responsibility of Subcommittee D18.22 on Soil as a Medium for Plant Growth.

Current edition approved August 10, 2000. Published November 2000. Originally published as D 2974 – 71. Last previous edition D 2974 – 87 (1995).

[2] *Annual Book of ASTM Standards*, Vol 04.08.

[3] *Annual Book of ASTM Standards*, Vol 04.06.

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meeting the requirements of Standard D 4753 for a balance or scale of 0.01 g readability.

6.4 *Rubber Sheet, Oil Cloth*, or other non-absorbent material.

6.5 *Evaporating Dishes*, of high silica or porcelain of not less than 100-mL capacity.

6.6 *Blender*, high-speed.

6.7 *Aluminum Foil*, heavy-duty.

6.8 *Porcelain Pan, Spoons*, and equipment of the like.

6.9 *Desiccator.*

7. Sampling and Test Specimens

7.1 Place a representative field sample on a square rubber sheet, oil cloth, or equivalent material and mix thoroughly.

7.2 Reduce the sample to the quantity required for a test specimen by quartering.

7.3 Place the test specimen and the remaining sample in separate waterproof containers.

7.4 Work rapidly to prevent moisture loss or perform the operation in a room with a high humidity.

8. Procedure

8.1 *Moisture Content Determination*

8.1.1 *Test Method A*

8.1.1.1 Record to the nearest 0.01 g the mass of a high silica or porcelain evaporating dish fitted with a heavy-duty aluminum foil cover. The dish shall have a capacity of not less than 100 mL.

8.1.1.2 Following the instruction in section 4.1 above, place a test specimen of at least 50 g in the container described in 8.1.1.1. Crush soft lumps with a spoon or spatula. The thickness of peat in the container should not exceed 3 cm.

8.1.1.3 Cover immediately with the aluminum foil cover and record the mass to the nearest 0.01 g.

8.1.1.4 Dry uncovered for at least 16 h at 105°C or until there is no change in mass of the sample after further drying periods in excess of 1 h. Remove from the oven, cover tightly, cool in a desiccator, and record the mass to the nearest 0.01 g.

8.1.2 *Calculations for Test Method A*

8.1.2.1 Calculate the moisture content as follows:

$$\text{Moisture Content, \%} = [(A - B) \times 100]/A \quad (1)$$

where:

A = mass of the as-received test specimen, g, and

B = mass of the oven-dried specimen, g.

8.1.2.1.1 This calculation is used primarily for agriculture, forestry, energy, and horticultural purposes and the result should be referred to as the moisture content as a percentage of as-received or total mass.

8.1.2.2 An alternative calculation is as follows:

$$\text{Moisture Content, \%} = [(A - B) \times 100]/B \quad (2)$$

where:

A = as-received test specimen, g, and

B = mass of the oven-dried specimen, g.

8.1.2.2.1 This calculation is used primarily for geotechnical purposes and the result should be referred to as the moisture content as a percentage of oven-dried mass.

8.1.2.3 Take care to indicate the calculation method used.

8.1.3 *Test Method B*

8.1.3.1 This test method should be used if pH, nitrogen content, cation exchange capacity, and the like are to be tested.

8.1.3.2 Following the instructions in section 4.1 above, select a 100 to 300 g representative test specimen. Determine the mass of this test specimen to the nearest 0.01 g and spread it evenly on a large flat pan. Crush soft lumps with a spoon or spatula and let the sample come to moisture equilibrium with room air. This will require at least 24 h. Stir occasionally to maintain maximum air exposure of the entire sample. When the mass of the sample reaches a constant value, calculate the moisture removed during air drying as a percentage of the as-received mass.

8.1.3.3 Grind a representative portion of the air-dried sample for 1 to 2 min in a high-speed blender. Use the ground portion for moisture, ash, nitrogen, cation exchange capacity tests, and the like.

8.1.3.4 Thoroughly mix the air-dried, ground sample. Weigh to the nearest 0.01 g the equivalent of 50 g of test specimen on an as-received basis. Determine the amount, in grams, of air-dried sample equivalent to 50 g of as-received sample, as follows:

$$\text{Equivalent Sample Mass, g} = 50.0 - [(50 \times M)/100] \quad (3)$$

where:

M = moisture removed in air drying, %.

8.1.3.5 Place the sample in a container as described in 8.1.1 and proceed as in Method A.

8.1.4 *Calculations for Test Method B*

8.1.4.1 Calculate the moisture content as follows:

$$\text{Moisture Content, \%} = (50 - B) \times 2 \quad (4)$$

where:

B = oven-dried sample, g.

8.1.4.1.1 This calculation gives moisture content as a percentage of as-received mass.

8.1.4.2 An alternative calculation is as follows:

$$\text{Moisture Content, \%} = [(50 - B) \times 100]/B \quad (5)$$

8.1.4.2.1 This calculation gives moisture content as a percentage of oven-dried mass.

8.2 *Ash Content Determination*

8.2.1 *Test Method C*

8.2.1.1 Determine the mass of a covered high-silica or porcelain dish to the nearest 0.01 g.

8.2.1.2 Place a part of or all of the oven-dried test specimen from a moisture determination in the dish and determine the mass of the dish and specimen.

8.2.1.3 Remove the cover and place the dish in a muffle furnace. Gradually bring the temperature in the furnace to 440°C and hold until the specimen is completely ashed (no change of mass occurs after a further period of heating).

8.2.1.4 Cover with the retained aluminum foil cover, cool in a desiccator, and determine the mass to the nearest 0.01 g.

8.2.1.5 This test method should be used for all geotechnical and general classification purposes.

8.2.2 *Test Method D*

8.2.2.1 Determine the mass of a covered high-silica or porcelain dish to the nearest 0.01 g.

8.2.2.2 Place a part of or all of the oven-dried test specimen from a moisture determination in the dish and determine the mass of the dish and specimen to the nearest 0.01 g.

8.2.2.3 Remove the cover and place the dish in a muffle furnace. Gradually bring the temperature in the furnace to 750°C and hold until the specimen is completely ashed (no change of mass occurs after a further period of heating).

8.2.2.4 Cover with the retained aluminum foil cover, cool in a desiccator, and determine the mass to the nearest 0.01 g.

8.2.2.5 This test method should be used when peats are being evaluated for use as a fuel.

8.2.3 *Calculation for Test Methods C and D*

8.2.3.1 Calculate the ash content as follows:

$$\text{Ash Content, \%} = (C \times 100)/B \quad (6)$$

where:

C = ash, g, and

B = oven-dried test specimen, g.

8.3 *Organic Matter Determination*

8.3.1 *Calculation*

8.3.1.1 Determine the amount of organic matter by difference, as follows:

$$\text{Organic matter, \%} = 100.0 - D \quad (7)$$

where:

D = ash content, %.

9. Report

9.1 Report the following information:

9.1.1 Results for organic matter and ash content, to the nearest 0.1 %.

9.1.2 Furnace temperature used for ash content determinations.

9.1.3 Whether moisture contents are by proportion of as-received mass or oven-dried mass.

9.1.3.1 Express results for moisture content as a percentage of as-received mass to the nearest 0.1 %.

9.1.3.2 Express results for moisture content as a percentage of oven-dried mass as follows:

(a) Below 100 % to the nearest 1 %.

(b) Between 100 % and 500 % to the nearest 5 %.

(c) Between 500 % and 1000 % to the nearest 10 %.

(d) Above 1000 % to the nearest 20 %.

10. Precision and Bias

10.1 *Precision*—Test data on precision is not presented due to the nature of the soil materials tested by this test method. It is either not feasible or too costly at this time to have ten or more laboratories participate in a round-robin testing program.

10.1.1 The Subcommittee D 18.06 is seeking any data from the users of this test method that might be used to make a limited statement on precision.

10.2 *Bias*—There is no accepted reference value for this test method, therefore, bias cannot be determined.

11. Keywords

11.1 ash content; moisture content; organic soil; peat; % organic matter

SUMMARY OF CHANGES

In accordance with Committee D18 policy, this section identifies the location of changes to this standard since the last edition (95) that may impact the use of the standard.

(1) Section 1.2—Added second sentence to update SI statement.

(2) Inserted new Section 2 on Referenced Documents and new Section 3 on Terminology. Renumbered subsequent sections as needed.

(3) Inserted new Section 5 on Significance and Use and renumbered subsequent sections as needed.

(4) Renumbered Section 5—Inserted standard Note 1 referencing D 3740 and renumbered following notes as needed.

(5) Inserted new footnotes 2 and 3 for referenced ASTM documents.

(6) Section 6.1—Inserted reference to E 145.

(7) Section 6 Apparatus—Inserted a balance or scale as 6.3 and a rubber sheet, etc. as 6.4.

(8) Changed heading of Section 7 from Preparation of Sample to Sampling and Test Specimens.

(9) Renumbered section 7.1—Clarified procedures for mixing, subsampling and storing material.

(10) Added Section 8 Procedure and renumbered sections on moisture content, ash content and organic matter to fall under procedure.

(11) Renumbered sections 8.1.1.2 and 8.1.3.2—Deleted "Mix the sample thoroughly and" with "Following the instructions in section 4.1 above."

(12) Renumbered sections 8.1.1.4, 8.1.3.2, 8.2.1.1, 8.2.1.4, 8.2.2.1, and 8.2.2.3—specified determining the mass to the nearest 0.01 g.

(13) Renumbered section 8.1.3.2—Changed "sample" to "test specimen."

(14) Updated Precision and Bias statement.

(15) Added Keywords section.

(16) Added Summary of Changes section.

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Analytical Methods

Total Extractable Petroleum Hydrocarbons

NJ-TPH-QAM 025-10/91

New Jersey Department of Environmental Protection
Office of Quality Assurance
Analytical Method

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MALCOLM PIRNIE, INC.
NORTHERN NEW JERSEY

Title:
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Date: 2/5/01 Revision: 5

Prepared by: Dr. Michael W. Miller

Location: **Master Sets**
DEP/OQA

Cleared for
Issue by: Joseph Aiello

1.0 SCOPE OF APPLICATION

1.1 Scope

This method utilizes a gas chromatograph fitted with a flame ionization detector (FID). The following petroleum analyses are included in the method:

1.1.1 Quantitative analysis of environmental samples (water, soil, sediment, and sludge) for residues from commercial petroleum products such as crude oil, diesel fuel, waste oil, fuels oils Nos. 2-6, lubricating oil, processed oils and bunker fuel.

The method determines Total Semi-Volatile Petroleum Products (TPHC), also known as Total Petroleum Hydrocarbons. TPHC includes paraffinic, naphthenic, and polynuclear aromatic hydrocarbons (PAHs).

The method must not be used for gasoline contaminated sites.

1.1.2 Fingerprint - Identification of unknown petroleum products by comparison of their chromatograms with chromatograms of known petroleum product profiles. Products that can be identified include diesel fuel, fuel oils Nos. 2-6, lubricating oils, bunker fuel and processed oils (2).

1.2 Applicable Program

Underground Storage Tanks (UST), New Jersey Spill Fund, Comprehensive Environmental Response Compensation and Liability Act (CERCLA), Industrial Site Recovery Act (ISRA), Sludge Residuals, and Resource Conservation and Recovery Act (RCRA).

1.3 Method Advantages

1.3.1 The method replaces the TPHC method based on Freon 113 extraction and analysis by infrared spectroscopy.

1.3.2 The FID response produces a TPHC chromatogram that can be used to identify the type of petroleum product present by matching the chromatogram of the unknown sample with the chromatograms of known petroleum products.

1.4 Method Limitations

1.4.1 Quantitative Studies

1.4.2.1 The TPHC is quantitatively restricted to the semi-volatile components since partial loss of volatiles (b.p. < 60°C) occurs during the extraction and/or concentration process.

1.4.2.2 The gas chromatographic conditions are not designed for compounds with carbon numbers greater than C40.

1.4.2.3 Benzene and hydrocarbons that elute from the column before heptane co-elute with the extraction solvent methylene chloride.

1.4.2 Identification Studies

1.4.1.1 The method is most successful with fresh spills of petroleum products. Weathering changes the chromatographic profile. Weathering can be simulated in the laboratory.

1.4.1.2 Absorption, adsorption, biological reactions, and chemical reactions occur in soil, changing the chromatographic profile which reduces the ability to make positive identifications. Method OQA-QAM-018 can be used for more detailed product analysis.

1.5 Matrix

1.5.1 Surface water, ground water, and wastewater.

1.5.2 Soil, sediments or high solids sludge (>50%).

2.0 SUMMARY OF METHOD

2.1 This quantitative TPHC method is adopted from the "Leaking Underground Fuel Tanks Field Manual" of the California State Water Resources Control Board (3). This method is also derived from "Test Methods for Evaluating Solid Waste" USEPA Method 8015B and the Florida Department of Environmental Protection, "Method for the Determination of Total Petroleum Range Organics"(4, 25).

2.2 This petroleum method is adapted with modifications from ASTM Method D3328-82, and the US Coast Guard Oil Spill Identification Procedure for Total Petroleum (1,2).

2.3 Petroleum residues are extracted from sample matrices with methylene chloride. Surrogate compounds are added to all samples before extraction. The methylene chloride extract is analyzed with a gas chromatograph fitted with a capillary column attached to a FID.

2.3.1 The TPHC is determined by integration of the FID chromatogram. Calibration of the gas chromatograph is done with a hydrocarbon standard C8-C40 or where justified and documented, based on historic site-specific data, a standard reference petroleum product.

2.3.2 Identification of unknown residues may be done by comparing their chromatograms with chromatograms of known petroleum products. Samples from old spills are compared to synthetically weathered samples if available. Identification is established when chromatograms match. Method QAM-018 must be used for detailed pattern recognition (6).

2.3.3 The sensitivity of the method is dependent on the level of interference rather than on instrumental limitations. The method detection limit (MDL) for TPHC in soil is approximately 10 ug/g and in water 30 ug/L. These MDLs can be achieved without concentrating the extract..

2.3.4 Dynamic Range

2.3.4.1 TPHC

Soil 30-1000 ug/g
Aqueous 0.1-500 mg/L

2.3.4.2 Individual Compounds

Soil 1.0-500 ug/g
Aqueous 0.2-200 ug/L

3.0 INTERFERENCES

3.1 Method interferences are reduced by washing all glassware with hot soapy water and then rinsing with tap water, distilled water, methanol, and methylene chloride.

3.2 High purity reagents such as Burdick and Jackson GC2 methylene chloride, Baker capillary grade methylene chloride or equivalent must be used to minimize interference problems.

3.3 Before processing any sample, the analyst should demonstrate daily, through the analysis of a method blank, that the entire system is interference-free.

3.4 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interference will vary considerably from source to source (e.g. fatty acids, biogenic materials, oxidized biodegradation products), depending upon the nature and diversity of the site being sampled. The cleanup procedure, EPA Method 3630B can be use to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the method detection limit (MDL) (4).

3.5 Naturally occurring alkanes may be detected by this method and may interfere with product identification. Naturally occuring plant waxes include odd carbon number alkanes from n-C_{25} through n-C_{35}, and exhbit a dominant odd/even chain length distribution. Leaf hydrocarbons also may be detected.

3.6 A vial septum should be penetrated and extracted with methylene chloride to evaluate the potential alkane distribution that could occur in re-analyzed extracts. Vial septums should be changed after each analysis.

3.7 Particulates interfer with the determination of disolved petrolem products in ground water. Petroleum products adsorb on the surface of particulates. The groundwater samples should be filtered through glass fiber filters to determine dissolved TPH.

4.0 SAFETY

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been defined precisely. Each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDS) should also be made available to all personnel involved in the chemical analysis. Additional reference to laboratory safety are available and have been identified for use by the analyst (8,9).

5.0 APPARATUS AND EQUIPMENT

5.1 Sampling Containers

5.1.1 Prior to use, wash bottles and cap liners with aqueous detergent solutions and rinse with tap water, distilled water, and methylene chloride. Allow the bottles and containers to air dry at room temperature, place in a 150°C oven for one hour, then remove and allow to cool in an area known to be free of organic analytes.

5.1.2 Screw cap bottle - 40 mL PTFE-faced silicone cap liners.

5.1.3 Narrow mouth bottles - 1 liter, amber, PTFE faced silicone cap liners.

5.1.4 Wide-mouth glass jar-four ounce, amber, PTFE faced silicone cap liners

5.2 Glassware

5.2.1 Serum bottles - 100 mL, 10 mL, 2 mL crimp-top, PTFE-faced silicone cap liners.

5.2.2 Pasteur pipets

5.2.3 Screw-cap Erlenmeyer flasks - 250 mL, with PTFE faced silicone cap liners.

5.2.4 Volumetric flasks - 10 mL, 25 mL, 100 mL

5.2.5 Kuderna-Danish apparatus (KD)

5.2.6 Sepratory funnels - 2 L Pyrex, Tefon stopcoat

5.2.7 Soxhlet Extractor

5.3 Apparatus

5.3.1 Rotary shaker table, 350 rpm minimum

5.3.2 Analytical balance capable of accurately weighing 0.0001 g.

5.3.3 A gas chromatograph with split/splitless injector, equipped with a capillary column, capable of temperature programming.

5.3.3.1 Column-30m long x .53mm ID, .5um film thickness dimethyl polysiloxane coating (Restek, J&W Scientific or equivalent). This column will allow for the resolution of alkanes from nC8 to nC40, as well as the resolution of phytane/nCl8 and pristane/nCl7. This column will also allow for the resolution of the petroleum products listed in Section 1.1 (21). Low bleed columns must be used. Equivalent columns maybe used.

5.3.3.2 Column - 30m long x 0.32mm ID, 0.25um film thickness, 95% dimethyl-5% diphenyl polysilxane (J&W Scientific, Restek or equivalent). This column has simillar resolution to 5.3.3.1 but high bp compounds elute later. Equivalent columns maybe used.

5.3.3.2 Column - 100m long x .25mm ID., 0.5um film thickness, capillary, Protocol DH (Supelco or equivalent (22).

5.3.3.3 Detector - Flame Ionization Detector (TPHC only)

5.3.4 An autosampler is recommended.

5.3.5 Boiling chips - Solvent extracted approximately 10/40 mesh.

5.3.6 Water bath - Top, with concentric ring cover, capable of temperature control. The bath should be used in a hood.

5.3.7 Gas-tight syringe - One milliliter (mL) with chromatographic needles.

5.3.8 Microsyringes – l0uL, 100uL, 200uL

5.3.9 Continuous liquid-liquid extraction apparatus.

5.3.10 Liquid chromatographic column - 400 x 20mm with course frit, teflon stopcock.

5.3.11 Magnetic stirrer and 2-inch Teflon coated stirring bars.

5.3.12 Nitrogen concentration system composed of a precleaned pasteur pipet, with a small plug of glass wool loaded at the tip end, and filled with approximately 1-2 cm of precleaned alumina. The top of the pipet is attached to a hydrocarbon free nitrogen gas source using precleaned Teflon tubing. This concentration step should be performed at room temperature or lower to retain light end compounds.

6.0 REAGENTS

6.1 Purity of Reagents - Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee and Analytical Reagents of the American Chemical Society.

6.2 Reagent water - Reagent water is defined as a water in which an interference is not observed at the MDL of each parameter of interest. (ASTM Specification D1193, Type ii).

6.3 Methylene chloride, methanol, carbon, disulfide and hexane - pesticide grade, Burdick and Jackson GC2, Baker Capillary Grade or equivalent.

6.4 Sodium sulfate - (ACS) granular, anhydrous. Purify by heating at 400°C for four hours in a shallow tray, cool in a desiccator and store in a sealed glass bottle.

6.5 Silica gel - Grade 923 (100/200) desiccant. Before use, activate for at least 16 hours at 130°C in a shallow glass tray that is loosely covered in foil. Cool and store as in Section 6.4.

6.6 Silica granular, fine (60-120 mesh) Fisher 5151-10. Purify by Soxhelt extraction with methylene chloride for four hours. Dry at 80°C. Store in glass bottle.

6.7 Hydrochloric acid, 1:1 - Mix equal volumes of (ACS) concentrated HCl and distilled water.

6.8 Stock Standards

6.8.1 Normal Paraffinic Hydrocarbons - Prepare a Methylene chloride solution containing a mixture of components ranging from octane to tetracontane

(nC8-nC40), or selected individual normal paraffins (2 mg/ml ea). The standard must include a minimum of 12 compounds including C8, C18, C20, C32, and C40. For product identification purposes the mixture also may contain C17, pristane and phytane (2 mg/ml ea.) . A separate pristane, phytane, C17, and C18 column resolution standard may be used. An appropriate dilution of the mixture is analyzed under normal analytical conditions to determine retention times and the Relative Response Factors for the Compounds. A 10% carbon disulfide/ 90% methlyene chloride solvent mixture may be used if standard do not remain in solution. (Mixtures are available from Supelco, Restek (31266), NSI Solutions and Ultrex).

6.8.2 Diesel and Fuel Oil Profile Standards - Where applicable prepare commercial diesel, waste motor oil and/or fuel standards in methylene chloride. Weigh 300mg oil to the nearest 0.1 mg, into a 10 mL volumetric flask. Dilute to volume with methylene chloride (30 mg/ml). Standards are available from Restek Inc., Bellefonte, PA.

6.8.3 Surrogates (SS) and Internal Standards (IS) - The surrogates (chlorobenzene, ortho-terphenyl [OTP] and tetracosane-d50), and internal standard (5-androstane) are prepared separately by carefully weighing 100 mg of each compound in a 100 mL volumetric flask. Dilute to volume with methylene chloride. The final concentration of each compound is one ug/ul. The laboratory is free to choose any two or more surrogates that cover the carbon range (C8 - C40). However chlorobenzene is required. Standards are available from Restek Inc.

6.8.4 Quality Control Check Standard (Blank Spike) - The QC check standard concentrate (30 mg/ml) of fuel oil #2 must be prepared by the laboratory using stock standards prepared independently from those used for calibration (Section 6.8.2). If the contamination at the site is known, other fuel standards can be used. Standards are available from Supelco, Restek or Ultrex.

6.8.5 Matrix spiking standard (MSS) - Prepare the MSS in methylene chloride from a Fuel oil #2 standard in Section 6.8.2 or another oil for site speific work . The laboratory may use the hydrocarbon calibration standard noted in section 6.8.1 as the MSS for unknown petroleum sources.

7.0 CALIBRATION

7.1 Initial Calibration

7.1.1 Rentention time windows

a. **Before establishing windows, make sure the GC system is within optimum operating conditions. Serial injections over less than a 72 hr period result in retention time windows that are too tight.**

b. **Calculate the mean and the standard deviation of the three retention times (use any function of retention time; including absolute retention time, or relative retention time) for each surrogate.**

c. Plus or minus three times the standard deviation of the mean retention times for each surrogate will be used to define the retention time window; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms. The default value for the retetion time shall be a minimum of +/- 0.05 minutes, if the standard deviation is zero.

d. Establish the midpoint of the retention time window for each surrogate by using the absolute retention for each surrogate from the mid-concentration standard of the initial calibration. The absolute retention time window equals the midpoint $\pm$ 3 SD, where the standard deviation is determined as described in Section b.

e. The laboratory must calculate retention time windows for each surrogate on each GC column and whenever a new GC column is installed. The data must be retained by the laboratory.

7.1.2 FID Internal Standard Calibration for Quantitation of TPHC - Calibrate the GC-FID with an initial fivepoint, (i.e., concentration of individnal components 1 ng/uL, 5ng/uL, 10ng/ul, 20 ng/uL, 50ng/uL), Total Petroleum Hydrocarbons calibration curve (Section 6.8.1). The lowest concentration point in the calibration curve should be near the MDL. The highest concentration point should be twice the expected sample concentration and within the linear instrument range. To maintain the standards in solution, a 10% carbon disulfide/90% methylene chloride solvent may be required. Prepare the calibration standard to contain 5.0 ng/ul of surrogate and GC internal standard. The relative standard deviation (RSD) for the surrogates and each calibration compound's relative response factor (RRF) must be less than or equal to 20%. If not, the calibration curve must be used to determine concentration. A minimum correlation coeffient of 0.95 is required. Also calculate the response for total petroleum hydrocarbons (TPHC) which is the average of the RRFs for the nC8-nC40 compounds (Section 11.2.2). The RSD must be less than 20%. The chromatograms should be checked for mass discrimination (Section 7.3). Standards with concentrations greater than 20 mg/L may need to be equilibrated to room temperature prior to analysis.

7.1.3 TPHC External Standard Calibration - The laboratory has the option of using an external calibration procedure. Prepare the standards as directed in Section 7.1.2 omitting the internal standard. Calculate response factors (RF) instead of relative response factors for each compound and the surrogates. The relative standard deviation (RSD) of each calibration compound's response factor (RF) must be less than 20%. If not the calibration curve must be used to determine concentration. A minimum correlation coefficient of 0.95 is required. Also

calculate the response for total petroleum hydrocarbons (TPHC) which is the average of the RFs for the nC8-nC40 compounds (Section 11.3).

7.1.4 TPHC Petroleum Product Calibration - If the laboratory has a site specific project and the petroleum product contamnation is known the GC_FID maybe calibrated using a reference petroleum product (Section 6.8.2). Calibrate the GC-FID with an initial five point, (i.e. concentration total petroleum 0.1 mg/ml, 0.2mg/ml, 1.0mg/ml, 2.0mg/ml, 5.0mg/ml) calibration curve. Calculate the response factor (RF) for TPHC (Section 11.2). The RSD of the TPHC responce factor must be less than 20%. If not the calibration curve must be used to detirmine concentration. A minimum correlation coefficient of 0.95 is required.

7.1.5 Petroleum Profile Calibration - If the method is used only for qualitative petroleum product profiling, a single point GC-FID retention time calibration is required. Prepare a 2 mg/ml standard from the products in section 6.8.2 (23). Prepare a 20 ng/ul carbon number standard from section 7.12.

7.2 Daily Calibration

7.2.1 The resolution check is required for fingerprint determination. The resolution of the chromatographic column should be checked daily. Inject two uL of the calibration mixture (10 ng/ul) (section 7.1.2) into the chromatograph. Visually inspect the chromatograms for separation between phytane and nC18.

If a standard fuel oil #2 is used as the calibration mixture, the resolution of the chromatograph column can be monitored by visually checking the resolution of the pair, nC17-Pristane and nC18-phytane. These compounds occur in all fuel oil #2 products.

7.2.2 The working calibration curves or calibration factors for TPHC, must be verified on each working day and after every 12 hours by the measurement of one or more calibration standards, (10 ng/ul). Calculate the percent difference (D%) between the verified RF/RRF and the inital responses RF/RRF for TPHC and the surrogates. The %D must not exceed 20%. If the %D exceeds 20% the instrument must be recalibrated. Reanalysis of all samples analyzed after a non compliant standard is required.

7.2.3 The retention times of surrogates in the calibration verification standard analyzed at the beginning of the analytical shift must fall within the absolute retention time windows calculated in Sec. 7.1.1b. The purpose of this check is to ensure that retention times do not continually drift further from those used to established the widths of the retention time windows. If the retention time of any surrogate at the beginning of the analytical shift does not fall within the $\pm$ 3 SD

window (minimum +/- 0.05 min.), then a new initial calibration is necessary unless system maintenance (Sec. 7.11) corrects the problem.

In addition, the retention times of all surrogates in the subsequent calibration verification standards analyzed during the analytical shift must fall within the absolute retention time windows established in Sec. 7.1.1d.

7.2.4 Surrogate Standards (SS), GC Internal Standard (IS) - The SS and IS responses and retention times in the calibration check standard must be evaluated during or immediately after data acquisition. If the retention time(s) for the SS or IS is outside the determined RT window, the chromatographic system must be inspected for malfunctions and corrections must be made. If the area(s) for the SS or IS changes by +/- 50% from the last daily calibration standard check, the GC must be inspected for malfunctions and corrections must be made.

7.3 Mass Discrimination

7.3.1 Mass discrimination can take place in the injection port. The heavier molecules do not enter the column as a defined plug of vapor with the lighter molecules.

7.3.2 Mass discrimination is minimized by placing a small plug of silanized glass wool one centimeter from the base of the glass injection liner. The end of the capillary column is placed just below the glass wool.

7.3.4 The calibration chromatogram (Section 7.1.1) is inspected for mass discrimination. The response factor ratio C32/C20 should be greater than 0.8. If the ratio is less, reposition the column in the glass liner until mass discrimination is minimized.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses this method is required to operate a formal quality control program which conforms with New Jersey Regulation N.J.A.C. 7:18-4.7 (13). The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of QC samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with laboratory established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

8.1.1 The analyst must make an initial, one-time demonstration of the ability to generate acceptable accuracy and precision with this method (Section 8.2).

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted to improve the separations by changing the GC conditions or column. Each time such a modification is made to the method, the analyst is required to repeat and document the procedure in Section 8.2.

8.1.3 Each day before calibration and after the calibration, the analyst should analyze a reagent blank (instrument blank) to demonstrate that interferences from the analytical system are under control.

8.1.4 With each sample batch, the analyst must analyze a method blank to demonstrate that interferences from sample extraction are under control. Target compounds' concentrations in the blank should be no more than 5x MDL. If blank levels for any component are above 5x MDL and the sample concentrations present in the samples are greater than 10X then the samples may be quantified and qualified. If the blank concentration is greater than 5X MDL and the sample concentrations present in the samples are less than 10 X the blank level, the affected samples should be re-extracted and re-analyzed. If a sample cannot be re-extracted or re-analyzed, the data should be qualified as such. Samples should not be blank corrected.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.3. The frequency of the check standard analyses is equivalent to 5% of all samples analyzed.

8.1.6 The laboratory must spike all samples with the surrogates to monitor recovery. This procedure is described in Section 8.4.

8.1.7 The laboratory must spike a minimum of five percent or one per batch, which ever is more frequent of all samples in each matrix, with the MSS (Section 6.8.5) to monitor and evaluate laboratory data quality. This procedure is described in Section 8.5.

8.2 To establish the ability to generate acceptable precision and accuracy, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing fuel oil #2 at a concentration of 30 mg/ml in methylene chloride (Section 6.8.4). The QC check sample concentrates must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Aqueous

Analyze four 1 L aliquots (TPHC) of the well-mixed reagent water spiked with 0. 5 mL QC check sample concentrate and 20 uL of each surrogate according to the method beginning in Section 10.1.

8.2.3 Soil and Sediment

a. Prepare a TPHC QC check sample to contain 200 ug/g of a reference oil (6.8.2) by adding 0.2 mL of QC standard concentrate to 30g of reagent sodium sulfate (6.4). Also add the appropriate surrogates.

b. Analyze four aliquots of silica spiked with QC check standard concentrate according to the method beginning in section 10.3.

8.2.4 For each matrix calculate the average recovery (X) and the standard deviation of the recovery (s) for #2 fuel, using the four results. The average percent recovery should be between 70-120%. samples. The laboratory is to establish the criteria for the standard deviations as described in USEPA Method 8000 A (4).

8.2.5 The FID retention times of the surrogates and internal standards must match the calibration standard as described in 7.2.3.

8.3 The laboratory must analyze a Total Petroleum Hydrocarbon (TPHC) QC check sample with every 5% of the samples. The check sample shall be prepared as directed in Section 8.2.1. The recovery of TPHC shall be in ranges specified in Section 8.2. The FID retention times of the surrogates and internal standards must match the previous calibration as described in 7.2.3.

8.4 As a quality control check, the laboratory must spike all samples with the surrogates chosen in Section 6.8.3 and calculate the percent recovery (P) of the Surrogate based on the FID response.

$$\%P = \frac{A_x}{A_s} \times 100$$

A_x = Area response of SS or IS in check sample

A_s = Average area response of SS or IS in standard

8.4.1 For the surrogate standards, the laboratory must develop separate accuracy statements of laboratory performance for each matrix. An accuracy statement for the method is defined as Percent Recovery $\pm$ Standard Deviation ($P \pm s$). The accuracy statement should be developed by the analysis of four aliquots as described in Section 8.2, followed by the calculation of P and s. Alternatively, the

analyst may use four data points gathered through the requirement for continuing quality control in Section 8.3. The accuracy statements should be updated regularly. The initial recovery may be set 60 to 120 percent.

8.4.2 Calculate upper and lower control limits for %P for the surrogate standard in each matrix.

Upper Control Limit (UCL) = P +3s
Lower Control Limit (LCL) = P - 3s

The UCL and LCL can be used to construct control charts that are useful in observing trends in performance (14).

8.4.3 The following corrective actions can be taken when the percent recovery of chlorobenzene, androstane and/or tetracosane-d50 are outside of the recovery range:

8.4.3.1 Check calculations to assure there are no errors.

8.4.3.2 Check instrument performance, check the sample preparation procedure for loses due to temperture control and internal standard and surrogate solutions for degradation contamination, etc.

8.4.3.3 Reanalyze the sample or extract if the steps above fail to reveal a problem. If reanalysis yields surrogate recoveries within the stated limites, the reanaysis data should be used.

8.4.3.4 If the surrogate could not be measured because the sample was diluted prior to analysis, qualify the surrogate recovery. If the surrogate co-elutes with a compound (as in coal tar), report only the recovery of the backup surrogate tetracosane-d50. Qualify the out of range surrogate on the data table. No additional corrective action is required.

8.5 Matrix Spike Analysis - The laboratory must, on an ongoing basis, spike (MS) and analyze at least 5% of the samples for each matrix from each sample site being monitored to assess accuracy. The spike should be the matrix spiking standard (MSS) (Section 6.8.5).

8.5.1 Report the recovery as the average of the individual recoveries of the components nC8-nC40, if the hydrocarbon standard is used.

8.5.2 The laboratory should establish there own acceptance criteria for % recovery (R) as in Section 8.2.4. Recoveries of > 70% should be achieved.

8.6 Sample Duplicate - The laboratory must, on an ongoing basis, analyze 5% of the samples for each matrix in duplicate. Both results are to be reported. (No specific criteria concerning the relative precent difference (RPD) exists at this time. However, results should not differ by more than 50%.) The laboratory should establish their own acceptance creteria for RPD based on control charts. A matrix spike duplicate may be used if no postive TPHC samples are in the batch.

8.7 Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

8.8 The laboratory shall determine the method detection limits (MDLs) for the fuels of interest using the methods of 40 CFR 136 Appendix B (7). The MDLs must be confirmed weekly by analyzing a low level standard (2x MDL).

9.0 SAMPLE COLLECTION PRESERVATION

9.1 Aqueous Matrix

9.1.1 Collect a representative water sample in a 1L narrow mouth bottle. A delay between sampling and analysis of greater than four hours requires sample preservation by the addition of 5ml HCl (Section 6.7). Confirmation of a pH < 2 must be obtained in the field.

9.1.2 Sample must be chilled to 4+/-2°C on the day of collection and stored at 4+/-2°C until analyzed.

9.1.3 Samples must be extracted within seven days from the time of collection or five days from verified sample time of receipt (VSTR). Extracts must be analyzed within 40 days of extraction.

9.2 Solid Matrix

9.2.1 Collect a representative soil-sediment sample in a four-ounce, wide-mouth jar with a minimum of air space.

9.2.2 Samples must be chilled at 4+/-2°C on the day of collection and stored at 4+/-2°C until analyzed.

9.2.3 Samples must be extracted within seven days from the time of collection or five days from VSTR. Extracts must be analyzed within 40 days of extraction.

10.0 PROCEDURES

10.1 Dissolved Product

10.1.1 Sealed Extraction (14)

a. Mark the liquid level on the outside of the one liter bottle. Check the sample for floating product. Measure/adjust pH to 2 with 6N HCl if necessary.

b. Add a two inch teflon stirring bar, 30 ul of surrogate standards (Section 6.8.3), and 30 mL of methylene chloride. Seal the sample bottle.

c. Place the bottle on a magnetic stirrer. Adjust the speed so that there is a vortex. Stir for five minutes and then release any pressure. Continue stirring for 15 minutes.

d. Transfer the methylene chloride extract to a serum bottle for storage using a Pasteur pipet. Add 30 mL of methylene chloride to the sample bottle, seal, return to the magnetic stirrer and stir for twenty minutes. Fill the empty sample bottle to the mark with water. Determine the sample volume in a liter graduated cylinder.

e. Combine the methylene chloride extracts, filter and dry the extract through glass wool and sodium sulfate. Adjust the extract volume to 50 mL in a volumetric flask. Store the extract in a 100 mL crimp top serum bottle at 4°C.

f. Emulsions

1. Emulsions can be broken by centrification

2. Continuous extraction can be used on samples known to form emulsions, USEPA Method 3520 (4).

g. Screen the extract before concentrating (Section 10.4). Dry and Concentrate the extract as in section 10.1.2.e through 10.1.2i.

10.1.2 Separatory Funnel Extraction (7)

a. Aqueous samples are usually extracted using separatory funnel techniques. If emulsions prevent achieving acceptable solvent recovery

with separatory funnel extraction, continuous extraction (Section 10.1.2) may be used. The separatory funnel extraction scheme described below assumes a sample volume of 1 L. When a sample volume of 2 L is to be extracted, use 250, 100 and 100-mL volumes of methylene chloride for the serial extraction.

b. Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2 L separatory funnel. Measure/adjust pH to 2 with 6N HCL. Pipet 30 uL of the surrogate standard spiking solution into the separatory funnel and mix well (Section 6.8.3).

c. Add 60 mL of methylene chloride to the sample bottle, seal and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for two minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min.

If the analyst must employ mechanical techniques to the complete phase separation, the optimum technique depends upon the sample. The techniques may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250 mL Erlenmeyer flask with a glass stopper.

If the emulsion cannot be broken (recovery of less than 80% of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the extract to the chamber of a continuous extractor and proceed as described in Section 10.2.3.

d. Add a second 60 mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Label the combined extract. Screen the extract (Section 10.4) before concentrating.

e. Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D concentrator if the requirements of Section 8.2 are met.

f. Pour the combined extract through a solvent rinsed drying column (Section 5.3.10) containing about 10 cm of anhydrous sodium sulfate, and

collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

g. Add one or two clean boiling chips and attach a three-ball Snyder column to the evaporative flask for each fraction. Prewet each Snyder column by adding about 1 mL of methylene chloride to the top. Position the K-D apparatus in a hot water bath (60°C to 65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of the distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with one to two mL of methylene chloride. A five mL syringe is recommended for this operation.

h. Add another one or two clean boiling chips to the concentrator tube of each fraction and attach a two ball micro Snyder column. Prewet the Snyder column by adding about 0. 5 mL of methylene chloride to the top. Place the KD apparatus on a hot water bath and allow it to drain and cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with approximately 0.2 mL of methylene chloride. Adjust the final volume to 1.0 mL with the solvent. Transfer to a 1 ml GC autosampler vial and add 20 uL of the GC internal standard (5-androstane). If the internal standard method is used.

i. Determine the original sample volume by refilling the sample bottle to the mark with water and transferring the liquid to a 1000 mL graduated cylinder. Record sample volume to the nearest five mL.

j. Other extract concentation methods can be used if the recoveies of the surrogates and the QC check samples meet the requirements of the method.

10.2.3 Continuous Extraction (4)

a. Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Transfer the sample to the continuous

extractor. Measure/adjust pH to 2 with 6N HCl. Using a pipet, add 30uL of surrogate standard spiking solution and mix well. Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the extractor.

b. Repeat the sample bottle rinse with an additional 50 to 100 mL portion of methylene chloride and add the rinse to the extractor.

c. Add 200 to 500 mL of methylene chloride to the distilling flask, and sufficient reagent water to ensure proper operation, and extract for 24 hours. Allow to cool, then detach the distilling flask. Screen the extract (Section 10.4) before concentrating. Dry and concentrate the extract as in section 10.1.2.e through 10.1.2.i.

10.3 Sample preparation, soils and sediments (1,12)

10.3.1 Homogenize the soil sample with a solvent-rinsed stainless steel spatula. Weigh about five grams of the sample to +.01g into a tared aluminum pan. Dry at 105 degrees Celsius for 12 hours and calculate the percent solids content (Section 11.3.4).

10.3.2 Soxhlet Extraction - If the samples contain residual oil and tar, the EPA soxhlet extraction method 3540 should be used (2). Method 3540 may be used for all sample types.

a. Quickly blend 10-30g of the solid sample with 10-30g of anhydrous sodium sulfate and place in an extraction thimble. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the Soxhlet extractor is an acceptable alternative for the thimble. Add 30uL of the surrogate standard spiking solution onto the sample. The blending of the soil with the anhydrous sodium sulfate can lead to the loss of volitile components (C8-C12). If the sample is expected of containing a large volitle component such as Jet fuel, this drying process may be omitted.

b. Place 300 mL of the extraction solvent into a 500-mL round-botton flask containing one or two clean boiling chips. Attach the flask to the extractor and extract sample for 16-24 hours at 4-6 cycles/hr.

c. Allow the extract to cool after the extraction is complete. Screen the extract before continuing (Section 10.4). Dry and conceutrate the extract as in Section 10.1.2e through 10.12h.

10.3.3 Gyrotory Shaker Extraction

a. Add 30g (+/- .1 g) (wet weight) of the sample with a stainless steel spatula to a 250 mL acid-cleaned, solvent-rinsed, capped Erlenmeyer flask. Mix in 30 g of sodium sulfate. If the sample has excessive moisture, add additional amounts of sodium sulfate. This procedure must be done quickly to reduce evaporation losses.

b. Add 50 mL of methylene chloride, 30 uL of surrogate standard spiking solution, screw on the top, and shake the mixture vigorously for 1 minute, vent the flask (Section 6.8.3).

c. Place the 250 mL flask on a rotary shaker unit, positioned behind a safety shield, in a fume hood. Adjust the agitation rate of the shaker device to 400 RPM and extract the samples under these conditions for exactly 30 minutes.

d. After 30 minutes, the rotary shaker should be turned off and Erlenmeyer flasks removed to a stationary location. The analyst should permit suspended solids and particulate matter in the flasks to settle for approximately 30 minutes.

e. Using a pasteur pipet, carefully transfer the supernatant extract to a 100 mL crimp top serum bottle for storage. Do not agitate the sediment layer.

f. Extract the sample with two additional 30mL volumes of methylene chloride. The sample should be sonicated for 0.5 minutes before the last extraction. This will insure the complete dispersion of the soil. Combine all of the extracts, in the serum bottle for storage. Screen the extract before continuing (Section 10.4). Dry and concentrate the extract as in section 10.1.2e through 10.1.2.h.

10.3.5 Other Extraction Methods

a. Extraction methods listed in SW846 may be used such as 3545 Pressurized Fluid Extraction, 3541 Automated Soxhlet Extraction and 3550 Sonication.

b. The laboratory must conduct a one time demonstration of the ability to

generate acceptable accuracy and precision (Sectin 8.2). The demonstration must include comparison results with real samples that cover the C8-C40 carbon range. The laboratory must meet the sensitivity

requirements of Section 2.3.3, the dynamic range of section 2.3.4, and the surrogate recovers of section 8.4.1.

c. Routine analysis using alternate extraction methods must meet the surrogate reqiurements of section 8.4.1.

10.4 Preliminary Analysis of Extracts (Screening)

10.4.1 Adjust the chromatograph for maximum sensitivity.

10.4.2 Inject 1 uL of the sample extract using an auto sampler.

10.4.3 A complete profile of the extract should be obtained without saturating the detectors. The largest peak should be a minimum of 50% and a maximum of 90% full span. If the response is too high, the extract should be diluted. if the response is too low, concentrate the extract. If the response meets the criteria, determine the extract volume and go to section 10.5 or 10.6.

10.5 Cleanup for Quantitation (4)

10.5.1 Should the sample require additional cleanup due to interfering compounds, polar compounds or a large unresolved hump without destinct peaks, in the chromatogram, use EPA Method 3630 - silica gel cleanup. Combine fraction 1 (pentane; aliphatics) and fraction 2 (methylene chloride/pentane [2: 3 v/v] aromatics) for total petroleum hydrocarbons (TPHC) analysis.

10.6 Chromatographic Analysis

10.6.1 One milliliter of extract ready for analysis should be transferred to a one mL GC auto sampler vial.

10.6.2 All extracts, standards and blanks, should contain the GC internal standard (30 ug/L) when applicable.

10.6.3 Inject one to two uL of extract using an autosampler device or the solvent plug method.

10.7 Recommended Chromatographic Conditions (21)

10.7.1 Temperature Program for RTX-1 Column:

Initial Value	40°C
Initial Time	2.00 min

Program Rate	12.00°C/min
Final Value	320°C
Final Time	10 min
Total Run Time	35 min
Carrier Gas	He

10.7.2 Injection Port Temperature 330°C

10.7.3 Detector Temperature 330°C

10.7.4 Instrument Performance

a. All of the peaks contained in the standard chromatograms must be sharp and symmetrical. Peak tailing must be corrected. If only the compounds eluting before ethylbenzene give random response, have unusually wide peak width, are poorly resolved, or are missing, the problem is usually traceable to the injection port temperature.

b. Check the precision between consecutive QC check samples. A properly operating system should perform with an average relative standard deviation of less than 10%. Poor precision is generally traceable to pneumatic leaks.

c. Monitor the retention time for each analyte using data generated from calibration standards. If individual retention times vary by more than ±3 standard deviations (7.1.1) over a twelve hour period, the source of retention data variance must be corrected before acceptable data can be generated.

d. The instrument sensitivity must be maximized. Injection of 2ul of a 1ng/ul hydrocarbon standard should yield a detector signal-to-noise ratio of between 5:1 and 15:1 for the individual alkanes.

10.8 Analysis Sequence

10.8.1 This method uses a 12hr clock. The time sequence begins with the analysis of the first initial calibration standard. Continuing calibrations must be verified every 12hrs.

10.8.2 Sequence

1. Instrument Blank
2. Initial Calibration

3. Samples (including Method Blanks, and QC samples)
4. Continuing Calibration (every 12hrs.)

11.0 CALCULATIONS

11.1 Concentration of Petroleum Hydrocarbons

11.1.1 To calculate the concentration of total petroleum hydrocarbons in the sample, the area response attributed to the petroleum must first be determined. This area includes all of the resolved peaks and the unresolved "envelope". This total area must be adjusted to remove area response of the internal standards, solvent, surrogates and the GC column bleed.

11.1.2 Establishing the baseline

a. Column bleed is defined as the reproducible baseline shift that occurs during temperature programming of the GC column oven. To determine this area, a methylene chloride blank injection should be analyzed at the beginning of the day and after every 12 hours to determine the baseline response. The baseline is then set at a stable reproducible point just before the solvent peak. This baseline should be extended horizontally to the end of the run. The area for the blank run that must be subtracted from the actual sample run, includes all of the area between C_8 and C_{40}.

Baseline response within ± 20%

b. The baseline for the sample should be set in the same manner. The area in the sample will contain the area attributed to petroleum and that attributable to the baseline. The petroleum area must be calculated by subtracting the baseline area and area for the standards from the total area. The TPHC is then calculated according to the equation in Section 11.1.4.

c. As the concentration of TPHC in the sample approaches the detection limit, the baseline correction becomes more critical.

11.1.3. Mass discrimination must be kept to a minimum by placing a small plug of silanized glass wool one cm from the base of the glass injection liner. The capillary column should be placed just below the glass wool. A full range alkane standard should be run to test the degree a mass discrimination before performing any actual sample analyses. The reponse factor ratio of C_{32}/C_{20} should be greater than 0.8. If less than 0.8, reposition the column in the glass liner until the mass discrimination is minimized.

11.1.4 Concentration based on Internal Standard

RRT variation - Initial or CCC

a. From sample analysis, determine the total area (A) of the unknown and calculate the concentration. The analyst must take care when calculating total product areas that the appropriate baseline is used.

(1) Aqueous Matrix

$$C = \frac{(A)\ (C_{is})\ (D)\ (Ve)}{(RRF)\ (A_{is})\ (V_o)\ (Vi)}$$

Where:

C = Concentration of Analyte or concentration of Total Petroleum Products, ug/L

A = Area response of compound or TPH to be measured.

D = Dilution Factor

C_{is} = Concentration of internal standard added to extract

A_{is} = Area response of internal standard

RRF = Relative response factor of analyte (section 11. 2.2). For TPHC RRF is the average of all the nC8-nC40 RRFs.

V_e = Final volume of extract, uL

V_i = Volume of extract injected, uL

V_o = Volume of sample, L

(2) Soil and Sediment

$$C = \frac{(A)\ (C_{is})\ (D)\quad Ve}{(RRF)\ (S)\ (A_{is})\ \ Vi}$$

C = Concentration of compound to be measured, or Concentration of TPHC, ug/g

S = Dry sample weight, grams

11.2 The FID Relative Response Factor (RRF) calculation for a specific compound or TPHC.

$$RRF = \frac{C_{is} \times A_{cs}}{A_{is} \times C_{cs}}$$

Where:

C_{cs} = Concentration of calibration compound or TPHC standard, ug/ml

C_{is} = Concentration of internal standard, 5-androstane, ug/ml

A_{is} = Area Response of internal standard

C_{cs} = Area of calibration compound or TPHC standard

11.3 External standard calibration - The concentration of each analyte in the sample may be determined by calculating the amount of analyte injected, from the peak response, using the calibration curve or the calibration factor determined in Step 7.1.3. The concentration of a specific analyte is calculated as follows:

(1) Aqueous samples

$$\text{Concentration (ug/L)} = \frac{(A)\,(D)\,(Vc)}{RF\,(V_o)\,(Vi)}$$

RF = Response factor of analyte (Section 7.1.2) or TPHC average response of all th nC8 - nC40 RFs.

(2) Nonaqueous

$$\text{Concentration (ug/g)} = \frac{(A)\,(D)\,(Vc)}{RF\,(s)\,(Vi)}$$

11.4 Matching Chromatographic Patterns - The following provides the basis for identification of the type of petroleum product. Method OQA-QAM-018 should be used to make more definative identifications.

11.4.1 Interpretation (from ASTM D 3328, (1))

a. Basis of Matching - The source of a spilled petroleum oil can be identified by comparison of the chromatogram to that of a suspected source oil or

that of a reference oil. Identical petroleum products give identical chromatographic peak patterns.

b. Chromatogram Features - The major features of the chromatogram that are used for comparison are listed as follows:

A FID chromatogram shows the features of a homologous series of normal paraffins, the isoprenoid hydrocarbons pristine and phytane, the other resolved peaks and the unresolved envelope. All of these features are used to characterize petroleum oil.

c. Weathering effects: - When petroleum is spilled on open water or spilled on open ground, weathering will progress rapidly. A thin slick on open water may lose significant amounts of its components, up to uC15, 271°C, atmospheric boiling point, within 48 hours of being spilled. Soil samples will lose the soluble fraction through leaching. Biological degradation of petroleum begins within seven days. It is important to be aware of the effects of weathering when matching chromatograms of spill samples more than a few hours old. It is advisable to compare only those portions of chromatograms boiling above pentadecane in order to minimize the difference resulting from weathering. Reference oils can be weathered in the laboratory using the method of Reference 10.

Light distillate fuels cannot survive heavy weathering and have few hydrocarbons above C15. Comparison of the residues of these oils can only be done qualitatively - from about C8-C15.

d. A direct comparison of chromatograms will establish identity or nonidentity between samples. The comparison involves a peak-for- peak matching, noting differences or similarities in relative peak height. If the chromatograms are the same on the basis of the peak-for-peak matching, there is a high probability that the samples are from the same source. A mismatch occurs when the chromatograms are different. The differences may be due to the presence of one or more components or petroleum products in one sample relative to another. Spill samples may contain components such as cleaning detergents, plasticizer, paint vehicles, etc. The presence of one or two components in a spill sample which are absent in a suspect petroleum oil is not absolutely indicative of non-identity.

e. If the ratio of pristine/phytane in the unknown and reference petroleum oil match with $\pm$ 15%, the fingerprint match is confirmed.

11.5 Percent Recovery of Surrogate Standard (5)

Percent recovery is calculated using the 5-androstane GC internal standard, (C_{is}).

$$\% \text{ SS recovery} = \frac{(A_{ot})(C_{is}) \quad x\ 100}{(C_{ot})(A_{is})}$$

Where: C_{ot} = Concentration of surrogate

A_{ot} = Area of surrogate

SS = Surrogate

Percent recovery based on External Calibration

$$\% \text{ SS recovery} = \frac{C_{of}}{C_{ot}} \quad x\ 100$$

Where: C_{of} = Concentration of surrogate found

11.6 Percent Solids (P)

$$P = \frac{D_s}{T_s} \quad x\ 100$$

D_s = Weight dry Sample, g

T_s = Weight wet Sample, g

11.7 Dry Weight (S)

$$S = \frac{\text{Wet Weight x P}}{100}$$

12.0 REPORTING REQUIREMENTS AND DELIVERABLES

The following minimal information must be provided to the Department on request. The Laboratory must keep this information on file and available for inspection by the Department as per N.J.A.C. 7:18 (16).

12.1 Chain of custody documents. For every sample submitted to the laboratory, both field and laboratory chain of custody documents MUST be provided at the end of the final data report. The chain of custody must show the signatures of the sample custodian, extraction supervisors and any other personnel who handled the sample. It must clearly track the movement of the sample through the laboratory by showing the relinquishing and acceptance of the sample by each person.

12.2 Methodology Review

The laboratory shall provide a brief narrative outlining the essential points of each method actually employed in the analysis of the samples submitted to the laboratory.

12.3 Non-Conformance Summary Report

The laboratory shall describe in narrative and/or tabular from any item which does not conform to the requirements of this method. This shall include but is not limited to a discussion of missed holding times, of failed Quality Assurance/Quality Control criteria, sample matrix effects on the analysis, sample dilutions, re-analyses, corrective actions taken and deviations from the analytical method specified on the analytical request form or the preparative methods permitted.

12.4 Sample Data Package - must contain the following information in sequence:

12.4.1 Quantitative Sample Results Summary (uncorrected for blank), Blank Results and Method Detection Limits.

12.4.2 Qualative Sample Result Summary (For fingerprint work)

12.4.3 Quantitation Reports

12.4.4 Sample Chromatograms

The chromatograms must be clearly labeled with the following information:

a. Sample identification number.
b. Volume injected.
c. Date and time of injection.
d. GC Column identification.
e. GC instrument identification - exact instrument employed.
f. Positively identified compounds, either directly above the peak or on a printout of retention times, if the retention times are printed on chromatograms.
g. Internal Standards labeled.

h. Surrogate labeled.
i. Analyst signature.

12.5 Quality Control Summary - must contain the following items:

a. Surrogate Recovery Summary
b. QC Check Sample Recovery
c. Method Blank Summary
d. Matrix Spike Summary
e. Duplicate Summary

12.6 Standard Data Packages - must contain the following items:

a. Initial Calibration Data Summary
b. Continuing Calibration Data Summary
c. Chromatograms of Standards and Quantitation Reports
d. Chromatograms of Reference Standards where applicable

12.7 Raw QC Data Package - additionally must contain the following items:

a. Blank Chromatograms
b. QC Check Sample Chromatograms
c. Blank spike Chromatograms.

12.8 Qualitative Sample Results Summary - List Sample Fingerprint matches (ASTM D3328(I)).

a. Based upon the visual comparison of source chromatograms, and after considering weathering, report the sample of unknown origin as belonging to one of the categories below:

1. Match - The chromatogram is identical to one, or more, of the samples submitted for comparison.

2. Probable Match - The chromatogram is similar to one, or more, of the samples submitted for comparison, except: (a) for changes which can be attributed to weathering, or (b) differences attributable to specific contamination.

3. Indeterminate - The chromatogram is similar to one, or more, of the samples submitted for comparison, except for certain differences as in 2, of such magnitude that it is impossible to determine whether the

unknown is the same petroleum oil heavily weathered, or a totally different oil.

4. Mismatch - Unlike the samples submitted for comparison.

b. Compare unknowns to a library of the products listed in Section 1.1.

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Figure 1 - Calibration Standard 50 ug/Kg (C8-C42)

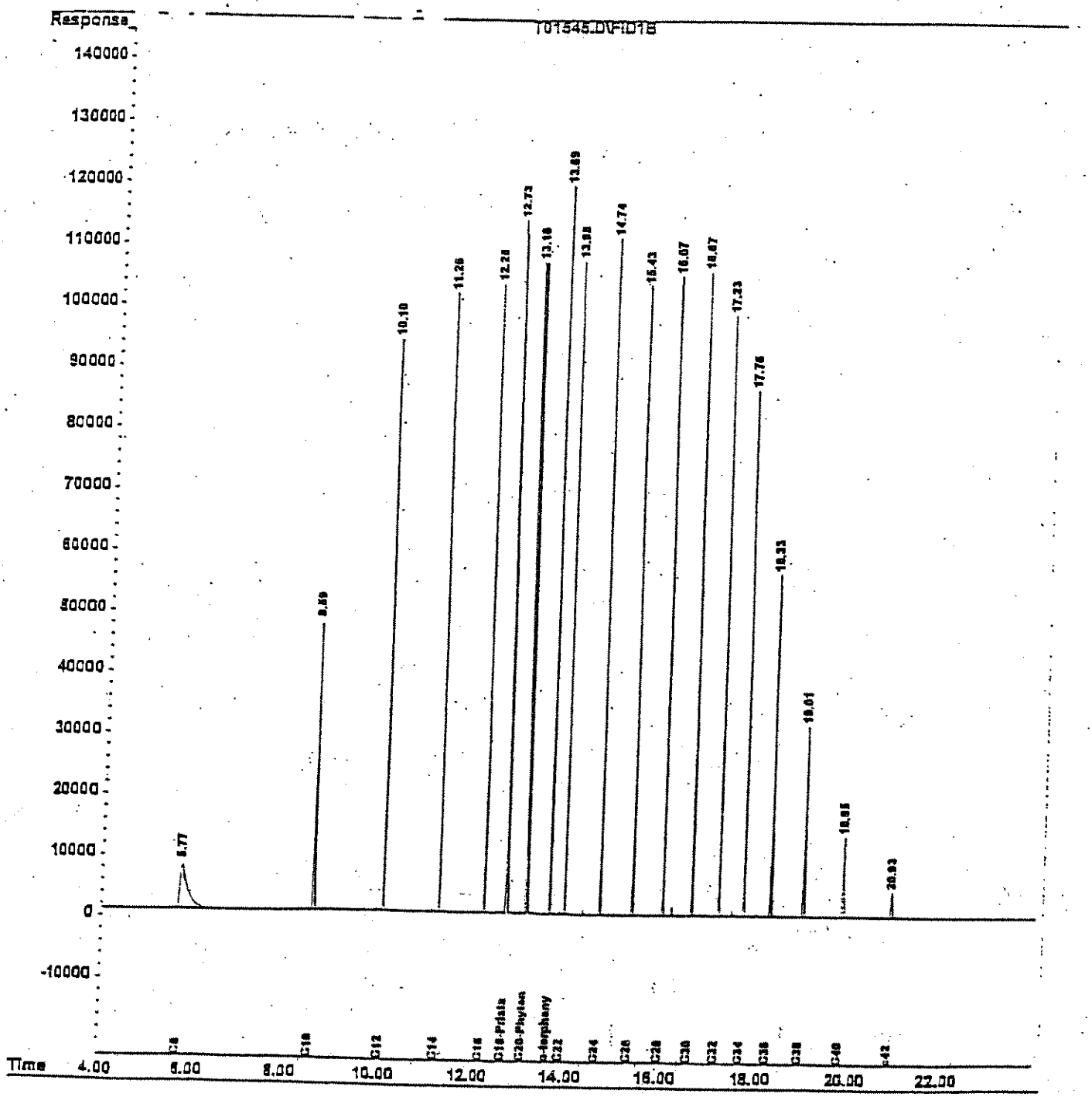


Figure 2 - MDL Study 250 ug/Kg in Soil

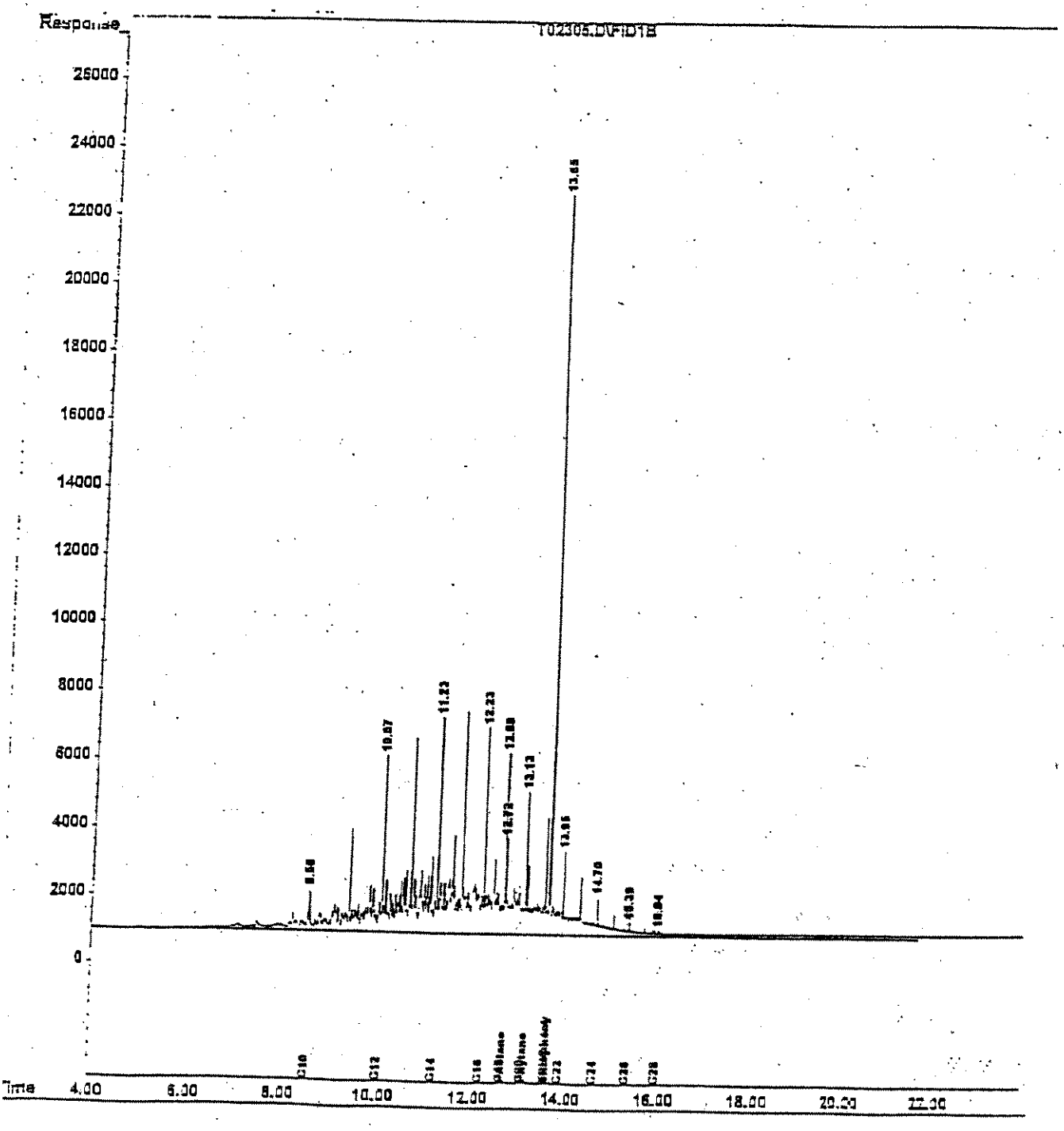


Figure 3 - Methylene Chloride Blank

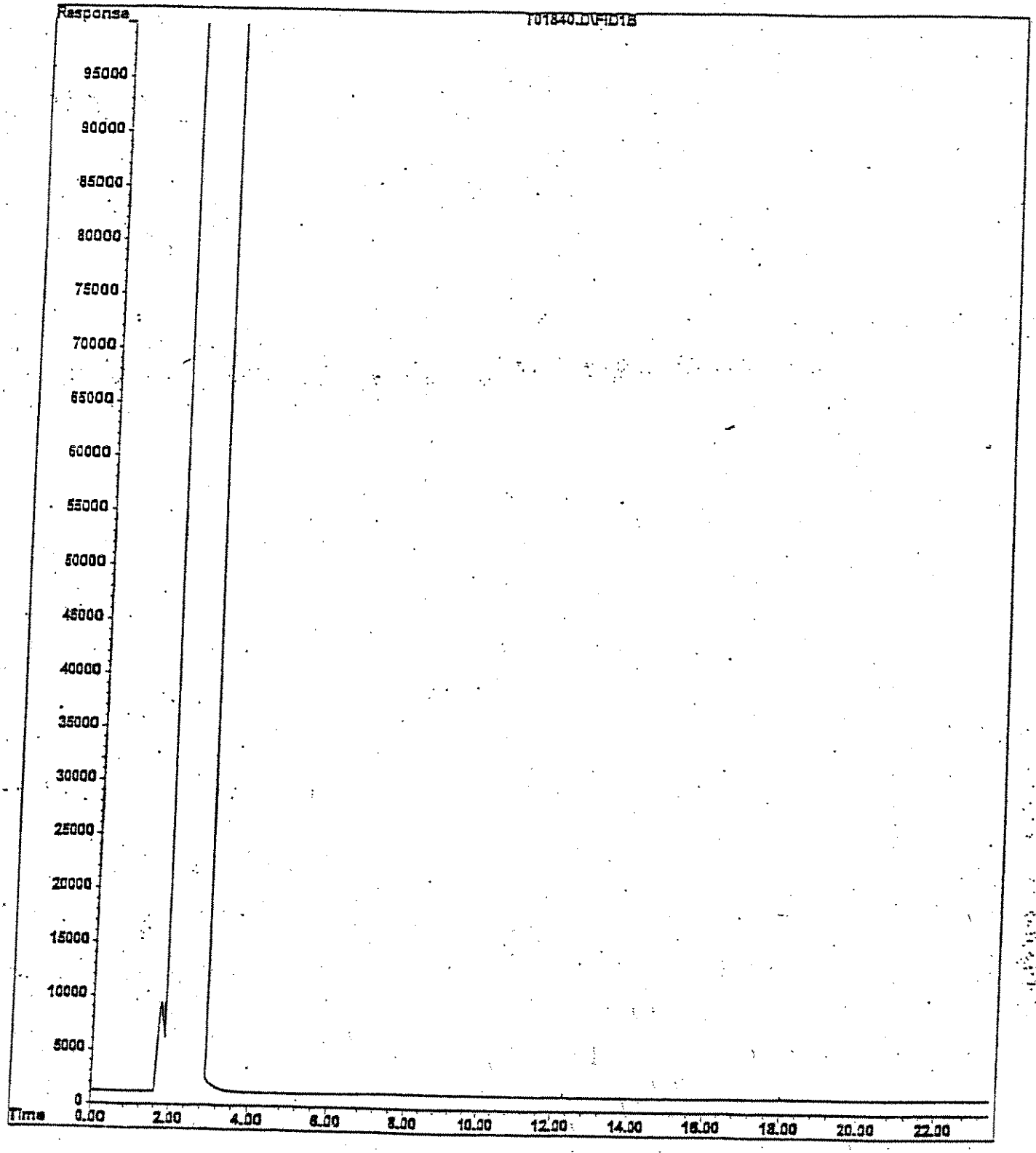
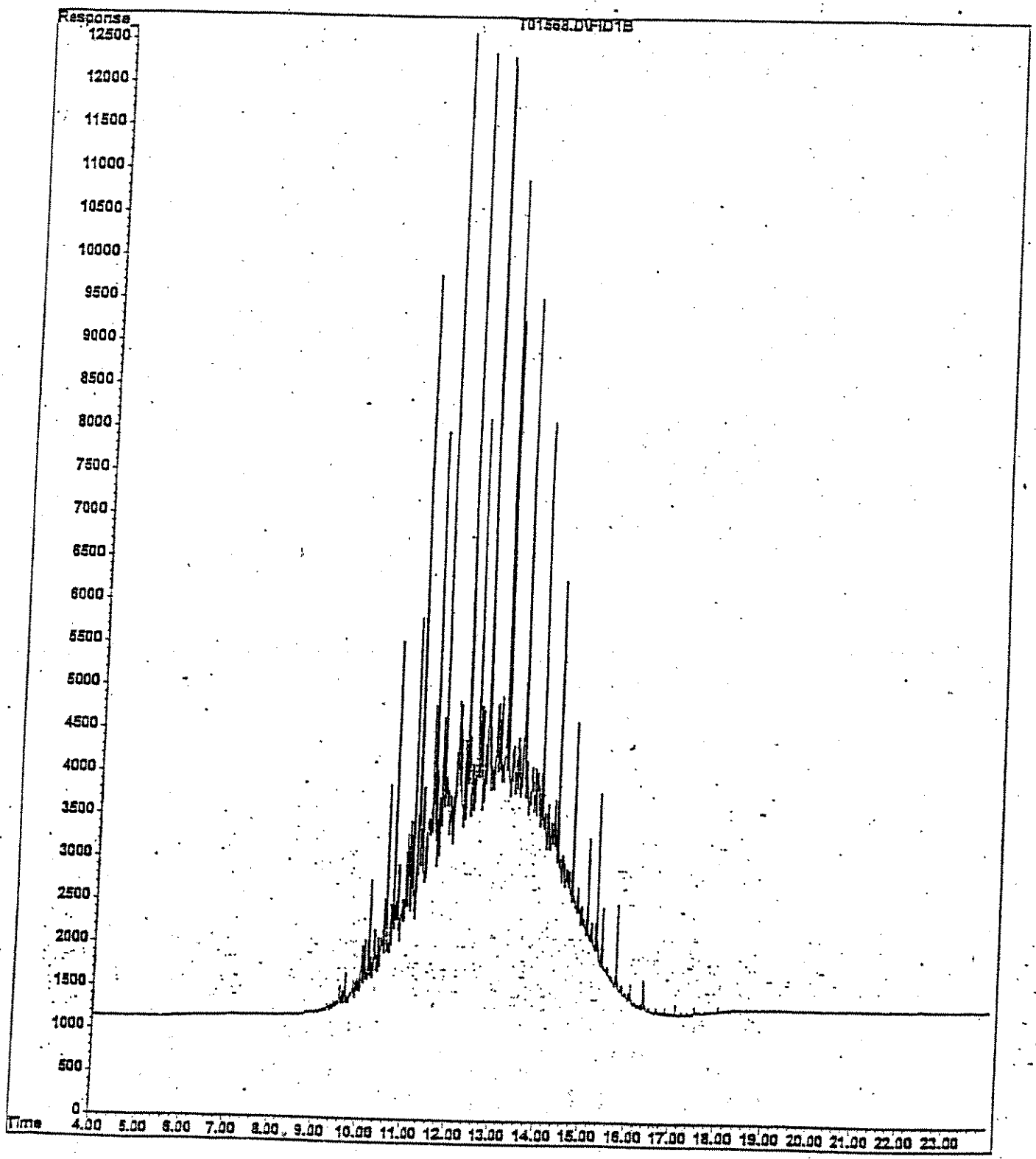


Figure 4 - Diesel Fuel #2 / Methylene Chloride Soxhlet Extraction



Analytical Methods

Organotins

STL SOPs:

LM-GC-ALKYLTINS REV. 7
LP-OP-3510-OR560
LP-OP-3550-OR560

STANDARD OPERATING PROCEDURE FOR ORGANO-TIN COMPOUNDS

Applicable Matrices: Water, Soil, Sediment, Waste, Tissue
Standard Compound List and Reporting Limits: See Table 1

APPROVAL SIGNATURES

Laboratory Director:	Michael F. Wheeler, Ph.D.	Date: 12/29/03
QA Manager:	Kirstin L. McCracken	Date: 12/29/03
GC Supervisor:	Jennifer L. Clements	Date: 12/29/03

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1.0 SCOPE AND APPLICATION

1.1 This SOP describes the laboratory procedure used to determine the concentration of alkyltins in aqueous, soil, sediment, waste and tissue extracts. This SOP is applicable to GC/FPD analysis only. The extraction and derivatization procedure are given in laboratory SOPs LM-OP-Alkyltins for aqueous and soil matrices.

1.2. The routine compound list, reporting limit, and accuracy and precision limits for each compound in aqueous and soil matrices is given in Table 1, Section 17.0.

2.0 SUMMARY OF METHOD

2.1. Samples are extracted with hexane/tropolone and are derivatized with a grignard reagent following the procedures given in the above referenced extraction SOPs. The tin chlorides are determined by gas chromatography with a flame photometric detector (GC/FPD) and the results are reported as tins.

2.2. This SOP is based on Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846) and NOAA Status and Trends.

3.0 DEFINITIONS

3.1 A list of terms and definitions is given in Appendix B.

4.0 INTERFERENCES

4.1 Method interference may be caused by contaminants in the extraction solvent. Solvents should be stored in an area away from organochlorine compounds to minimize contamination.

4.2. Matrix interferences may be caused by contaminants coextracted from the sample. The extent of the intereferences will vary considerably depending on the nature and diversity of the samples.

4.3. The hexyl magnesium bromide should be lot tested for contamination.

5.0 SAFETY

5.1 All laboratory employees shall be trained on and adhere to the safety policies and procedures that are given in the STL Corporate Safety Manual and in this SOP.

5.1.1. Safety Concerns or Requirements

The gas chromatograph contains zones that have elevated temperatures. The analyst should be aware of the locations of those zones, and should cool them to room temperature prior to working on the instrument. The GC also has areas of high voltage. Depending on the type of work involved, the instrument should be turned off or disconnected from its source of power prior to extensive maintenance.

5.1.2. Primary Materials Used

Table 2, Section 17.0 lists materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the MSDS. The table does not include all materials used in the procedure. A complete list of materials used can be found in section 7.0. Employees that perform this procedure must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Any questions regarding the safe handling of these materials should be directed to the laboratory's Environmental Health and Safety Coordinator.

6.0 EQUIPMENT AND SUPPLIES

6.1. Autosampler Vials

6.2 Class "A" volumetric flasks

6.3 Class "A" volumetric syringes (Hamilton) ±1% accuracy

6.4 Class "A" volumetric pipets or equivalent

6.5 Disposable glass pasteur-type pipets

6.6 Gas Chromatograph - An analytical system complete with a temperature programmable gas chromatograph equipped with a split/splitless or purge packed injection port, two flame photometric detectors, and an auto sampler.

6.7 Recommended Column: A dual fused silica capillary column system that will provide simultaneous primary and confirmation analyses.

- RTX-35 (30m x 0.32mm ID x 0.25 um)
- RTX-5 (30m x 0.32mm ID x 0.50 um)
- Equivalent columns may be used, provided the elution orders are documented and compound separations are maintained.

6.8 Dectector: Flame Photometric Detectors

6.9 Autosampler: Capable of making 2 uL injections.

6.10 Data System –Capable of handling a minimum of 200 chromatographic peaks per detector.

- Fison's Vax based Multichrom Version 2.0 or higher (Data Acquisition)

- Target Version 3.5 or higher (Processing & Report Generation)

7.0 REAGENTS AND STANDARDS

7.1. Solvents: Hexane, Acetone, Methylene Chloride. Store away from other solvents.

7.2. Stock standard solutions are purchased pre-certified from commercial vendors. Working standard solutions are prepared in the laboratory by dissolving a volume of standard solution in solvent and diluting to a specified volume. The recommended "recipes" for the standards used in this procedure are provided in Appendix A.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1 Sample extracts must be stored refrigerated at a temperature of 4°C (±2) until analysis.

8.2 The analytical holding time is 40 days from the date of extraction.

8.3 Unless otherwise specified by a federal, state or client specific requirement, extracts are stored from the time of receipt until 30 days after delivery of the reconciled data package report and then disposed of in a manner that complies with all applicable regulations.

9.0 QUALITY CONTROL

9.1 Method Blank (MB)

A method blank is analyzed per preparation batch of 20 or fewer samples. The concentration of target analyte in the MB must be less than or equal to the reporting limit. If a target analyte is found in the MB, the source of contamination is investigated and actions are taken to minimize or eliminate the problem. Samples processed with the contaminated method blank should be re-extracted and reanalyzed or data should be qualified if the concentration of target analyte in the blank is at or above the reporting limit and is greater than 1/10 the amount measured in any sample or if the blank contamination otherwise affected the sample results per the project data quality objectives. Unless otherwise noted in the sampling and analysis plan, for DOD work, the concentration of target analytes in the MB must be less than or equal to 1/2 RL except for common laboratory contaminants, which must be less than or equal to the RL.

9.2. Laboratory Control Sample (LCS)

A laboratory control sample is analyzed per preparation batch of 20 or fewer samples. The recovery of the LCS should be within the acceptance criteria given in Table 1. If the LCS recovery is not within limits, the problem should be investigated and corrected. The LCS and all samples in the associated batch should be re-extracted and reanalyzed or the data should be reported with appropriate data qualifiers.

9.3. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

Matrix spikes are used to assess the effect of the sample matrix on the precision and

accuracy of the method. The results of matrix spike are sample/matrix specific and are not used to determine validity of an entire analytical batch. The client should determine the frequency of the MS/MSD analysis on their project samples as part of their project data quality objectives. The minimum frequency recommended for matrix spike analysis is one MS/MSD per 20 project samples per matrix.

The recovery of the MS/MSD should be within the advisory limits given in Table 1, and the RPD between the MS and the MSD should be ≤30%. If the results are outside this range, the data should be qualified and reported or project data quality objectives should be used to determine appropriate corrective action.

9.4. Sample Duplicate

Sample duplicates are analyzed at the frequency specified by the client and they are used to provide the data user with information on the heterogeneity of the sample matrix or to determine the precision of intralaboratory analytical processes for the sample matrix. The RPD between the two portions of samples should be less than or ≤30%. If the results are outside this range, the data should be qualified and reported or project data quality objectives should be used to determine appropriate corrective action.

9.5. Surrogates

All field and QC samples are fortified with surrogate spike prior to extraction and surrogate spike is added to the calibration standards. The surrogate recovery should be within the acceptance criteria given in Table 1. If recovery is outside this range, the effect on individual sample results should be evaluated. QC and field samples should be re-extracted and reanalyzed for the failed surrogates if sufficient sample is available. If obvious chromatographic interference with the surrogate is present, reanalysis may not be necessary. Consult project specific data quality objectives to determine appropriate corrective action. Any results reported from analyses with surrogate recoveries outside acceptance criteria should be reported with appropriate data qualifiers.

9.6. Retention Time Windows (RT)

The laboratory uses default RT windows for each analyte and surrogate established by using the retention time for each analyte and surrogate from the mid-point standard (Level 4) of the initial calibration ± 0.05 RRT units. The retention time of the surrogate in the calibration standards are used to track retention time shifts and when the observed retention time of the surrogate is outside the established retention time window, the default RT window may be extended in the same direction as the retention time shift.

10.0 CALIBRATION AND STANDARDIZATION

10.1. Chromatographic Conditions & Pre-Calibration Routine

Attach a five-meter guard column to the injection port and the analytical columns (via a glass "y") then attach the analytical columns to the FPD's. Set the initial temperature to 100°C and hold for 3.0 minutes. Ramp 20°C per minute to 290°C and hold for 1.0 minute. Set the detector temperature to 290°C and the injection port temperature to

225°C. Use helium as the carrier gas. Set the helium flow to approximately 6.0-10.0 mL/min. The hydrogen flow and zero air flow should be optimized for optimum sensitivity but is generally set to approximately 175 mL/min total flow. Set the autosampler injection volume to 3uL.

10.2. Initial Calibration, Instrument Performance & Analytical Sequence

The instrument is calibrated using an internal standard (tetra-n-propyltin) calibration procedure with a minimum of five different concentrations for target analytes.

Analyze a hexane blank to verify that the system is free of contaminants. If contamination is found, investigate the source and correct prior to analysis of the calibration and retention time standards.

Prepare the mixed calibration standards using the procedure described in Appendix A. Analyze each calibration standard and using one of the following options, determine if the calibration is acceptable. If criteria are not met, correct the problem and repeat the initial calibration.

Option 1: Linear-Least Squares Regression (Preferred Method)

Calculate the correlation coefficient. If r is $\geq$ 0.995 or (r^2) is $\geq$ 0.990 for the curve is considered acceptable.

Option 2: Response Factor

Calculate %RSD of the instrument response against the concentration of the calibration standard for each target analyte. If the %RSD is $\leq$ 20 % for each analyte, the curve is considered acceptable.

10.3. Initial Calibration Verification (ICV)

Immediately following initial calibration, analyze the second source calibration verification standard (ICV) standard. The recovery of the ICV should be within ±25% of its expected value. If it is not, the problem should be investigated and corrected prior to further analysis. Recommended corrective actions are provided in Table 3, Section 17.0.

10.4. Continuing Calibration Verification (CCV)

Analyze a CCV daily before sample analysis, after every 10 field samples and at the end of the analysis sequence. All analytes should be within ±25%D of the expected value. If the CCV is not within criteria, correct the problem and reanalyze. If repeat failure, correct the problem and verify performance with two consecutive CCVs that pass criteria or repeat the initial calibration. If a CCV exhibits a high response (> 25%D) and the analyte is not detected in the samples, then the verification standard has demonstrated that the analyte would have been detected if present and reanalysis of samples is not necessary.

11.0 PROCEDURE

11.1 GC Analysis

All calibration standards and samples are spiked with Internal Standard (Tetra-n-propyltin) before analysis. Samples are analyzed in an analytical sequence that begins with instrument calibration or a daily CCV followed by analysis of sample extracts. Samples are analyzed with the same instrument operating conditions that were used for initial calibration and must be bracketed by acceptable CCV and retention time criteria. The sequence ends when the CCV results indicate the calibration relationship is no longer valid.

An example analysis sequence that includes initial calibration is given below:

Instrument Blank
50 ppb Tin standard
100 ppb Tin standard
250 ppb Tin standard
500 ppb Tin standard
1000 ppb Tin standard
Instrument Blank
Tin ICV

10 Field Samples
250 ppb Tin standard
10 Field Samples
250 ppb Tin standard

Transfer the 100 uL of extract and 10 uL of Internal Standard (Tetra-n-propyltin) to an auto sampler vial and place the vials in the autosampler. Enter the sample ID's into the data acquisition program, start the analytical sequence and acquire the data.

11.2. Qualitative & Quantitative Analysis

Evaluate the resulting chromatograms and calculated sample concentrations. Evaluate the QC results against the performance standards given in Section 9.0 and perform corrective action as necessary. Dilute and reanalyze any samples whose concentration exceeds the range of the calibration. *Note: A summary of acceptance criteria for each QC item is provided in Table 3 Section 17.3 along with recommended corrective actions.*

Identify target analytes using the retention times established during initial calibration. Report quantitative results in appropriate units and significant figures and correct the results for sample volume, dilution factor and percent solids.

12.0. CALCULATIONS

12.1. Aqueous Sample Concentration

$$Concentration_{sample}\,(ug/L) = Amt_{extract}\,(ug/L) \times \frac{extract\ volume\ (L)}{sample\ volume\ (L)} \times df$$

Where:
df= dilution factor

12.2. Soil Sample Concentration

$$Concentration_{sample}\,(ug/Kg) = Amt_{extract}\,(ug/L) \times \frac{extract\ \ volume(L)}{sample\ \ volume(Kg)} \times \frac{100}{\%\ solid} \times df$$

Where:
df= dilution factor

12.3. Percent Recovery (%R) (LCS and CCV)

$$\%R = \frac{SR}{SA} * 100\%$$

Where:
SR= Sample Result
SA=Concentration of Spike Added

12.4. Percent Recovery (%R) (Matrix Spike)

$$MSRecovery(\%) = \frac{SSR - SR}{SA} * 100\%$$

Where:
SSR= Matrix Spike Result
SR= Sample Result
SA=Concentration of Spike Added

12.5. Precision (RPD)

$$\%RPD = \frac{|D_1 - D_2|}{\frac{D_1 + D_2}{2}} * 100$$

Where:
D1 = Sample result/Matrix spike result
D2 = Matrix duplicate result/Matrix spike duplicate result

13.0 DATA ASSESSMENT, CRITERIA & CORRECTIVE ACTION

13.1. Samples, standards and QC samples are reviewed against the performance criteria given in section 9.0 for Quality Control. If the results do not fall within the established limits or criteria, corrective action should be performed. If corrective action is not taken or unsuccessful, the situation should be documented and reported in the project narrative. Primary review of the data is performed by the analyst(s) that performed the procedure. Secondary review is performed by a senior analyst or a data review analyst. All data that does not meet established criteria must be flagged with the appropriate data qualifier and noted in the project narrative.

14.0 METHOD PERFORMANCE

14.1. An Initial Demonstration of Capability is required for each analyst before unsupervised performance of this method.

14.2. A Method Detection Limit (MDL) determination for each test method referenced in this SOP is performed following the procedure described in the reference method, 40CFR, Part 136, Appendix B and laboratory SOP LP-LB-009. The MDL is verified or repeated when a significant change to the method occurs. Significant changes include the use of alternate reagents or standard reference materials, new instrumentation or the use of alternate sample preparation procedures.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1. Where reasonably feasible, technological changes have been implemented to minimize the production of hazardous waste and minimize potential source of pollution to the environment.

15.2. Hazardous waste generated by this procedure is accumulated in satellite containers located in the work area. The satellite containers are labeled "Hazardous Waste" along with the type of waste category generated. Authorized personnel routinely transfer the contents of the satellite containers to the hazardous waste storage room for future disposal in accordance with Federal, State and Local regulations. The procedures for waste management are further given in laboratory SOP LP-LB-001 *Hazardous Waste.*

16.0 REFERENCES

16.1. Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846), Third Edition, September 1986, Final Update I, July 1992, Final Update IIA, August 1993, Final Update II, September 1994; Final Update IIB, January 1995; Final Update III, December 1996.

16.2. Sampling and Analytical Methods of the National Status and Trends Program, National Benthic Surveillance and Mussel Watch Projects 1984-1992, Vol. IV, NOAA Technical Memorandum, NOS ORCA 71.

17.0 TABLES, DIAGRAMS, FLOWCHARTS

Table 1: *Target Analyte List, Reporting Limits, Accuracy and Precision Limits*
Table 2*: Primary Materials Used*
Table 3: *QC Summary and Recommended Corrective Action*

Table 1: Routine Compound List, Reporting Limits and Precision & Accuracy Limits

Compound	Reporting Limit		Accuracy Limit (%R)		Precision %RPD
	Water (ug/L)	Soil (ug/Kg)	Water	Soil	
Tetrabutlytin	.050	1.7	30-150	30-160	≤30
Tributyltin	.045	1.5	30-150	30-160	≤30
Dibutyltin	.039	1.3	30-150	30-160	≤30
Monobutyltin	.031	1.0	0-48	0-48	≤30

The alkyltin chloride compounds are quantitated and reported as unsubstituted alkyltin compounds. The factors used to convert from the alkytin chloride to the alkytin are listed below.

Analyte	Conversion Factor	Report as
Tetrabutyltin	---	tetrabutyltin
tributyltin chloride	0.89	tributyltin
dibutyltin dichloride	0.77	dibutyltin
monobutyltin trichloride	0.62	monobutyltin
tripentyltin chloride (SS)	0.90	tripentyltin
tetrapropyltin (ISTD)	--	tetrapropyltin

Conversion Factors are determined from the following formula:

$$Conversion\ Factor = \frac{MWT - MWC}{MWT}$$

Where:
MWT= Total molecular weight of the analyte
MWC= Number of chlorides * molecular weight of chloride (molecular weight of chloride = 35.5)

Table 2: Primary Materials Used

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Sulfuric	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

Table 3: QC Summary, Acceptance Criteria and Recommended Corrective Action (Tins)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
ICAL	Initially prior to sample analysis, Repeat failure of CCV	Option 1: r≥ 0.995 Option 2: RSD ≤ 20% for each analyte	Correct Problem Recalibrate
Second Source ICV	Once after each ICAL	%R ± 25	Correct Problem, Remake Standards Recalibrate
RT Window Establishment	Once per ICAL	Center of RT window set at mid-point of ICAL	NA
RT Window Verification	Each CCV	Analytes within established RT window	Correct Problem Reanalyze all samples analyzed since last acceptable CCV If necessary, repeat ICAL and re-set RT window
CCV	Daily before sample analysis, after every 10 field samples and at the end of the analytical sequence	All analytes within ±25% of expected value **High Bias CCV with no detects in associated samples may be acceptable*	Correct Problem Reanalyze, Repeat Calibration Reanalyze samples since last passing CCV
Method Blank	One per prep batch of 20 or fewer samples	No analytes detected above RL DOD <1/2 RL	Correct Problem Reprep & reanalyze method blank and all associate samples
LCS	One per prep batch of 20 or fewer samples	%R within limits given in Table 1 or within limits specified by project *High Bias LCS with no detects in associated samples may be acceptable*	Correct Problem Reprep & reanalyze method blank and associate samples for failed analytes
MS/MSD	One pair per 20 samples	%R & RPD within limits given in Table 1 or within limits specified by project	Consult Project DQO's
Sample Duplicate	Per client request	RPD within limits given in Table 1 or within limits specified by project	Consult Project DQO's
Surrogate Spike	All field and QC samples	%R within limits given in Table 1 or within limits specified by project	Reprep & Reanalyze if sufficient sample available.
2nd Column Confirmation	All positive results	RPD≤ 25	Flag Results

Appendix A: Standard Preparation Tables

The standard preparation tables provided are accurate only when the specified concentrations and volumes are used. Any time the concentration or volume of any of the components change, the analyst must adjust the "recipe" accordingly. See laboratory SOP LP-LB-002 *Standard Preparation* for further guidance. All prepared standards must be labeled with the lot number, name of the standard, concentration, and the expiration date. The expiration date for the prepared standard is 6 months from the date or preparation or date of expiration of the parent standard(s), whichever is sooner.

All working calibration standards for this method are made by the organic prep department and derivatized before analysis.

Table Legend:

Cstock = Concentration of Parent Standard(s)
Vstock = Volume of Parent Standard
Vspike = Volume of Prepared Standard
Cspike =Theoretical Concentration of Prepared Standard

Parent Stock Standard(s)	***Cstock (ug/mL)***	***Vstock (uL)***	***Vspike (mL)***	***Cspike (ug/mL)***
Tetra-n-propyltin	2000	625	250	5.0

Appendix B: Terms & Definitions

Batch: environmental samples, which are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria.

Calibration Curve: the graphical relationship between the known values or a series of calibration standards and their instrument response.

Continuing Calibration Verification (CCV): a single or multi-parameter calibration standard used to verify the stability of the method over time. Usually from the same source as the calibration curve.

Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

Initial Calibration: Analysis of analytical standards for a series of different specified concentrations used to define the quantitative response, linearity and dynamic range of the instrument for target analytes.

Initial Calibration Verification (ICV): solution prepared from a separate source from that which is used to prepare the calibration curve.

Intermediate Standard: a solution made from one or more stock standards at a concentration between the stock and working standard. Intermediate standards may be certified stock standard solutions purchased from a vendor and are also known as secondary standards.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure.

Matrix Duplicate (MD): duplicate aliquot of a sample processed and analyzed independently; under the same laboratory conditions; also referred to as Sample Duplicate.

Matrix Spike (MS): a field sample to which a known amount of target analyte(s) is added.

Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).

Method Detection Limit (MDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific measurement system. The MDL is a statistical estimation at a specified confidence interval of

the concentration at which relative uncertainty is ±100%. The MDL represents a range where qualitative detection occurs. Quantitative results are not produced in this range.

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

Reporting Limit (RL): the level to which data is reported for a specific test method and/or sample. The RL must be minimally at or above the MDL.

Stock Standard: a solution made with one or more neat standards usually with a high concentration. Also known as a primary standard. Stock standards may be certified solutions purchased from a vendor.

STANDARD OPERATING PROCEDURE
SEPARATORY FUNNEL EXTRACTION FOR ALKYL TIN

Applicable Matrix: Non-Potable Water

APPROVAL SIGNATURES

Laboratory Director: Michael F. Wheeler, Ph.D. Date: 4/27/05

QA Manager: Kirstin L. McCracken Date: 04/27/05

Department Manager: Jon Zygmuntowicz Date: 4/27/05

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1.0 SCOPE AND APPLICATION

1.1. This SOP describes the laboratory procedure for isolating organic compounds from non-potable water samples in preparation for analysis by GC/ECD.

2.0 SUMMARY OF METHOD

2.1. A measured volume of sample, usually 1 L, is extracted at a pH of less than 2 with 0.05% tropolone-hexane using the separatory funnel extraction technique. The extract is concentrated using Kuderna-Danish (K-D) technique, derivitized, and exchanged into hexane in preparation for Florisil Cleanup. After cleanup, the extract is ready for analysis by GC following the procedures in laboratory SOP LP-GC-Alkyltins.

3.0 DEFINITIONS

3.1. Definitions are included in Appendix A.

4.0 INTERFERENCES

4.1. Method interference may be caused by contaminants in solvents, reagents, glassware and other sample processing equipment that can cause interference and/or elevated baselines in chromatography. All reagents and solvents used during this procedure should be reagent grade or high purity in order to minimize interference. All glassware must be cleaned in accordance with laboratory SOP LP-OP-Glass and rinsed with acetone prior to use.

5.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.

5.1 Specific Safety Concerns or Requirements

The use of separatory funnels to extract aqueous samples creates excessive pressure. Initial venting should be done immediately after the sample container has been sealed and inverted. Vent the funnel into the hood away from people and other samples. This is considered a high-risk activity, and a face shield should be worn over safety glasses or goggle when it is performed.

5.2 Primary Materials Used

Table 1, Section 17.0 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the MSDS. The table does not include all materials used in the procedure. A complete list of materials used can be found in section 7.0. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Any questions regarding

the safe handling of these materials should be directed to the laboratory's Environmental Health and Safety Coordinator.

6.0 EQUIPMENT AND SUPPLIES

6.1. Separatory funnel - 2 liter, with Teflon stopcock and stopper

6.2. Drying funnel - 75 mm Glass Funnel with Pyrex glass wool at bottom

6.3. Kuderna-Danish (K-D) apparatus:

- Concentrator tube - 10 mL, graduated (AMK KD-0015 or equivalent)
- Evaporation flask - 500 mL (AMK KD-0015 or equivalent). Attach to concentrator tube with clamps or equivalent.
- Snyder column - Three-ball macro (AMK KD-0018 or equivalent)
- Snyder column - Two-ball micro (AMK KD-0013 or equivalent)

6.4. Solvents vapor recovery system (Kontes K-545000-1006 or K-547300- 0000, Ace Glass 6614-30, or equivalent)

6.5. Boiling chips - Solvent-extracted, approximately 10/40 mesh (silicon carbide or equivalent).

6.6. Water bath - Heated, capable of temperature control ($\pm$ 5°C).

6.7. pH meter

6.8. Adjustable Power Pipette – volumetric range of 0.5 mL to 2.0 mL.

6.9. Graduated cylinder - 1 liter (Class A)

6.10. Fiberglass wool, 8 um.

6.11. Vials and caps: 1.8 and 16 mL with Teflon lined septa and screw caps

6.12. Wrist shaker

7.0 REAGENTS AND STANDARDS

7.1. Reagents

Reagent water: Milli-Q System

Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray,

Silica Gel / Florisil Cartridges, 21 g: Restek, cat # 24049 or equivalent.

Hydrochloric Acid (HCL): J.T. Baker, Cat# 9530-33

Hydrochloric acid solution (1:1 v/v): Slowly add 50 mL of concentrated HCl to 50 mL of organic-free reagent water in a 1L container.

Hexane C_6H_{14}: Pesticide quality or equivalent.

Acetone (CH3)2CO: Pesticide quality or equivalent.

Tropolone: Aldrich, 98%, Cat# T89702

0.05% Tropolone-Hexane Solution: Add 2.00 g of 99% purity tropolone to 4 L of hexane in a 4L amber bottle.(what type of container?). Tumble for 1 hour. Prepare this solution each day extraction is performed.

Triethylamine, $(C_2H_5)_3N$- Pesticide quality or equivalent

Hexyl magnesium bromide, $CH_3(CH_2)_5MgBr$- Pesticide quality or equivalent

7.2. Standards

Surrogate and spike solutions are prepared from certified stock standard solutions purchased from commercial vendors. The components and concentration for preparation of the working standards may vary. In general, a known volume of stock standard solution is diluted in an appropriate solvent to achieve the desired concentration. The preparation of working standard solutions is documented in a logbook designated for this purpose. The lot number of the prepared surrogate and spike standards is documented on the extraction log along with the concentration and volume of standard solution used.

8.0 SAMPLE HANDLING AND PRESERVATION

8.1 Samples should be collected in 1 L amber glass bottles, fitted with screw caps lined with Teflon. If amber containers are not available, alternate measures should be taken to protect the samples from light sources. After collection, the samples must be cooled and maintained at a temperature of 4°C (±2°C) from the time of collection until sample extraction. Sample extracts must be stored separately from original sample containers in a temperature controlled storage areas maintained at 4°C (±2°C).

8.2 The extraction holding time is 7 days from date of collection.

8.3 Unless otherwise specified by client or regulatory program, after extraction and analysis samples are retained for 30 days and then disposed of in accordance with applicable regulations.

9.0 QUALITY CONTROL

9.1. A method blank (MB) and lab control sample (LCS) are included with each preparation batch of 20 or fewer field samples. A matrix spike/matrix spike duplicate (MS/MSD) should be prepared with each extraction batch when sufficient sample is available. Sample duplicates are performed per client request.

9.2 Prior to extraction all field and QC samples are fortified with surrogate spike solution and the LCS and MS/MSD are fortified with spike solution.

9.2. The criteria used to assess quality control samples are given in the analytical SOP for the determinative method.

10.0 CALIBRATION AND STANDARDIZATION

10.1. Calibrate the pH meter on each day of use, prior to use using pH 4 and 7 buffer solutions.

10.2 Check the calibration of the balance each day of use prior to use with at least 3 Class S weights that bracket the range of use.

10.3 Check the accuracy of the mechanical pipettes each day of use prior to use.

11.0 PROCEDURE

11.1. Equipment Set-Up

For each sample:

Add a plug of Pyrex glass wool to a 75 mm glass funnel. Add a sufficient amount of purified sodium sulfate to each funnel such that the funnel is approximately ¾ full. Rinse the funnel with ~30 mL of 0.05% tropolone-hexane solution.

Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporation flask then attach a K-D setup to each drying funnel.

11.2 Extraction

Mark the meniscus of the aqueous on the sample container (1L) with a permanent marker. Pour the entire sample into the 2 L separatory funnel.

Note: If high analyte concentrations are anticipated, a smaller sample volume may be taken and diluted to 1L with reagent water. If smaller volumes are used, it may be necessary to adjust the volume of surrogate and spike solution. Consult with the Department Supervisor for further guidance.

Add the appropriate volume of surrogate solution to each field and QC sample then add the appropriate volume of spike solution to the LCS and MS/MSD. Refer to the laboratory prepared benchsheet (extraction log) for details on the type, concentration and volume of surrogate and spike standard solutions.

Rinse each sample container with 60 mL of 0.05% tropolone-hexane and transfer this rinse solvent to the separatory funnel. Fill the sample container with water to the mark of the meniscus and measure the volume of water using a graduated cylinder. Record the sample volume on the extraction log. For the method blank and LCS, use 1 L of reagent water.

Check the pH of each sample with the pH meter and adjust the pH to <2 using 1:1 HCl solution.

Seal and shake the separatory funnel vigorously for 15-20 seconds with periodic venting to release excess pressure. Place the separatory funnel on the mechanical shaker and shake for 2 minutes.

Initial venting should be done immediately after the separatory funnel has been sealed and shaken once. Venting of the separatory funnel should be into a hood to avoid needless exposure of the analyst to solvent vapors.

Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, use mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.

The organic solvent phase will float on top of the aqueous phase. Collect the water phase in a clean 1 L amber bottle. Drain the organic solvent layer through the sodium sulfate drying funnel into the K-D concentrator. Repeat the extraction two more times using fresh portions of solvent. Rinse the drying funnel with ~ 15mL of 0.05% tropolone-hexane solution.

11.2. Extract Concentration

11.2.1 Macro Snyder K-D Technique

Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15-20° C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Attach the solvent vapor recovery glassware (condenser and collection device) to the Snyder column of the K-D apparatus following manufacturer's instructions. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood.

When the apparent volume of liquid reaches < 10mL, remove the Synder column from the water bath and allow it to drain and cool for 10 minutes. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of hexane. Concentrate the extract to a volume of 2~3mL using the micro-Synder column technique.

11.2.2 Micro-Snyder Column Technique

Add one or two clean boiling chips to the concentrator tube and attach a two ball micro-Snyder column. Place the concentrator tube into the water bath so that the concentrator tube is partially immersed in hot water. Adjust the vertical position of the concentrator tube and/or the temperature of the water bath to complete the concentration of the extract in 5-10 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with solvent. Continuously monitor the distillation process to ensure sample extracts do not evaporate too quickly.

When the apparent volume of extract reaches ~2-3 mL, remove the Snyder column, rinse the rinse concentration tube with ~0.2 mL hexane. Transfer the extract to a 16 mL vial and rinse the concentrator tube with ~ 1mL of hexane. Transfer the rinse into the vial.

11.3. Extract Derivitization

Add 150 µl of triethylamine and 0.80 mL of Hexyl magnesium bromide to each extract. Cap the vial and shake the extract using the mechanical wrist shaker for 60 minutes.

Caution: *Hexyl magnesium bromide is very hazardous and ether based. Do not use near any heat source.*

After the shake step is complete, slowly add a sufficient amount of 1:1 HCl to each extract to dissolve the precipitate. Perform this step in a fume hood because the addition of HCl produces a gas.

Centrifuge each extract to separate the solvent extract from the acid. Transfer the extract layer to a K-D concentrator tube. Rinse the acid layer with 2.0 mL of hexane then transfer the rinse to the concentrator tube.

Concentrate the samples 1-2 mL using the micro synder column technique. Solvent exchange the samples with ~ 10mL of hexane. Concentrate the samples back to 1-2mL using the microsynder column technique.

11.4 Extract Cleanup

Pre-clean silica/florisil cartridges by attaching the cartridges to the vacuum box using a teflon insert. Elute 100 mL of methylene chloride through each cartridge followed by 100 mL of hexane at gravity flow rate. Remove the cartridge and teflon insert and connect it to the top of a KD flask. Elute the sample extract through the cartridge and rinse with 100 mL of hexane.

Concentrate the extracts using macro and micro-snyder techniques. When the apparent volume of liquid reaches <1 mL, remove the Snyder column and rinse the concentrator tube with ~0.2 mL of hexane.

Adjust the final volume of sample extracts to 1.0 mL with hexane. Transfer the extract to a labeled PTFE-lined screw cap vial in preparation for analysis.

11.5 Preparation of Standard Curve

Extract the curve standards following the procedures given in Section 11.1 through 11.5. Adjust the final volume of the curve standards to 5.0 mL in hexane.

12.0 CALCULATIONS

12.1 This section is not applicable to this SOP.

13.0 DATA ASSESSMENT, CRITERIA & CORRECTIVE ACTION

13.1 The extraction log is completed the primary analyst who also performs primary review of his or her work. The extraction log is reviewed for accuracy and completeness by the Department Supervisor, or designee prior to the transfer of paperwork and extracts to the analytical department. Problems encountered during the extraction process are documented on the extraction log.

14.0 METHOD PERFORMANCE

14.1 Each analyst must complete an Initial Demonstration of Capability prior to unsupervised performance of this method.

14.2 A Method Detection Limit (MDL) Study is performed at initial method set-up when there are significant changes made to the procedure. The procedure and acceptance criteria for MDL studies are given in laboratory SOP LP-LB-009 *Method Detection Limits.*

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this SOP and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2 Waste Streams

The following waste streams are produced when this method is carried out.

- Organic Solvents
- Extracted water samples
- Vials containing extracts

Neutralize extracted water samples with 50 g of baking soda prior to disposition in the non-regulated water waste stream. Transfer the waste stream(s) to the appropriate satellite container(s) located in your work area. Notify authorized personnel when it is time to transfer the contents of the satellite containers to the hazardous waste storage room for future disposal in accordance with Federal, State and Local regulations. The procedures for waste management are further given in laboratory SOP LP-LB-001 *Hazardous Waste*.

16.0 REFERENCES

16.1 Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846), Third Edition, September 1986, Final Update I, July 1992, Final Update IIA, August 1993, Final Update II, September 1994; Final Update IIB, January 1995; Final Update III, December 1996.

16.2 Sampling and Analytical Methods of the National Status and Trends Program, National Benthic Surveillance and Mussel Watch Projects 1984-1992, Vol. IV, NOAA Technical Memorandum, NOS ORCA 71.

16.3 A Manual for the Analysis of Butyltins in Environmental Samples, The Virginia Institute of Marine Science, College of William and Mary, Gloucester Point, Virginia, November 1996.

17.0 TABLES, DIAGRAMS, FLOWCHARTS

17.1 Table 1: Primary Materials Used

Table 1: Primary Materials Used

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Methylene chloride	Cancer causing	25 ppm (TWA)	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

Appendix A: Terms & Definitions

Acceptance Criteria: Specified limits placed on characteristics of an item, process or service.

Aliquot: A discrete, measured, representative portion of a sample taken for analysis.

Analyst: The designated individual who performs the extraction / test method and the one who is responsible for applying required laboratory practices and other pertinent quality control measures to meet the required level of quality specified by the project or by the laboratory's quality system.

Batch: environmental samples, which are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria.

Conformance: An affirmative indication or judgment that a product or service has met the requirements of the relevant specification, contract or regulation; also the state of meeting requirements.

Corrective Action: action taken to eliminate the causes of an existing non-conformance, defect, or other undesirable situation in order to prevent recurrence.

Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure.

Matrix: The component or substrate that contains the anlayte of interest.

Matrix Spike (MS): a field sample to which a known amount of target analyte(s) is added.

Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure.

Method Detection Limit (MDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific measurement system. The MDL is a statistical estimation at a specified confidence interval of the concentration at which relative uncertainty is ±100%. The MDL represents a range where qualitative detection occurs. Quantitative results are not produced in this range.

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves.

Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of its users.

Reporting Limit (RL): the level to which data is reported for a specific test method and/or sample. The RL must be minimally at or above the MDL.

Sample Duplicate (SD): duplicate aliquot of a sample processed and analyzed independently; under the same laboratory conditions.

Spike: A known mass of target anlayte added to a blank sample or sub-sample used to determine recovery efficiency or for other quality control measures.

Stock Standard: a solution made with one or more neat standards usually with a high concentration. Also known as a primary standard. Stock standards may be certified solutions purchased from a vendor.

Surrogate: A substance with properties that mimic the analyte of interest but it is unlikely to be found in environmental samples.

SEVERN TRENT STL

METHOD 3550_OR560
STANDARD OPERATING PROCEDURE
FOR ALKYL TIN ULTRASONIC EXTRACTION

Applicable Matrices: Solid/Tissue

APPROVAL SIGNATURES

Laboratory Director: _____ Date: 12/29/03
Michael F. Wheeler, Ph.D.

QA Manager: _____ Date: 12/29/03
Kirstin L. McCracken

Organic Extraction Manager: _____ Date: 12/30/03
Jon Zygmuntowicz

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1.0 SCOPE AND APPLICATION

1.1. This SOP describes the laboratory procedure for isolating organic compounds from solid and tissue samples in preparation for analysis by a variety of chromatographic procedures.

2.0 SUMMARY OF METHOD

2.1. A known mass of sample, usually 30 grams is transferred into a beaker. The soil sample is sonicated and tissue sample is tissuemized. The extract is then dried and concentrated using a Kuderna- Danish (K-D) apparatus. The extract is then derivitized, hexane exchanged and silica gel/florisil cleaned. The final extract is 1.0mL.

2.2. This procedure is based on EPA Method SW-846, 3550B.

3.0 DEFINITIONS

3.1. Definitions are included in Appendix A.

4.0 INTERFERENCES

4.1. Method interference may be caused by contaminants in solvents, reagents, glassware and other sample processing equipment that can cause interference and/or elevated baselines in chromatography. All reagents and solvents used during this procedure should be reagent grade or high purity in order to minimize interference. All glassware must be cleaned in accordance with laboratory SOP LP-OP-Glass and rinsed with acetone prior to use.

5.0 SAFETY

5.1. The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be minimized when reasonably possible. A reference file of Material Safety Data Sheets (MSDS) is made available to all personnel.

5.2. Safety glasses, gloves and protective clothing (lab coat) must be worn while performing this method.

5.3. All laboratory personnel must be familiar with the laboratory environmental health and safety plan described in the STL Corporate Safety Manual.

6.0 EQUIPMENT AND SUPPLIES

6.1. Kuderna-Danish Apparatus:

6.1.1. Concentrator tube - 10 ml graduated (AMK KD-0018 or equivalent)

6.1.2. Evaporation flask - 500 ml (AMK KD-0015 or equivalent) attached to concentrator tube with clip.

6.2. Snyder column - three ball macro (AMK KD-0011) and two ball micro (AMK KD-0013).

6.3. Heating mantle rheostat controlled for water bath capable of temperature control (± 5°C).

6.4. Boiling chips - silicon carbide, approximately 10/40 mesh, solvent extracted with methylene chloride.

6.5. Disposable glass Pasteur pipettes and bulb.

6.6. High Intensity Ultrasonic Processor - Tekmar 600-watt Model Dual Output with pulsing capability, 3/4" standard disrupter horn (1/8" disrupter horn for medium level extractions).

6.7. Tissuemizer-Fisher Scientific, Power-gen 700 with 20mm rotor shaft.

6.8. Balance - capable of weighing 100 g to ± 0.01 gram.

6.9. Filtering funnels - 100-mm diameter for filtration/drying.

6.10. Filter paper - No. 541 Whatman 18.5 cm circles, or equivalent.

6.11. Beakers - 400 mL. Stainless steel or Teflon spatulas.

6.12. Adjustable pipette for surrogate and matrix spiking solutions.

6.13. 5 and 10 ml comparison vials.

6.14. Vials and caps: 1.8, 4, 8, and 16 ml with Teflon lined septa and screw caps.

6.15. Wrist Action shaker.

6.16. Vacuum Box with teflon inserts.

7.0 REAGENTS AND STANDARDS

7.1. Reagents:

Reagent grade chemicals shall be used. Unless otherwise specified, all reagents shall conform to the specifications of the American Chemical Society or equivalent national standard where such specifications are available.

7.1.1. Sodium Sulfate (granular, anhydrous), Na2SO4. Purify by placing in oven set at 400°C for 4 hours.

7.1.2. 21 Gram Silica Gel/ Florisil Cartridges- Restek, cat # 24049

7.1.3. Methylene Chloride, CH2C12- Pesticide quality or equivalent

7.1.4. Hexane, C6H14- Pesticide quality or equivalent

7.1.5. Acetone, (CH3)2CO- Pesticide quality or equivalent

7.1.6. Hydrochloric acid solution (1:1 v/v), HCl. Slowly add 50 ml of HCl to 50 ml of organic-free reagent water.

7.1.7. 0.05% Tropolone/Hexane solution. Add 2.00g of 99% Tropolone to 4L Hexane and tumble for an hour. This solution is to be made fresh each day extraction is performed.

7.1.8. Triethylamine, $(C_2H_5)_3N$- Pesticide quality or equivalent

7.1.9. Hexyl magnesium bromide, $CH_3(CH_2)_5MgBr$- Pesticide quality or equivalent

7.2. Stock Standard Solutions

Purchase standard solutions pre-made, pre-certified or prepare by accurately measuring a volume of stock standard *(Vstock)*, dissolving the stock standard in solvent and diluting to volume *(Vspike)* in a volumetric flask. The "recipes" for the preparation of standard solutions used for each determinative method are provided in lab SOP-LP-OP-Standards, refer to Table 1 in Appendix A of this SOP.

8.0 SAMPLE HANDLING AND PRESERVATION

8.1. Sample Collection and Preservation:

8.1.1. Soil samples may be collected in level 3, pre-cleaned, certified 250ml amber wide mouth glass containers. Specific requirements for site sample collection may be outlined in the client site sampling plan.

8.1.2. All samples must be iced or refrigerated at 4°C (±2 °C) from the time of collection until extraction. Sediment and tissue samples may be frozen upon receipt and holding times will begin from the point that the samples are brought back to room temperature.

8.2. Required Holding Times:

8.2.1. Extraction of soil/sediment samples by sonication must be started within 14 days of sample collections. Soil/sediment samples collected for EPH extraction must be started within 7 days, and soil/sediment samples collected for New York State extraction must be started within 10 days of collection. CLP methods must be completed within 10 days of receipt or 14 days from collect, whichever comes first.

8.2.2. All extracts must be analyzed within forty days of sample extraction.

8.3. Samples, extracts and digestates are stored from the time of receipt in the laboratory until 60 days after delivery of the reconciled data package report. Unless otherwise specified by a federal, state or client-specific protocol, samples, extracts and digestates are disposed of after 60 days in a manner that complies with all applicable regulations.

9.0 QUALITY CONTROL

9.1. A method blank and lab control sample (LCS) must be performed with each preparation batch. A matrix spike/matrix spike duplicate is performed at the frequency specified in the client project plan or at a frequency of one MS/MSD per every 20 field samples per site-specific matrix over time. If insufficient sample volume is available to perform the MS/MSD, a lab control sample duplicate (LCSD) must be performed.

9.2. All field samples, QC samples (MB, LCS, LCSD) and the matrix spikes (MS/MSD) are fortified with surrogate standard prior to extraction.

9.3. The LCS, LCSD, and the matrix spikes (MS/MSD) are fortified with spike solution that contains all analytes of interest prior to extraction.

9.4. The criteria that are used to assess quality control samples are described in the SOP for the determinative method.

10.0 CALIBRATION AND STANDARDIZATION

10.1. pH meter: Calibrate on day of use following procedures described in laboratory SOP LP-LB-0011 Organic Maintenance.

10.2. Autopipettes: Calibrate on day of use following procedures described in laboratory SOP LP-LB-0008 Pipette Calibration.

11.0 PROCEDURE

11.1. Prepare glassware using the procedures described in laboratory SOP LP-OP-Glass.

11.1.1. In the inverted hood, place an 100mm glass funnel. Fold a 185mm Whatman® 54 filter, or equivalent, and place in the funnel.

11.1.2. Fill funnel ~3/4 full of baked sodium sulfate, rinse with ~30 ml Tropolone/hexane. Discard solvent rinse and place K-D setup (see section 6.1) under funnel.

11.2. Obtain samples from sample management and obtain preparation bench sheet. Sign any internal COCs from sample management.

11.3. Tare the balance with a cleaned and labeled 400-ml beaker on it.

11.4. Mix sample thoroughly, especially composite samples. Discard any foreign objects such as sticks, leaves and rocks. Tissue Samples may need to be homogenized prior to extraction. (See SOP LM-OP-HOMOG).

11.5. Weigh 30 grams of sample to the nearest +/- 0.05 grams into the 400ml beaker. Tissue samples are prepared following SOP LM-OP-TISSUE. See Table 1 for specific method requirements.

11.6. Prepare the remaining samples, method blank, laboratory control sample and matrix spike and matrix spike duplicate if required. The soil/tissue method blank and the laboratory control sample (LCS) consist of 30 grams of baked granular sodium sulfate in each.

11.7. Add sufficient volume of granular sodium sulfate (until free flowing) to sample in 400 ml beaker, and mix thoroughly with a Teflon spatula. If the sample/sodium sulfate mixture does not have a dry sandy texture, more sodium sulfate may be added to the sample.

11.8. Using a calibrated adjustable pipette, add 10ml of 1:1 HCl and mix.

11.9. Using a calibrated adjustable pipette, add the appropriate surrogate solution to all samples. (See Table 1)

11.10. Using a calibrated adjustable pipette, add spiking solution to the LCS and each matrix spike sample. (See Table 1)

11.11. Immediately add 100 ml of 0.05% tropolone/hexane and stir with the spatula. Tissue samples are extracted following SOP-LM-OP-TISSUE. Soil samples are extracted as specified below.

11.12. Sonication:

11.12.1. Sonicator Tuning - Each instrument must be tuned each day used.
Tuning procedures are as follows:

Attach one converter to the bottom connector only. Set pulsar to off (For TM-500 sonicator only). Set output control to 10. Set % duty cycle, making sure it reads 50. Momentarily hold down tune switch and rotate the tuning control clockwise or counterclockwise until a minimum reading is obtained on the power meter. (Meter should read less than 20%). Re-attach upper converter if using both converters. Record attunement in designated logbook.

11.12.2. Sonicating:

After tuning, clean horns 3 times with reagent water, acetone, hexane, and a Kimwipe. Place the samples underneath horns, and drop converters down into acoustic enclosure. Adjust jackstands so that horns are approximately ¾ inch into the solvent. Set timer for 2 minutes, and turn on power.

11.13. After the sonication is complete decant the extraction solvent through a sodium sulfate funnel into a labeled 500 ml K-D set up.

11.14. Sonicate the sample 2 more times with 0.05% tropolone/hexane. After the sonication is complete decant the extraction solvent through the sodium sulfate funnel into the same K-D set up.

11.15. Rinse down the sodium sulfate funnels with ~30 ml $MeCl_2$ or Hexane, depending on extraction solvent. When the funnels have completely drained, remove the funnels from the K-D apparatus and discard the sodium sulfate.

11.16. Extract Concentration:

11.16.1. Concentrate tissue and soil samples using Macro Snyder K-D technique:

Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Pre-wet the Snyder column by adding about 1-mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15-20° C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Attach the solvent vapor recovery glassware (condenser and collection device) to the Snyder column of the K-D apparatus following manufacturer's instructions. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches just <10-ml, Hexane exchange (if specified in table 1 of Appendix A), and boil down to <10-ml. If Hexane exchange is not required, remove the K-D apparatus from the water bath and allow it to cool and drain for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2-mL of solvent (see Table 1). The extract is further concentrated by using the microsynder column techniques.

11.16.2. Micro-Snyder Column Technique:

Add one or two clean boiling chips to the concentrator tube and attach a two ball micro-Snyder column. Place the concentrator tube into the water batch so that the concentrator tube is partially immersed in hot water. Adjust the vertical position of the concentrator tube and/or the temperature of the water bath to ensure that concentration of the extract is complete within 5-10 minutes.

Caution: Care should be taken with 8270 PAH- it should not be boiled below 1ml, compounds volatize easily.

11.16.3. Continuously monitor the distillation process to ensure sample extracts do not evaporate too quickly. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with solvent. When the volume of liquid in the concentrator tube reaches 5-mls (much lower and monobutyl tin is lost), remove from the hot water bath. Bring extract to the appropriate concentration to perform cleanup methods indicated in Appendix A table 1. Cleanup methods are described in SOP LM-OP-Cleanup.

11.17. Add 150µl Triethylamine.

11.18. Add 0.80ml Hexyl magnesium bromide. Place mixture on wrist shaker for 60 minutes.

11.19. Slowly add 1:1 HCl to dissolve precipitate. **Caution:** Samples give off a gas, so be sure to do this in the hood.

11.20. Remove extract from acid and add to clean K-D bottom. Hexane exchange with 10ml of hexane.

11.21. Concentrate samples to ~5ml. Pre-clean a 21g silica/florisil cartridge by attaching the cartridge to the vacuum box using a teflon insert. Using vacuum, elute 100mL of Methylene Chloride through the cartridge followed by 100mL of Hexane. Remove the cartridge with teflon insert and place on top of KD flask.

11.22. Elute sample through cartridge with 100ml of hexane and collect in KD flask.

11.23. Concentrate samples using macro and micro-snyder techniques. Continuously monitor the distillation process to ensure sample extracts do not evaporate too quickly. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with solvent. When the volume of liquid in the concentrator tube reaches <1.0 ml . Remove the Snyder column, rinse the concentrator tube with ~0.2 mls of Hexane. Adjust the final volume to 1.0mL.

11.24. Nitrogen Blowdown Technique (if necessary):

This technique may be employed if there is difficulty boiling down a sample due to high viscosity.

11.24.1. Place the concentrator tube in a warm bath (65°C) and evaporate the solvent to final volume (See Table 1), The internal wall of the tube must be rinsed several times with the appropriate solvent during the evaporation. While evaporating, the solvent level in the tube must be positioned to prevent water from condensing into the sample. (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry.

CAUTION: When the volume of solvent is reduced below 1ml, semivolatile analytes may be lost.

11.24.2. Final volume is determined using a calibrated, graduated concentrator tube for sample volumes ≤ 1.0ml. Calibrated comparison vials are used for volumes greater than 1.0ml.

11.25. Transfer sample to a labeled PTFE-lined screw cap vial.

11.26. Complete the preparation bench sheet, enter data into the Organic Extraction Module, attach all corresponding papers and submit paperwork and samples to supervisor or designee to route to the analytical department.

11.27. An alkyl tin curve is generated for GC as requested. See Table 1 for spiking specifics.

12.0 CALCULATIONS

See Method SOP for the determinative method being performed.

13.0 DATA ASSESSMENT, CRITERIA & CORRECTIVE ACTION

13.1. All data generated in the extraction laboratory shall be reviewed and documented by the primary lab analyst, and then are reviewed for accuracy by the Department Supervisor, or designee prior to the transfer of paperwork and extracts to the analytical department.

13.2. Problems encountered during the extraction process are documented using the nonconformance form in Q-Pulse. The NCR documents the non-conformance condition, investigation of root-cause, action taken, and the result of action taken. The NCR is maintained as part of the data record for the project file.

13.3. Data that does not meet the minimum acceptance criteria is flagged using data qualifiers. When necessary a complete description of the outage is written in the case narrative provided with the data package report.

13.4. For systematic problems noted, a corrective action report is initiated for investigation and follow-up.

14.0 METHOD PERFORMANCE

See Method SOP for the determinative method being performed.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation.

15.1.1. The extraction laboratory uses a chilled water solvent recovery system during extract concentration. As the extract concentrates, the waste solvent is condensed, collected into a 55-gallon drum and disposed in accordance with state and local regulations.

15.2. The quantity of chemicals purchased and prepared should be based on expected use during the shelf life as well as the disposal costs for unused material.

15.3. There is a regulated system within the laboratory to assure proper waste disposal. All containers are labeled with proper identification and warning labels.

15.4. The laboratory optimizes technology to minimize pollution and reduce the production of hazardous waste whenever possible.

15.5. The laboratory procedures for waste management comply with applicable federal, state, and local regulations and are described in SOP LP-LB-001HAZWD.

16.0 REFERENCES

16.1. Code of Federal Regulations, Title 40, Part 136; U.S. Government Printing Office: Washington, DC, July 1, 1997.

16.2. National Environmental Laboratory Accreditation Conference, Constitution, Bylaws, and Standards, EPA600/R-98/151, US EPA Office of Research and Development, July 1999.

16.3. Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846), Third Edition, September 1986, Final Update I, July 1992, Final Update IIA, August 1993, Final Update II, September 1994; Final Update IIB, January 1995; Final Update III, December 1996.

17.0 TABLES, DIAGRAMS, FLOWCHARTS

Method 3550_OR560
Alkyl Tin Sonication/Tissuemize Extraction
Table 1

Test Method Summary OR560 : Alkyl Tin Extraction

Test Method	Bench Sheet	EX pH	Surrogate Volume (mL)	Spike Volume (mL)	Additional Spike Volume (mL)	Solvent	Exchange Solvent	Pre-cleanup Volume (mL)	Post Cleanup Volume (mL)*	Theoretical Final Volume (ml)	Cleanup				
											GPC	Florisil	Acid	Sulfur	Silica
3550	3550_OR560/Tissuemizer_OR560	ACIDIC	1.0ppm Tripentyl Tin Chloride 0.500	1.0ppm Tin Mtx 0.500	N/A	0.05% Tropolone/ Hexane	Hexane	~5	1.0	1.0	N/A	YES	N/A	N/A	YES
CURVE	CURVE_OR560	N/A	1.0ppm Tripentyl Tin Chloride 0.050;0.100; 1.250; 0.500; 1.000	1.0ppm Tin Mtx 0.050; 0.100; 1.250; 0.500; 1.000	Second Source: 1.0ppm Tin Surr. 1.250; 1.0ppm Tin Mtx 1.250	0.05% Tropolone/ Hexane	Hexane	~5	1.0 / 5.0	1.0; 1.0; 5.0; 1.0; 1.0; 5.0 (2nd source)	N/A	YES	N/A	N/A	YES

*Post-cleanup volume is the volume sent down to MS and GC.

Appendix A: Terms & Definitions

Batch: environmental samples, which are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of a similar matrix, meeting the above mentioned criteria. Where no preparation method exists (example, volatile organics, water) the batch is defined as environmental samples that are analyzed together with the same process and personnel, using the same lots of reagents, not to exceed 20 environmental samples. An analytical batch is composed of prepared environmental samples, extracts, digestates or concentrates that are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

Calibration Curve: the graphical relationship between the known values or a series of calibration standards and their instrument response.

Chain of Custody (COC): an unbroken trail of accountability that ensures the physical security of samples, data and records.

Continuing Calibration Verification (CCV): a single or multi-parameter calibration standard used to verify the stability of the method over time. Usually from the same source as the calibration curve.

Corrective Action: action taken to eliminate the causes of an existing non-conformance, defect, or other undesirable situation in order to prevent recurrence.

Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.

Equipment Blank: a portion of the final rinse water used after decontamination of field equipment; also referred to as Rinsate Blank and Equipment Rinsate.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

Initial Calibration: Analysis of analytical standards for a series of different specified concentrations used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

Initial Calibration Verification (ICV): solution prepared from a separate source from that which is used to prepare the calibration curve.

Internal Chain of Custody: an unbroken trail of accountability that ensures the physical security of samples, data and records. Internal Chain of Custody refers to additional documentation procedures implemented within the laboratory that includes special sample storage requirements, and documentation of all signatures and/or initials, dates, and times of personnel handling specific samples or sample aliquots.

Intermediate Standard: a solution made from one or more stock standards at a concentration between the stock and working standard. Intermediate standards may be certified stock standard solutions purchased from a vendor and are also known as secondary standards.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure.

Matrix Duplicate (MD): duplicate aliquot of a sample processed and analyzed independently; under the same laboratory conditions; also referred to as Sample Duplicate.

Matrix Spike (MS): a field sample to which a known amount of target analyte(s) is added.

Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).

Method Detection Limit (MDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific measurement system. The MDL is a statistical estimation at a specified confidence interval of the concentration at which relative uncertainty is ±100%. The MDL represents a range where qualitative detection occurs. Quantitative results are not produced in this range.

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

Reporting Limit (RL): the level to which data is reported for a specific test method and/or sample. The RL must be minimally at or above the MDL.

Stock Standard: a solution made with one or more neat standards usually with a high concentration. Also known as a primary standard. Stock standards may be certified solutions purchased from a vendor.

Analytical Methods

PCB Congeners and Homologues

1668A

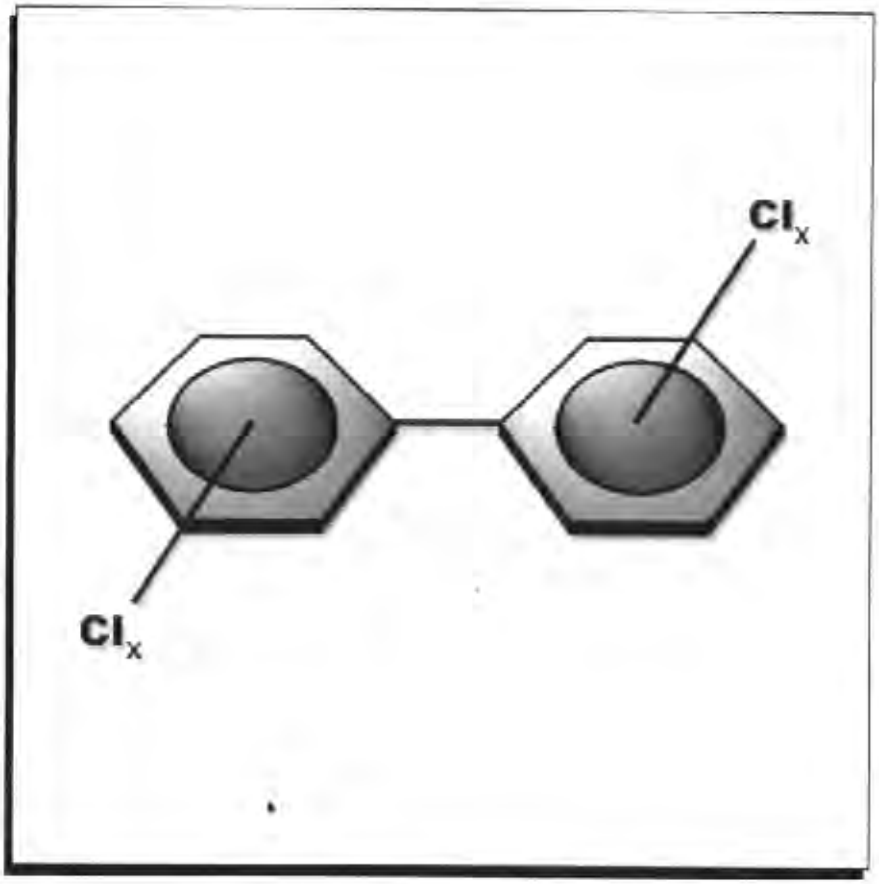
United States
Environmental Protection
Agency

Office of Water
(4303)

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December 1999

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Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS



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Disclaimer

Method 1668A has been reviewed and approved for publication by the Engineering and Analysis Division of the U.S. Environmental Protection Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Annex A A1

Introduction

Method 1668 was developed by the U.S. Environmental Protection Agency's (EPA's) Office of Science and Technology for congener-specific determination of the polychlorinated biphenyl (PCB) congeners designated as toxic by the World Health Organization. Revision A of Method 1668 has been expanded to include congener-specific determination of more than 150 chlorinated biphenyl (CB) congeners. The toxic PCBs and the beginning and ending level-of-chlorination CBs are determined by isotope dilution high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The remaining CBs are determined by internal standard HRGC/HRMS. Method 1668A is applicable to aqueous, solid, tissue, and multi-phase matrices.

Method 1668A is based on validation in a single laboratory. The basic revision of Method 1668 was validated in two laboratories.

Questions concerning this method or its application should be addressed to:

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Note: This method is performance based. The laboratory is permitted to omit any step or modify any procedure provided that all performance requirements in this method are met. The laboratory may not omit any quality control analyses. The terms "shall," "must," and "may not" define procedures required for producing reliable results. The terms "should" and "may" indicate optional steps that may be modified or omitted if the laboratory can demonstrate that the modified method produces results equivalent or superior to results produced by this method.

Method 1668, Revision A

Chlorinated biphenyl congeners in water, soil, sediment, biosolids and tissue by HRGC/HRMS

1.0 Scope and application

1.1 Method 1668, Revision A (Method 1668A, the Method) is for determination of chlorinated biphenyl congeners (CBs) in water, soil, sediment, biosolids, tissue, and other sample matrices by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS).

1.1.1 The CBs that can be determined by this Method are the 12 polychlorinated biphenyls (PCBs) designated as toxic by the World Health Organization (WHO) plus the remaining 197 CBs, approximately 125 of which are resolved adequately on an SPB-octyl gas chromatographic column to be determined as individual congeners. The remaining approximately 70 congeners are determined as mixtures of isomers (co-elutions).

1.1.2 The 12 PCBs designated as toxic by WHO (Toxics, also known as dioxin-like PCBs; DLPCBs) and the earliest and latest eluted congener at each level of chlorination (LOC CBs) are determined by the isotope dilution quantitation technique; the remaining congeners are determined by the internal standard quantitation technique.

1.1.3 This Method allows determination of the PCB toxicity equivalent (TEQ_{PCB}) for the Toxics in a sample using toxicity equivalency factors (TEFs; Reference 1) and allows unique determination of 19 of 21 CBs of interest to the National Oceanic and Atmospheric Administration (NOAA; Reference 2). A second-column option is provided for resolution of the two toxic PCB congeners (with IUPAC numbers 156 and 157) that are not resolved on the SPB-octyl column and for resolution of other CB congeners.

1.1.4 This Method also allows estimation of homolog totals by level of chlorination (LOC) and estimation of total CBs in a sample by summation of the concentrations of the CB congeners and congener groups.

1.1.5 The list of 209 CBs is given in Table 1 with the Toxics, the CBs of interest to NOAA, and the LOC CBs identified.

1.2 This Method is for use in data gathering and monitoring associated with the Clean Water Act, the Resource Conservation and Recovery Act, the Comprehensive Environmental

Response, Compensation and Liability Act, and the Safe Drinking Water Act. It is based on a compilation of methods from the technical literature (References 3-5) and on EPA Method 1613.

1.3 The detection limits and quantitation levels in this Method are usually dependent on the level of interferences and laboratory background levels rather than instrumental limitations. The estimated minimum levels of quantitation (EMLs) in Table 2 are the levels at which the CBs can be determined with laboratory contamination present. The estimated method detection limit (EMDL) for CB 126 in water is 5 pg/L (picograms-per-liter, parts-per-quadrillion) with no interferences present.

1.4 The GC/MS portions of this Method are for use only by analysts experienced with HRGC/HRMS or under the close supervision of such qualified persons. Each laboratory that uses this Method must demonstrate the ability to generate acceptable results using the procedure in Section 9.2.

1.5 This Method is "performance-based." The laboratory is permitted to modify the Method to overcome interferences or lower the cost of measurements, provided that all performance criteria are met. The requirements for establishing Method equivalency are given in Section 9.1.2.

1.6 Any modification of this Method, beyond those expressly permitted, shall be considered a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

2.0 Summary of Method

Flow charts that summarize procedures for sample preparation, extraction, and analysis are given in Figure 1 for aqueous and solid samples, Figure 2 for multi-phase samples, and Figure 3 for tissue samples.

2.1 Extraction

2.1.1 Aqueous samples (samples containing less than one percent solids)—Stable isotopically labeled analogs of the Toxics and labeled LOC CBs are spiked into a 1-L sample. The sample is extracted using solid-phase extraction (SPE), separatory funnel extraction (SFE), or continuous liquid/liquid extraction (CLLE).

2.1.2 Solid, semi-solid, and multi-phase samples (excluding tissue)—The labeled compounds are spiked into a sample containing 10 g (dry weight) of solids. Samples containing multiple phases are pressure filtered and any aqueous liquid is discarded. Coarse solids are ground or homogenized. Any non-aqueous liquid from multi-phase samples is combined with the solids and extracted in a Soxhlet/Dean-Stark (SDS) extractor. The extract is concentrated for cleanup.

2.1.3 Fish and other tissue—A 20-g aliquot of sample is homogenized, and a 10-g aliquot is spiked with the labeled compounds. The sample is mixed with anhydrous sodium sulfate, allowed to dry for 12 - 24 hours, and extracted for 18-24 hours using methylene chloride:hexane (1:1) in a Soxhlet extractor. The extract is evaporated to dryness, and the lipid content is determined.

2.2 After extraction, a labeled cleanup standard is spiked into the extract which is then cleaned up using back-extraction with sulfuric acid and/or base, and gel permeation, silica gel, or Florisil chromatography. Activated carbon and high-performance liquid chromatography (HPLC) can be used for further isolation of specific congener groups. Prior to the cleanup procedures cited above, tissue extracts are cleaned up using an anthropogenic isolation column.

2.3 After cleanup, the extract is concentrated to 20 µL. Immediately prior to injection, labeled injection internal standards are added to each extract and an aliquot of the extract is injected into the gas chromatograph (GC). The analytes are separated by the GC and detected by a high-resolution (≥10,000) mass spectrometer. Two exact m/z's are monitored at each level of chlorination (LOC) throughout a pre-determined retention time window.

2.4 An individual CB congener is identified by comparing the GC retention time and ion-abundance ratio of two exact m/z's with the corresponding retention time of an authentic standard and the theoretical or acquired ion-abundance ratio of the two exact m/z's. Isomer specificity for certain of the CB congeners is achieved using GC columns that resolve these congeners.

2.5 Quantitative analysis is performed in one of two ways using selected ion current profile (SICP) areas.

2.5.1 For the Toxics and the LOC CBs, the GC/MS is multi-point calibrated and the concentration is determined using the isotope dilution technique.

2.5.2 For all congeners other than the Toxics and LOC CBs, the GC/MS is calibrated at a single concentration and the concentrations are determined using the internal standard technique.

2.5.3 For the labeled Toxics, labeled LOC CBs, and the cleanup standards, the GC/MS is calibrated using replicates at a single concentration and the concentrations of these labeled compounds in samples are determined using the internal standard technique.

2.6 The quality of the analysis is assured through reproducible calibration and testing of the extraction, cleanup, and GC/MS systems.

3.0 Definitions

Definitions are given in the glossary at the end of this Method

4.0 Contamination and interferences

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts, elevated baselines, and/or lock-mass suppression causing misinterpretation of chromatograms. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Where possible, reagents are cleaned by extraction or solvent rinse. Environmentally abundant CBs, as well as toxic congeners 105, 114, 118, 123, 156, 157, and 167 have been shown to be very difficult to completely eliminate from the laboratory at levels lower than the EMDLs in this Method (Table 2), and baking of glassware in a kiln or furnace at 450 - 500 °C may be necessary to remove these and other contaminants

4.2 Proper cleaning of glassware is extremely important, because glassware may not only contaminate the samples but may also remove the analytes of interest by adsorption on the glass surface.

4.2.1 Glassware should be rinsed with solvent and washed with a detergent solution as soon after use as is practical. Sonication of glassware containing a detergent solution for approximately 30 seconds may aid in cleaning. Glassware with removable parts, particularly separatory funnels with fluoropolymer stopcocks, must be disassembled prior to detergent washing.

4.2.2 After detergent washing, glassware should be rinsed immediately, first with methanol, then with hot tap water. The tap water rinse is followed by another methanol rinse, then acetone, and then methylene chloride.

4.2.3 Baking of glassware in a kiln or other high temperature furnace (300 - 500 °C) may be warranted after particularly dirty samples are encountered. The kiln or furnace should be vented to prevent laboratory contamination by CB vapors. Baking should be minimized, as repeated baking of glassware may cause active sites on the glass surface that may irreversibly adsorb CBs.

4.2.4 Immediately prior to use, the Soxhlet apparatus should be pre-extracted with toluene for approximately 3 hours (see Sections 12.3.1-12.3.3). The extraction apparatus (Section 6.4) should be rinsed with methylene chloride/toluene (80/20 mixture).

4.2.5 A separate set of glassware may to necessary to effectively preclude contamination when low-level samples are analyzed.

4.3 All materials used in the analysis must be demonstrated to be free from interferences by running reference matrix method blanks (Section 9.5) initially and with each sample batch (samples started through the extraction process on a given 12-hour shift, to a maximum of 20 samples).

4.3.1 The reference matrix must simulate, as closely as possible, the sample matrix under test. Ideally, the reference matrix should not contain the CBs in detectable amounts, but should contain potential interferents in the concentrations expected to be found in the samples to be analyzed.

4.3.2 When a reference matrix that simulates the sample matrix under test is not available, reagent water (Section 7.6.1) can be used to simulate water samples; playground sand (Section 7.6.2) or white quartz sand (Section 7.3.2) can be used to simulate soils; filter paper (Section 7.6.3) can be used to simulate papers and similar materials; and corn oil (Section 7.6.4) can be used to simulate tissues.

4.4 Interferences co-extracted from samples will vary considerably from source to source, depending on the diversity of the site being sampled. Interfering compounds may be present at concentrations several orders of magnitude higher than the CBs. The most frequently encountered interferences are chlorinated dioxins and dibenzofurans, methoxy biphenyls, hydroxydiphenyl ethers, benzylphenyl ethers, brominated diphenyl ethers, polynuclear aromatics, polychlorinated naphthalenes, and pesticides. Because very low levels of CBs are measured by this Method, the elimination of interferences is essential. The cleanup steps given in Section 13 can be used to reduce or eliminate these interferences and thereby permit reliable determination of the CBs at the levels shown in Table 2.

4.5 Each piece of reusable glassware should be numbered to associate that glassware with the processing of a particular sample. This will assist the laboratory in tracking possible sources of contamination for individual samples, identifying glassware associated with highly contaminated samples that may require extra cleaning, and determining when glassware should be discarded.

4.6 Contamination of calibration solutions—The EMDLs and EMLs in Table 2 are the levels that can be achieved with normal laboratory backgrounds present. Many of the EMLs are greater than the equivalent concentrations of the calibration solutions. In order to prevent contamination of the calibration solutions with the backgrounds allowed by the EMLs, the calibration solutions must be prepared in an area free from CB contamination using glassware free from contamination. If these requirements cannot be met or are difficult to meet in the laboratory, the laboratory should prepare the calibration solutions in a contamination-free facility or have a vendor prepare the calibration standards and guarantee freedom from contamination.

4.7 Cleanup of tissue—The natural lipid content of tissue can interfere in the analysis of tissue samples for the CBs. The lipid contents of different species and portions of tissue

can vary widely. Lipids are soluble to varying degrees in various organic solvents and may be present in sufficient quantity to overwhelm the column chromatographic cleanup procedures used for cleanup of sample extracts. Lipids must be removed by the anthropogenic isolation column procedure in Section 13.6, followed by the gel permeation chromatography procedure in Section 13.2. Florisil (Section 13.7) is recommended as an additional cleanup step.

4.8 If the laboratory air is a potential source of CB contamination, samples, reagents, glassware, and other materials should be dried in a glove box or other area free from contamination.

5.0 Safety

5.1 The toxicity or carcinogenicity of each chemical used in this Method has not been precisely determined; however, each compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level.

5.1.1 PCBs have been tentatively classified as known or suspected human or mammalian carcinogens. On the basis of the available toxicological and physical properties of the CBs, pure standards should be handled only by highly trained personnel thoroughly familiar with handling and cautionary procedures and the associated risks.

5.1.2 It is recommended that the laboratory purchase dilute standard solutions of the analytes in this Method. However, if primary solutions are prepared, they must be prepared in a hood, and a NIOSH/MESA approved toxic gas respirator must be worn when high concentrations are handled.

5.2 The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this Method. A reference file of material safety data sheets (MSDSs) should also be made available to all personnel involved in these analyses. It is also suggested that the laboratory perform personal hygiene monitoring of each analyst who uses this Method and that the results of this monitoring be made available to the analyst. Additional information on laboratory safety can be found in References 6-9. The references and bibliography at the end of Reference 8 are particularly comprehensive in dealing with the general subject of laboratory safety.

5.3 The pure CBs and samples suspected to contain these compounds are handled using essentially the same techniques employed in handling radioactive or infectious materials. Well-ventilated, controlled access laboratories are required. Assistance in evaluating the health hazards of particular laboratory conditions may be obtained from certain consulting laboratories and from State Departments of Health or Labor, many of which have an industrial health service. Each laboratory must develop a strict safety program for handling these compounds. The practices in Reference 10 for handling chlorinated

dibenzo-*p*-dioxins and dibenzofurans (CDDs/CDFs) are also recommended for handling the CBs.

5.3.1 Facility—When finely divided samples (dusts, soils, dry chemicals) are handled, all operations (including removal of samples from sample containers, weighing, transferring, and mixing) should be performed in a glove box demonstrated to be leak tight or in a fume hood demonstrated to have adequate air flow. Gross losses to the laboratory ventilation system must not be allowed. Handling of the dilute solutions normally used in analytical and animal work presents no inhalation hazards except in the case of an accident.

5.3.2 Protective equipment—Disposable plastic gloves, apron or lab coat, safety glasses or mask, and a glove box or fume hood adequate for radioactive work should be used. During analytical operations that may give rise to aerosols or dusts, personnel should wear respirators equipped with activated carbon filters. Eye protection (preferably full face shields) must be worn while working with exposed samples or pure analytical standards. Latex gloves are commonly used to reduce exposure of the hands. When handling samples suspected or known to contain high concentrations of the CBs, an additional set of gloves can also be worn beneath the latex gloves.

5.3.3 Training—Workers must be trained in the proper method of removing contaminated gloves and clothing without contacting the exterior surfaces.

5.3.4 Personal hygiene—Hands and forearms should be washed thoroughly after each manipulation and before breaks (coffee, lunch, and shift).

5.3.5 Confinement—Isolated work areas posted with signs, segregated glassware and tools, and plastic absorbent paper on bench tops will aid in confining contamination.

5.3.6 Effluent vapors—The effluent of the sample splitter from the gas chromatograph (GC) and from roughing pumps on the mass spectrometer (MS) should pass through either a column of activated charcoal or be bubbled through a trap containing oil or high-boiling alcohols to condense CB vapors.

5.3.7 Waste Handling—Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans. Janitors and other personnel should be trained in the safe handling of waste.

5.3.8 Decontamination.

5.3.8.1 Decontamination of personnel—Use any mild soap with plenty of scrubbing action.

5.3.8.2 Glassware, tools, and surfaces—Chlorothene NU Solvent is a less toxic solvent that should be effective in removing CBs. Satisfactory cleaning may be accomplished by rinsing with Chlorothene, then washing with any detergent and water. If glassware is first rinsed with solvent, the wash water may be disposed of in the sewer. Given the cost of disposal, it is prudent to minimize solvent wastes.

5.3.9 Laundry—Clothing known to be contaminated should be collected in plastic bags. Persons that convey the bags and launder the clothing should be advised of the hazard and trained in proper handling. The clothing may be put into a washer without contact if the launderer knows of the potential problem. The washer should be run through a cycle before being used again for other clothing.

5.3.10 Wipe tests—A useful method of determining cleanliness of work surfaces and tools is to perform a wipe test of the surface suspected of being contaminated.

5.3.10.1 Using a piece of filter paper moistened with Chlorothene or other solvent, wipe an area approximately 10 x 10 cm.

5.3.10.2 Extract and analyze the wipe by GC with an electron capture detector (ECD) or by this Method.

5.3.10.2 Using the area wiped (e.g., 10 x 10 cm = 0.01 m^2), calculate the concentration in $\mu g/m^2$. A concentration less than 1 $\mu g/m^2$ indicates acceptable cleanliness; anything higher warrants further cleaning. More than 100 $\mu g/m^2$ constitutes an acute hazard and requires prompt cleaning before further use of the equipment or work space, and indicates that unacceptable work practices have been employed.

6.0 Apparatus and materials

Note: *Brand names, suppliers, and part numbers are for illustration purposes only and no endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here. Meeting the performance requirements of this Method is the responsibility of the laboratory.*

6.1 Sampling equipment for discrete or composite sampling.

6.1.1 Sample bottles and caps.

6.1.1.1 Liquid samples (waters, sludges and similar materials containing 5 percent solids or less)—Sample bottle, amber glass, 1.1-L minimum, with screw cap.

6.1.1.2 Solid samples (soils, sediments, sludges, paper pulps, filter cake, compost, and similar materials that contain more than 5 percent solids)—Sample bottle, wide mouth, amber glass, 500-mL minimum.

6.1.1.3 If amber bottles are not available, samples must be protected from light.

6.1.1.4 Bottle caps—Threaded to fit sample bottles. Caps must be lined with fluoropolymer.

6.1.1.5 Cleaning.

6.1.1.5.1 Bottles are detergent water washed, then solvent rinsed before use.

6.1.1.5.2 Liners are detergent water washed and rinsed with reagent water (Section 7.6.1).

6.1.2 Compositing equipment—Automatic or manual compositing system incorporating glass containers cleaned per bottle cleaning procedure above. Only glass or fluoropolymer tubing must be used. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used in the pump only. Before use, the tubing must be thoroughly rinsed with methanol, followed by repeated rinsing with reagent water to minimize sample contamination. An integrating flow meter is used to collect proportional composite samples.

6.2 Equipment for glassware cleaning.

Note: *If blanks from bottles or other glassware or with fewer cleaning steps than required above show no detectable CB contamination, unnecessary cleaning steps and equipment may be eliminated.*

6.2.1 Laboratory sink with overhead fume hood.

6.2.2 Kiln—Capable of reaching 450 °C within 2 hours and maintaining 450 - 500 °C within ± 10 °C, with temperature controller and safety switch (Cress Manufacturing Co, Santa Fe Springs, CA, B31H, X31TS, or equivalent). See the precautions in Section 4.2.3.

6.3 Equipment for sample preparation.

6.3.1 Laboratory fume hood of sufficient size to contain the sample preparation equipment listed below

6.3.2 Glove box (optional)

6.3.3 Tissue homogenizer—VirTis Model 45 Macro homogenizer (American Scientific Products H-3515, or equivalent) with stainless steel Macro-shaft and Turbo-shear blade.

6.3.4 Meat grinder—Hobart, or equivalent, with 3- to 5-mm holes in inner plate.

6.3.5 Equipment for determining percent moisture

6.3.5.1 Oven—Capable of maintaining a temperature of 110 ± 5 °C

6.3.5.2 Desiccator

6.3.6 Balances

6.3.6.1 Analytical—Capable of weighing 0.1 mg

6.3.6.2 Top loading—Capable of weighing 10 mg

6.4 Extraction apparatus

6.4.1 Water samples

6.4.1.1 pH meter, with combination glass electrode

6.4.1.2 pH paper, wide range (Hydrion Papers, or equivalent)

6.4.1.3 Graduated cylinder, 1-L capacity

6.4.1.4 Liquid/liquid extraction—Separatory funnels, 250-, 500-, and 2000-mL, with fluoropolymer stopcocks

6.4.1.5 Solid-phase extraction

6.4.1.5.1 1-L filtration apparatus, including glass funnel, frit support, clamp, adapter, stopper, filtration flask, and vacuum tubing (Figure 4). For wastewater samples, the apparatus should accept 90 or 144 mm disks. For drinking water or other samples containing low solids, smaller disks may be used.

6.4.1.5.2 Vacuum source—Capable of maintaining 25 in. Hg, equipped with shutoff valve and vacuum gauge

6.4.1.5.3 Glass-fiber filter—Whatman GMF 150 (or equivalent), 1 micron pore size, to fit filtration apparatus in Section 6.4.1.5.1

6.4.1.5.4 Solid-phase extraction disk containing octadecyl (C_{18}) bonded silica uniformly enmeshed in an inert matrix—Fisher Scientific 14-378F (or equivalent), to fit filtration apparatus in Section 6.4.1.5.1

6.4.1.6 Continuous liquid/liquid extraction (CLLE)—Fluoropolymer or glass connecting joints and stopcocks without lubrication, 1.5-2 L capacity (Hershberg-Wolf Extractor, Cal-Glass, Costa Mesa, California, 1000 mL or 2000 mL, or equivalent).

6.4.2 Soxhlet/Dean-Stark (SDS) extractor (Figure 5 and Reference 11) for filters and solid/sludge samples

6.4.2.1 Soxhlet—50-mm ID, 200-mL capacity with 500-mL flask (Cal-Glass LG-6900, or equivalent, except substitute 500-mL round-bottom flask for 300-mL flat-bottom flask)

6.4.2.2 Thimble—43 × 123 to fit Soxhlet (Cal-Glass LG-6901-122, or equivalent)

6.4.2.3 Moisture trap—Dean Stark or Barret with fluoropolymer stopcock, to fit Soxhlet

6.4.2.4 Heating mantle—Hemispherical, to fit 500-mL round-bottom flask (Cal-Glass LG-8801-112, or equivalent)

6.4.2.5 Variable transformer—Powerstat (or equivalent), 110-volt, 10-amp

6.4.3 Beakers—400- to 500-mL

6.4.4 Spatulas—Stainless steel

6.5 Filtration apparatus

6.5.1 Pyrex glass wool—Solvent-extracted using a Soxhlet or SDS extractor for 3 hours minimum

6.5.2 Glass funnel—125- to 250-mL

6.5.3 Glass-fiber filter paper—Whatman GF/D (or equivalent), to fit glass funnel in Section 6.5.2.

6.5.4 Drying column—15- to 20-mm ID Pyrex chromatographic column equipped with coarse-glass frit or glass-wool plug

6.5.5 Buchner funnel—15-cm

6.5.6 Glass-fiber filter paper for Buchner funnel above

6.5.7 Filtration flasks—1.5- to 2.0-L, with side arm

6.5.8 Pressure filtration apparatus—Millipore YT30 142 HW, or equivalent

6.6 Centrifuge apparatus

6.6.1 Centrifuge—Capable of rotating 500-mL centrifuge bottles or 15-mL centrifuge tubes at 5,000 rpm minimum

6.6.2 Centrifuge bottles—500-mL, with screw-caps, to fit centrifuge

6.6.3 Centrifuge tubes—12- to 15-mL, with screw-caps, to fit centrifuge

6.7 Cleanup apparatus

6.7.1 Automated gel permeation chromatograph (Analytical Biochemical Labs, Inc, Columbia, MO, Model GPC Autoprep 1002, or equivalent)

6.7.1.1 Column—600-700 mm long × 25 mm ID glass, packed with 70 g of 200-400 mesh SX-3 Bio-beads (Bio-Rad Laboratories, Richmond, CA, or equivalent)

6.7.1.2 Syringe—10-mL, with Luer fitting

6.7.1.3 Syringe filter holder—stainless steel, and glass-fiber or fluoropolymer filters (Gelman 4310, or equivalent)

6.7.1.4 UV detectors—254-nm, preparative or semi-preparative flow cell (Isco, Inc., Type 6, Schmadzu, 5-mm path length; Beckman-Altex 152W, 8-µL micro-prep flow cell, 2-mm path; Pharmacia UV-1, 3-mm flow cell; LDC Milton-Roy UV-3, monitor #1203, or equivalent)xxx

6.7.2 Reverse-phase high-performance liquid chromatograph (Reference 4)

6.7.2.1 Pump—Perkin-Elmer Series 410, or equivalent

6.7.2.2 Injector—Perkin-Elmer ISS-100 Autosampler, or equivalent

6.7.2.3 6-Port switching valve—Valco N60, or equivalent

6.7.2.4 Column—Hypercarb, 100 x 4.6 mm, 5 µm particle size, Keystone Scientific, or equivalent

6.7.2.5 Detector—Altex 110A (or equivalent) operated at 0.02 AUFS at 235 nm

6.7.2.6 Fraction collector—Isco Foxy II, or equivalent

6.7.3 Pipets

6.7.3.1 Disposable, Pasteur, 150-mm long × 5-mm ID (Fisher Scientific 13-678-6A, or equivalent)

6.7.3.2 Disposable, serological, 50-mL (8- to 10- mm ID)

6.7.4 Glass chromatographic columns

6.7.4.1 150-mm long × 8-mm ID, (Kontes K-420155, or equivalent) with coarse-glass frit or glass-wool plug and 250-mL reservoir

6.7.4.2 200-mm long × 15-mm ID, with coarse-glass frit or glass-wool plug and 250-mL reservoir

6.7.4.3 300-mm long x 22-mm ID, with coarse-glass frit, 300-mL reservoir, and glass or fluoropolymer stopcock

6.7.5 Oven—For baking and storage of adsorbents, capable of maintaining a constant temperature (±5 °C) in the range of 105-250 °C

6.8 Concentration apparatus

6.8.1 Rotary evaporator—Buchi/Brinkman-American Scientific No. E5045-10 or equivalent, equipped with a variable temperature water bath

6.8.1.1 Vacuum source for rotary evaporator equipped with shutoff valve at the evaporator and vacuum gauge

6.8.1.2 A recirculating water pump and chiller are recommended, as use of tap water for cooling the evaporator wastes large volumes of water

and can lead to inconsistent performance as water temperatures and pressures vary.

6.8.1.3 Round-bottom flask—100-mL and 500-mL or larger, with ground-glass fitting compatible with the rotary evaporator

6.8.2 Kuderna-Danish (K-D) concentrator

6.8.2.1 Concentrator tube—10-mL, graduated (Kontes K-570050-1025, or equivalent) with calibration verified. Ground-glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

6.8.2.2 Evaporation flask—500-mL (Kontes K-570001-0500, or equivalent), attached to concentrator tube with springs (Kontes K-662750-0012 or equivalent)

6.8.2.3 Snyder column—Three-ball macro (Kontes K-503000-0232, or equivalent)

6.8.2.4 Boiling chips

6.8.2.4.1 Glass or silicon carbide—Approximately 10/40 mesh, extracted with methylene chloride and baked at 450 °C for one hour minimum

6.8.2.4.2 Fluoropolymer (optional)—Extracted with methylene chloride

6.8.2.5 Water bath—Heated, with concentric ring cover, capable of maintaining a temperature within ±2 °C, installed in a fume hood

6.8.3 Nitrogen blowdown apparatus—Equipped with water bath controlled in the range of 30 - 60 °C (N-Evap, Organomation Associates, Inc., South Berlin, MA, or equivalent), installed in a fume hood

6.8.4 Sample vials

6.8.4.1 Amber glass, 2- to 5-mL with fluoropolymer-lined screw-cap

6.8.4.2 Glass, 0.3-mL, conical, with fluoropolymer-lined screw or crimp cap

6.9 Gas chromatograph—Must have splitless or on-column injection port for capillary column, temperature program with isothermal hold, and must meet all of the performance specifications in Section 10.

6.9.1 GC column—Any GC column or column system (2 or more columns) that provides unique resolution and identification of the Toxics for determination of a TEQ_{PCB} using TEFs (Reference 1). Isomers may be unresolved so long as they have the same TEF and response factor and so long as these unresolved isomers are uniquely resolved from all other congeners. For example, the SPB-octyl column (Section 6.9.1.3) achieves unique GC resolution of all Toxics except congeners with IUPAC numbers 156 and 157. This isomeric pair is uniquely resolved from all other congeners and these congeners have the same TEF and response factor.

6.9.1.1 If an SPB-octyl column is used, it must meet the specification in Section 6.9.1 and the following additional specifications:

6.9.1.1.1 The retention time for decachlorobiphenyl (DFB; PCB 209) must be greater than 55 minutes.

6.9.1.1.2 The column must uniquely resolve congeners 34 from 23 and 187 from 182, and congeners 156 and 157 must co-elute within 2 seconds at the peak maximum. Unique resolution means a valley height less than 40 percent of the shorter of the two peaks that result when the Diluted combined 209 congener solution (Section 7.10.2.2) is analyzed (see Figures 6 and 7).

6.9.1.1.3 The column must be replaced when any of the criteria in Sections 6.9.1 - 6.9.1.1.2 are not met.

6.9.1.2 If a column or column system alternate to the SPB-octyl column is used, specifications similar to those for the SPB-octyl column (Sections 6.9.1 - 6.9.1.1.2) must be developed and be functionally equivalent to those specifications.

6.9.1.3 Suggested column—30±5-m long × 0.25±0.02-mm ID; 0.25-µm film SPB-octyl (Supelco 2-4218, or equivalent). This column is capable of meeting the requirements in Sections 6.9.1 - 6.9.1.1.2.

Note: *The SPB-octyl column is subject to rapid degradation when exposed to oxygen. The analyst should exclude oxygen from the carrier gas, should eliminate air leaks, and should cool the injector, column, and transfer line before opening the column to the atmosphere. For further information on precluding oxidation, contact the column manufacturer.*

6.9.1.4 Column for resolution of additional congeners—See Annex A for details on the DB-1 column. The DB-1 column is optional and is capable of uniquely resolving the congener pair with IUPAC

156 and 157. When used in combination with the SPB-octyl column (Section 6.9.1.3), the two-column system is capable of resolving a total of approximately 180 CB congeners.

6.10 Mass spectrometer—28- to 40-eV electron impact ionization, must be capable of selectively monitoring a minimum of 22 exact m/z's minimum at high resolution (≥10,000) during a period less than 1.5 seconds, and must meet all of the performance specifications in Section 10.

6.11 GC/MS interface—The mass spectrometer (MS) must be interfaced to the GC such that the end of the capillary column terminates within 1 cm of the ion source but does not intercept the electron or ion beams.

6.12 Data system—Capable of collecting, recording, storing, and processing MS data.

6.12.1 Data acquisition—The signal at each exact m/z must be collected repetitively throughout the monitoring period and stored on a mass storage device.

6.12.2 Response factors and multipoint calibrations—The data system must record and maintain lists of response factors (response ratios for isotope dilution) and multipoint calibrations. Computations of relative standard deviation (RSD) are used to test calibration linearity. Statistics on initial (Section 9.4) and ongoing (Section 15.5.4) performance should be computed and maintained, either on the instrument data system, or on a separate computer system.

7.0 Reagents and standards

7.1 pH adjustment and back-extraction

7.1.1 Potassium hydroxide—Dissolve 20 g reagent grade KOH in 100 mL reagent water.

7.1.2 Sulfuric acid—Reagent grade (specific gravity 1.84).

7.1.3 Hydrochloric acid—Reagent grade, 6N.

7.1.4 Sodium chloride—Reagent grade, prepare at 5% (w/v) solution in reagent water.

7.2 Solution drying and evaporation

7.2.1 Solution drying—Sodium sulfate, reagent grade, granular, anhydrous (Baker 3375, or equivalent), rinsed with methylene chloride (20 mL/g), baked at 400 °C for 1 hour minimum, cooled in a desiccator, and stored in a pre-cleaned glass bottle with screw-cap that prevents moisture from entering. If, after heating, the sodium sulfate develops a noticeable grayish cast (due to the presence of carbon

in the crystal matrix), that batch of reagent is not suitable for use and should be discarded. Extraction with methylene chloride (as opposed to simple rinsing) and baking at a lower temperature may produce sodium sulfate that is suitable for use.

7.2.2 Tissue drying—Sodium sulfate, reagent grade, powdered, treated and stored as in Section 7.2.1.

7.2.3 Prepurified nitrogen.

7.3 Extraction

7.3.1 Solvents—Acetone, toluene, cyclohexane, hexane, methanol, methylene chloride, isooctane, and nonane; distilled in glass, pesticide quality, lot-certified to be free of interferences.

Note: *Some solvents; e.g., isooctane and nonane, may need to be re-distilled to eliminate CB backgrounds.*

7.3.2 White quartz sand, 60/70 mesh—For Soxhlet/Dean-Stark extraction (Aldrich Chemical, Cat. No. 27-437-9, or equivalent). Bake at 450 °C for 4 hour minimum.

7.4 GPC calibration solution—Prepare a solution containing 2.5 mg/mL corn oil, 0.05 mg/mL bis(2-ethylhexyl) phthalate (BEHP), 0.01 mg/mL methoxychlor, 0.002 mg/mL perylene, and 0.008 mg/mL sulfur, or at concentrations appropriate to the response of the detector.

7.5 Adsorbents for sample cleanup

7.5.1 Silica gel

7.5.1.1 Activated silica gel—100-200 mesh, Supelco 1-3651 (or equivalent), rinsed with methylene chloride, baked at 180 °C for a minimum of 1 hour, cooled in a desiccator, and stored in a precleaned glass bottle with screw-cap that prevents moisture from entering.

7.5.1.2 Acid silica gel (30% w/w)—Thoroughly mix 44 g of concentrated sulfuric acid with 100 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a screw-capped bottle with fluoropolymer-lined cap.

7.5.1.3 Basic silica gel—Thoroughly mix 30 g of 1N sodium hydroxide with 100 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a screw-capped bottle with fluoropolymer-lined cap.

7.5.1.4 Potassium silicate

7.5.1.4.1 Dissolve 56 g of high purity potassium hydroxide (Aldrich, or equivalent) in 300 mL of methanol in a 750- to 1000-mL flat-bottom flask.

7.5.1.4.2 Add 100 g of activated silica gel (Section 7.5.1.1) and a stirring bar, and stir on an explosion-proof hot plate at 60-70 °C for 1-2 hours.

7.5.1.4.3 Decant the liquid and rinse the potassium silicate twice with 100-mL portions of methanol, followed by a single rinse with 100 mL of methylene chloride.

7.5.1.4.4 Spread the potassium silicate on solvent-rinsed aluminum foil and dry for 2-4 hours in a hood. Observe the precaution in Section 4.8.

7.5.1.4.5 Activate overnight at 200-250 °C prior to use.

7.5.2 Carbon

7.5.2.1 Carbopak C—(Supelco 1-0258, or equivalent)

7.5.2.2 Celite 545—(Supelco 2-0199, or equivalent)

7.5.2.3 Thoroughly mix 18.0 g Carbopak C and 18.0 g Celite 545 to produce a 50% w/w mixture. Activate the mixture at 130 °C for a minimum of 6 hours. Store in a desiccator.

Note: *The carbon column has been included in this Method to allow separation of co-planar congeners 77, 126, and 169 from other congeners and interferences, should such separation be desired.*

7.5.3 Anthropogenic isolation column—Pack the column in Section 6.7.4.3 from bottom to top with the following:

7.5.3.1 2 g silica gel (Section 7.5.1.1)

7.5.3.2 2 g potassium silicate (Section 7.5.1.4)

7.5.3.3 2 g granular anhydrous sodium sulfate (Section 7.2.1)

7.5.3.4 10 g acid silica gel (Section 7.5.1.2)

7.5.3.5 2 g granular anhydrous sodium sulfate

7.5.4 Florisil column

7.5.4.1 Florisil—PR grade, 60-100 mesh (U.S. Silica Corp, Berkeley Springs, WV, or equivalent). Alternatively, prepacked Florisil columns may be used. Use the following procedure for Florisil activation and column packing.

7.5.4.1.1 Fill a clean 1- to 2-L bottle 1/2 to 2/3 full with Florisil and place in an oven at 130-150 °C for a minimum of three days to activate the Florisil.

7.5.4.1.2 Immediately prior to use, dry pack a 300-mm x 22-mm ID glass column (Section 6.7.4.3) bottom to top with 0.5-1.0 cm of warm to hot anhydrous sodium sulfate (Section 7.2.1), 10-10.5 cm of warm to hot activated Florisil (Section 7.5.4.1.1), and 1-2 cm of warm to hot anhydrous sodium sulfate. Allow the column to cool and wet immediately with 100 mL of n-hexane to prevent water from entering.

7.5.4.2 Using the procedure in Section 13.7.3, establish the elution pattern for each carton of Florisil or each lot of Florisil columns received.

7.6 Reference matrices—Matrices in which the CBs and interfering compounds are not detected by this Method.

7.6.1 Reagent water—Bottled water purchased locally, or prepared by passage through activated carbon.

7.6.2 High-solids reference matrix—Playground sand or similar material. Prepared by extraction with methylene chloride and/or baking at 450 °C for a minimum of 4 hours.

7.6.3 Paper reference matrix—Glass-fiber filter, Gelman type A, or equivalent. Cut paper to simulate the surface area of the paper sample being tested.

7.6.4 Tissue reference matrix—Corn or other vegetable oil.

7.6.5 Other matrices—This Method may be verified on any reference matrix by performing the tests given in Section 9.2. Ideally, the matrix should be free of the CBs, but in no case must the background level of the CBs in the reference matrix exceed the minimum levels in Table 2. If low background levels of the CBs are present in the reference matrix, the spike level of the analytes used in Section 9.2 should be increased to provide a spike-to-background ratio of approximately 5 (Reference 11).

7.7 Standard solutions—Prepare from materials of known purity and composition or purchase as solutions or mixtures with certification to their purity, concentration, and authenticity. If the chemical purity is 98 % or greater, the weight may be used without correction to calculate the concentration of the standard. Observe the safety precautions in Section 5 and the recommendation in Section 5.1.2.

7.7.1 For preparation of stock solutions from neat materials, dissolve an appropriate amount of assayed reference material in solvent. For example, weigh 1 to 2 mg of PCB 126 to three significant figures in a 10-mL ground-glass-stoppered volumetric flask and fill to the mark with nonane. After the compound is completely dissolved, transfer the solution to a clean 15-mL vial with fluoropolymer-lined cap.

7.7.2 When not being used, store standard solutions in the dark at room temperature in screw-capped vials with fluoropolymer-lined caps. Place a mark on the vial at the level of the solution so that solvent loss by evaporation can be detected. Replace the solution if solvent loss has occurred.

7.8 Native (unlabeled) stock solutions

7.8.1 Native Toxics/LOC stock solution—Prepare to contain the native Toxics and LOC CBs at the concentrations shown in Table 3, or purchase Accu-Standard M1668A-C-NT-LOC-WD-GCPC, or equivalent. If additional CBs are to be determined by isotope dilution (e.g., 170 and 180), include the additional native compounds in this stock solution.

7.8.2 Native 209 CB congener stock solutions—Solutions containing CB congeners to calibrate the SPB-octyl column.

Note: *If a column other than the SPB-octyl column is used, solutions that will allow separation of all 209 congeners on that column must be prepared.*

7.8.2.1 Native congener mix stock solutions for separation of individual congeners on the SPB-octyl column—Prepare the five solutions with the congeners listed in Table 4 at the concentrations shown in Table

3 or purchase Accu-Standard M-1668A-1, M-1668A-2, M-1668A-3, M-1668-4, and M-1668-5, or equivalent.

7.8.2.2 Combined 209 congener stock solution—Combine equal volumes of the standards in Section 7.8.2.1 to form a stock solution containing all CB congeners. This solution will be at 1/5 the concentration of the 5 individual solutions.

7.8.3 Stock solutions should be checked for signs of degradation prior to the preparation of calibration or performance test standards. Reference standards that can be used to determine the accuracy of standard solutions are available from several vendors.

7.9 Labeled compound stock solutions (Table 3)

7.9.1 Labeled Toxics/LOC/window-defining stock solution- Prepare in isooctane or nonane at the concentrations in Table 3 or purchase Cambridge Isotope Laboratories (CIL) EC-4977, or equivalent. If additional CBs are to be determined by isotope dilution (e.g., 170 and 180), include the additional labeled compounds in this stock solution.

7.9.2 Labeled cleanup standard stock solution-Prepare labeled CBs 28, 111, and 178 in iso-octane or nonane at the concentration shown in Table 3 or purchase CIL EC-4978, or equivalent.

7.9.3 Labeled injection internal standard stock solution—Prepare labeled CBs 9, 52, 101, 138, and 194 in nonane or isooctane at the concentrations shown in Table 3, or purchase CIL EC-4979, or equivalent.

7.10 Calibration standards

7.10.1 Calibration standards—Combine and dilute the solutions in Sections 7.8.1 and 7.9 to produce the calibration solutions in Table 5 or purchase CIL EC-4976, or equivalent, for the CS-1 to CS-5 set of calibration solutions. If a 6-point calibration is used, prepare the CS-0.2 solution or purchase CIL EC-4976-0.2, or equivalent. These solutions permit the relative response (labeled to native) and response factor to be measured as a function of concentration. The CS-3 standard (CIL EC-4976-3, or equivalent) is used for calibration verification (VER).

7.10.2 Solutions of congener mixes

7.10.2.1 Diluted individual solutions

7.10.2.1.1 The 5 individual solutions, when analyzed individually,

allow resolution of all 209 congeners on the SPB-octyl column, and are used for establishing retention time and other data for each congener. The elution order of the congeners present in each of the 5 solutions (Section 7.8.2.1) is given in Table 4.

7.10.2.1.2 Individually combine an aliquot of each individual mix stock solution (Section 7.8.2.1) with an aliquot of the Labeled Toxics/LOC/window-defining stock solution (Section 7.9.1), the Labeled cleanup standard stock solution (Section 7.9.2), and the Labeled injection internal standard stock solution (7.9.3) to produce concentrations of 100 ng/mL for the labeled compounds and 25, 50, and 75 ng/mL for the MoCB-TrCB, TeCB-HpCB, and OcCB-DeCB congeners, respectively, as shown in Table 3.

7.10.2.2 Diluted combined 209 congener solution

7.10.2.2.1 This solution combines the 5 individual mixes with the labeled compounds to allow single-point calibration of the congeners not included in the multi-point calibration, and establishes an average response factor for the co-eluting isomeric congeners.

7.10.2.2.2 Combine an aliquot of the combined 209 congener solution (Section 7.8.2.2) with an aliquot of the Labeled Toxics/LOC/window-defining stock solution (Section 7.9.1), the Labeled cleanup standard stock solution (Section 7.9.2), and the Labeled injection internal standard stock solution (7.9.3) to produce the same concentrations as in the diluted individual mix solutions (Section 7.10.2.1.2 and Table 3).

7.11 Native Toxics/LOC standard spiking solution—Used for determining initial precision and recovery (IPR; Section 9.2) and ongoing precision and recovery (OPR; Section 15.5). Dilute the Native Toxics/LOC stock solution (Section 7.8.1) with acetone to produce a concentration of the Toxics at 1 ng/mL, as shown in Table 3. When 1 mL of this solution spiked into the IPR (Section 9.2.1) or OPR (Section 15.5) and concentrated to a final volume of 20 μL, the concentration in the final volume will be 50 ng/mL (50 pg/μL). Prepare only the amount necessary for each reference matrix with each sample batch.

7.12 Labeled Toxics/LOC/window-defining standard spiking solution—This solution is spiked into each sample (Section 9.3) and into the IPR (Section 9.2.1), OPR (Section

15.5), and blank (Section 9.5) to measure recovery. Dilute the Labeled Toxics/LOC/ window-defining stock solution (Section 7.9.1) with acetone to produce a concentration of the labeled compounds at 2 ng/mL, as shown in Table 3. When 1 mL of this solution is spiked into an IPR, OPR, blank, or sample and concentrated to a final extract volume of 20 μL, the concentration in the final extract volume will be 100 ng/mL (100 pg/μL). Prepare only the amount necessary for each reference matrix with each sample batch.

7.13 Labeled cleanup standard spiking solution—This solution is spiked into each extract prior to cleanup to measure the efficiency of the cleanup process. Dilute the Labeled cleanup standard stock solution (Section 7.9.2) in methylene chloride to produce a concentration of the cleanup standards at 2 ng/mL, as shown in Table 3. When 1 mL of this solution is spiked into a sample extract and concentrated to a final volume of 20 μL, the concentration in the final volume will be 100 ng/mL (100 pg/μL).

7.14 Labeled injection internal standard spiking solution—This solution is added to each concentrated extract prior to injection into the HRGC/HRMS. Dilute the Labeled injection internal standard stock solution (Section 7.9.3) in nonane to produce a concentration of the injection internal standards at 1000 ng/mL, as shown in Table 3. When 2 μL of this solution is spiked into a 20 μL extract, the concentration of each injection internal standard will be nominally 100 ng/mL (100 pg/μL).

Note: *The addition of 2 μL of the Labeled injection internal standard spiking solution to a 20 μL final extract has the effect of diluting the concentration of the components in the extract by 10%. Provided all calibration solutions and all extracts undergo this dilution as a result of adding the Labeled injection internal standard spiking solution, the effect of the 10% solution is compensated, and correction for this dilution should not be made.*

7.15 QC Check Sample—A QC Check Sample should be obtained from a source independent of the calibration standards. Ideally, this check sample would be a certified Standard Reference Material (SRM) containing the CBs in known concentrations in a sample matrix similar to the matrix under test. The National Institute of Standards and Technology (NIST) in Gaithersburg, Maryland has SRMs for several individual CB congeners, and as Aroclors in transformer and motor oil, in combination with pesticides in cod liver oil, and in combination with 2,3,7,8-TCDD in human serum.

7.16 Stability of solutions—Standard solutions used for quantitative purposes (Sections 7.9 through 7.14) should be assayed periodically (e.g., every 6 months) against SRMs from NIST (if available), or certified reference materials from a source that will attest to the authenticity and concentration, to assure that the composition and concentrations have not changed.

8.0 Sample collection, preservation, storage, and holding times

8.1 Collect samples in amber glass containers following conventional sampling practices (Reference 13).

8.2 Aqueous samples

8.2.1 Samples that flow freely are collected as grab samples or in refrigerated bottles using automatic sampling equipment.

8.2.2 If residual chlorine is present, add 80 mg sodium thiosulfate per liter of water. EPA Methods 330.4 and 330.5 may be used to measure residual chlorine (Reference 11).

8.2.3 Adjust sample pH 2-3 with sulfuric acid.

8.2.4 Maintain aqueous samples in the dark at 0-4 °C from the time of collection until receipt at the laboratory. Store in the dark at 0-4 °C.

8.3 Solid samples

8.3.4 Solid samples are collected as grab samples using wide-mouth jars.

8.3.4 Maintain solid, semi-solid, oily, and mixed-phase samples in the dark at <4 °C from the time of collection until receipt at the laboratory. Store solid, semi-solid, oily, and mixed-phase samples in the dark at <-10 °C.

8.4 Fish and other tissue samples

8.4.1 Fish may be cleaned, filleted, or processed in other ways in the field, such that the laboratory may expect to receive whole fish, fish fillets, or other tissues for analysis.

8.4.2 Fish collected in the field should be wrapped in aluminum foil, and must be maintained at a temperature less than 4 °C from the time of collection until receipt at the laboratory. Ideally, fish should be frozen upon collection and shipped to the laboratory under dry ice.

8.4.3 Tissue samples must be frozen upon receipt at the laboratory and maintained in the dark at <-10 °C until prepared. Maintain unused sample in the dark at <-10 °C.

8.5 Holding times

8.5.1 There are no demonstrated maximum holding times associated with the CBs in

aqueous, solid, semi-solid, tissues, or other sample matrices. If stored in the dark at 0-4 °C and preserved as given above (if required), aqueous samples may be stored for up to one year. Similarly, if stored in the dark at <-10 °C, solid, semi-solid, multi-phase, and tissue samples may be stored for up to one year.

8.5.2 Store sample extracts in the dark at <-10 °C until analyzed. If stored in the dark at <-10 °C, sample extracts may be stored for up to one year.

9.0 Quality assurance/quality control

9.1 Each laboratory that uses this Method is required to operate a formal quality assurance program (Reference 15). The minimum requirements of this program consist of an initial demonstration of laboratory capability, analysis of samples spiked with labeled compounds to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the Method.

If the Method is to be applied to sample matrix other than water (e.g., soils, filter cake, compost, tissue) the most appropriate alternate reference matrix (Sections 7.6.2 - 7.6.5 and 7.15) is substituted for the reagent water matrix (Section 7.6.1) in all performance tests.

9.1.1 The laboratory must make an initial demonstration of the ability to generate acceptable precision and recovery with this Method. This demonstration is given in Section 9.2.

9.1.2 In recognition of advances that are occurring in analytical technology, and to overcome matrix interferences, the laboratory is permitted certain options to improve separations or lower the costs of measurements. These options include alternate extraction, concentration, and cleanup procedures, and changes in columns and detectors. Alternate determinative techniques, such as the substitution of spectroscopic or immuno-assay techniques, and changes that degrade Method performance, are not allowed. If an analytical technique other than the techniques specified in this Method is used, that technique must have a specificity equal to or greater than the specificity of the techniques in this Method for the analytes of interest.

9.1.2.1 Each time a modification is made to this Method, the laboratory is required to repeat the procedure in Section 9.2. If the detection limit of the Method will be affected by the change, the laboratory is required to demonstrate that the MDLs (40 CFR Part 136, Appendix B) are lower than one-third the regulatory compliance level or one-third the EMDLs in this Method, whichever are greater. If calibration will be affected by the change, the instrument must be

recalibrated per Section 10.

9.1.2.2 The laboratory is required to maintain records of modifications made to this Method. These records include the following, at a minimum:

9.1.2.2.1 The names, titles, addresses, and telephone numbers of the analyst(s) that performed the analyses and modification, and of the quality control officer that witnessed and will verify the analyses and modifications.

9.1.2.2.2 A listing of pollutant(s) measured, by name and CAS Registry number.

9.1.2.2.3 A narrative stating reason(s) for the modifications.

9.1.2.2.4 Results from all quality control (QC) tests comparing the modified method to this Method, including:

a) Calibration (Section 10).
b) Calibration verification (Section 15.3).
c) Initial precision and recovery (Section 9.2).
d) Labeled compound recovery (Section 9.3).
e) Analysis of blanks (Section 9.5).
f) Accuracy assessment (Section 9.4).

9.1.2.2.5 Data that will allow an independent reviewer to validate each determination by tracing the instrument output (peak height, area, or other signal) to the final result. These data are to include:

a) Sample numbers and other identifiers.
b) Extraction dates.
c) Analysis dates and times.
d) Analysis sequence/run chronology.
e) Sample weight or volume (Section 11).
f) Extract volume prior to each cleanup step (Section 13).
g) Extract volume after each cleanup step (Section 13).
h) Final extract volume prior to injection (Section 14).
i) Injection volume (Section 14.3).
j) Dilution data, differentiating between dilution of a sample or extract (Section 17.5).

k) Instrument and operating conditions.
l) Column (dimensions, liquid phase, solid support, film thickness, etc)
m) Operating conditions (temperatures, temperature program, flow rates)
n) Detector (type, operating conditions, etc).
o) Chromatograms, printer tapes, and other recordings of raw data.
p) Quantitation reports, data system outputs, and other data to link the raw data to the results reported.

9.1.2.3 Alternate HRGC columns and column systems—See Sections 6.9.1. If a column or column system alternate to those specified in this Method is used, that column or column system must meet the requirements in Section 6.9.1 - 6.9.1.1.3.

9.1.3 Analyses of method blanks are required to demonstrate freedom from contamination (Section 4.3). The procedures and criteria for analysis of a method blank are described in Sections 9.5 and 15.6.

9.1.4 The laboratory must spike all samples with labeled compounds to monitor Method performance. This test is described in Section 9.3. When results of these spikes indicate atypical Method performance for samples, the samples are diluted to bring Method performance within acceptable limits. Procedures for dilution are given in Section 17.5.

9.1.5 The laboratory must, on an ongoing basis, demonstrate through calibration verification and the analysis of the ongoing precision and recovery standard (OPR) and blanks that the analytical system is in control. These procedures are given in Sections 15.1 through 15.6.

9.1.6 The laboratory should maintain records to define the quality of data generated. Development of accuracy statements is described in Section 9.4.

9.2 Initial precision and recovery (IPR)—To establish the ability to generate acceptable precision and recovery, the laboratory must perform the following operations.

9.2.1 For low solids (aqueous) samples, extract, concentrate, and analyze four 1-L aliquots of reagent water spiked with 1 mL each of the Native Toxics/LOC spiking solution (Section 7.11), the Labeled Toxics/LOC/window-defining standard spiking solution (Section 7.12), and the Labeled cleanup standard spiking solution (Section 7.13), according to the procedures in Sections 11 through 18. For an alternative sample matrix, four aliquots of the alternative reference matrix (Section 7.6) are used. All sample processing steps that are to

be used for processing samples, including preparation (Section 11), extraction (Section 12), and cleanup (Section 13), must be included in this test.

9.2.2 Using results of the set of four analyses, compute the average percent recovery (X) of the extracts and the relative standard deviation (RSD) of the concentration for each compound, by isotope dilution for CBs with a labeled analog, and by internal standard for CBs without a labeled analog and for the labeled compounds.

9.2.3 For each CB and labeled compound, compare RSD and X with the corresponding limits for initial precision and recovery in Table 6. If RSD and X for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, any individual RSD exceeds the precision limit or any individual X falls outside the range for recovery, system performance is unacceptable for that compound. Correct the problem and repeat the test (Section 9.2).

9.3 To assess Method performance on the sample matrix, the laboratory must spike all samples with the Labeled Toxics/LOC/window-defining standard spiking solution (Section 7.12) and all sample extracts with the Labeled cleanup standard spiking solution (Section 7.13).

9.3.1 Analyze each sample according to the procedures in Sections 11 through 18.

9.3.2 Compute the percent recovery of the labeled Toxics/LOC/window-defining congeners and the labeled cleanup congeners using the internal standard method (Section 17.2).

9.3.3 The recovery of each labeled compound must be within the limits in Table 6. If the recovery of any compound falls outside of these limits, Method performance is unacceptable for that compound in that sample. Additional cleanup procedures must then be employed to attempt to bring the recovery within the normal range. If the recovery cannot be brought within the normal range after all cleanup procedures have been employed, water samples are diluted and smaller amounts of soils, sludges, sediments, and other matrices are analyzed per Section 18.

9.4 It is suggested but not required that recovery of labeled compounds from samples be assessed and records maintained.

9.4.1 After the analysis of 30 samples of a given matrix type (water, soil, sludge, pulp, etc.) for which the labeled compounds pass the tests in Section 9.3, compute the average percent recovery (R) and the standard deviation of the percent recovery (S_R) for the labeled compounds only. Express the assessment as a percent recovery interval from $R - 2S_R$ to $R + 2S_R$ for each matrix. For example, if R =

90% and S_R = 10% for five analyses of pulp, the recovery interval is expressed as 70 to 110%.

9.4.2 Update the accuracy assessment for each labeled compound in each matrix on a regular basis (e.g., after each five to ten new measurements).

9.5 Method blanks—A reference matrix Method blank is analyzed with each sample batch (Section 4.3) to demonstrate freedom from contamination. The matrix for the Method blank must be similar to the sample matrix for the batch, e.g., a 1-L reagent water blank (Section 7.6.1), high-solids reference matrix blank (Section 7.6.2), paper matrix blank (Section 7.6.3), tissue blank (Section 7.6.4), or alternative reference matrix blank (Section 7.6.5).

9.5.1 Spike 1.0 mL each of the Labeled Toxics/LOC/window-defining standard spiking solution (Section 7.12), and the Labeled cleanup standard spiking solution (Section 7.13) into the Method blank, according to the procedures in Sections 11 through 18. Prepare, extract, clean up, and concentrate the Method blank. Analyze the blank immediately after analysis of the OPR (Section 15.5) to demonstrate freedom from contamination.

9.5.2 If any CB (Table 1) is found in the blank at greater than the minimum level (Table 2) or one-third the regulatory compliance limit, whichever is greater, or if any potentially interfering compound is found in the blank at the minimum level for each CB given in Table 2 (assuming a response factor of 1 relative to the quantitation reference in Table 2 at that level of chlorination for a potentially interfering compound; i.e., a compound not listed in this Method), analysis of samples must be halted until the sample batch is re-extracted and the extracts re-analyzed, and the blank associated with the sample batch shows no evidence of contamination at these levels. All samples must be associated with an uncontaminated Method blank before the results for those samples may be reported or used for permitting or regulatory compliance purposes.

9.6 QC Check Sample—Analyze the QC Check Sample (Section 7.15) periodically to assure the accuracy of calibration standards and the overall reliability of the analytical process. It is suggested that the QC Check Sample be analyzed at least quarterly.

9.7 The specifications contained in this Method can be met if the apparatus used is calibrated properly and then maintained in a calibrated state. The standards used for calibration (Section 10), calibration verification (Section 15.3), and for initial (Section 9.2) and ongoing (Section 15.5) precision and recovery should be identical, so that the most precise results will be obtained. A GC/MS instrument will provide the most reproducible results if dedicated to the settings and conditions required for determination of CBs by this Method.

9.8 Depending on specific program requirements, field replicates may be collected to determine the precision of the sampling technique, and spiked samples may be required to determine the accuracy of the analysis when the internal standard method is used.

10.0 Calibration

10.1 Establish the operating conditions necessary to meet the retention times (RTs) and relative retention times (RRTs) for the CBs in Table 2.

10.1.1 Suggested GC operating conditions.

Injector temperature:	270 °C
Interface temperature:	290 °C
Initial temperature:	75 °C
Initial time:	2 minutes
Temperature program:	75-150 °C @ 15 °C/minute
	150-290 °C @ 2.5 °C/minute
Final time:	1 minute

Note: *All portions of the column that connect the GC to the ion source should remain at or above the interface temperature specified above during analysis to preclude condensation of less volatile compounds.*

The GC conditions may be optimized for compound separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, blanks, IPR and OPR standards, and samples.

10.1.2 Retention time calibration for the CB congeners.

10.1.2.1 Separately inject each of the diluted individual congener solutions (Section 7.10.2.1.2). Establish the beginning and ending retention times for the scan descriptors in Table 7. Scan descriptors other than those listed in Table 7 may be used provided the MLs in Table 2 are met. Store the retention time (RT) and relative retention time (RRT) for each congener in the data system.

10.1.2.2 The absolute retention time of CB 209 must exceed 55 minutes on the SPB-octyl column; otherwise, the GC temperature program must be adjusted and this test repeated until the minimum retention time criterion is met. If a GC column or column system alternate to the SPB-octyl column is used, a similar minimum retention time specification must be established for the alternate column or column systems so that interferences that may be encountered in environmental samples will be resolved from the analytes of interest.

This specification is deemed to be met if the retention time of CB 209 is greater than 55 minutes on such alternate column.

10.1.2.3 Inject the Diluted combined 209 congener solution (Section 7.10.2.2 and Table 5). Adjust the chromatographic conditions and scan descriptors until the RT and RRT for all congeners are within the windows in Table 2 and the column performance specifications in Sections 6.9.1 - 6.9.1.2 are met. If an alternate column is used, adjust the conditions for that column. If column performance is unacceptable, optimize the analysis conditions or replace the column and repeat the performance tests. Confirm that the scan descriptor changes at times when CBs do not elute.

10.1.2.4 After the column performance tests are passed (Section 10.1.2.2 - 10.1.2.3), store the RT and RRT for the resolved congeners and the RT and RRT for the isomeric congeners that co-elute.

10.2 Mass spectrometer (MS) resolution

10.2.1 Using PFK (or other reference substance) and a molecular leak, tune the instrument to meet the minimum required resolving power of 10,000 (10% valley) at m/z 330.9792 or any other significant PFK fragment in the range of 300 to 350. For each descriptor (Table 7), monitor and record the resolution and exact m/z's of three to five reference peaks covering the mass range of the descriptor. The level of PFK (or other reference substance) metered into the HRMS during analyses should be adjusted so that the amplitude of the most intense selected lock-mass m/z signal (regardless of the descriptor number) does not exceed 10% of the full-scale deflection for a given set of detector parameters. Under those conditions, sensitivity changes that might occur during the analysis can be more effectively monitored.

Note: *Different lots and types of PFK can contain varying levels of contamination, and excessive PFK (or other reference substance) may cause noise problems and contamination of the ion source necessitating increased frequency of source cleaning.*

10.2.2 The analysis time for CBs may exceed the long-term mass stability of the mass spectrometer. Because the instrument is operated in the high-resolution mode, mass drifts of a few ppm (e.g., 5 ppm in mass) can have serious adverse effects on instrument performance. Therefore, mass-drift correction is mandatory and a lock-mass m/z from perfluorokerosene (PFK) or other reference substance is used for drift correction. The lock-mass m/z is dependent on the exact m/z's monitored within each descriptor, as shown in Table 7. The deviation between the exact m/z and the theoretical m/z (Table 7) for each exact m/z monitored must be less than 5 ppm.

10.2.3 Obtain a selected ion current profile (SICP) at the two exact m/z's specified in Table 7 and at ≥10,000 resolving power at each LOC for the native congeners and congener groups and for the labeled congeners. Because of the extensive mass range covered in each function, it may not be possible to maintain 10,000 resolution throughout the mass range during the function. Therefore, resolution must be ≥8,000 throughout the mass range and must be ≥10,000 in the center of the mass range for each function.

10.2.4 If the HRMS has the capability to monitor resolution during the analysis, it is acceptable to terminate the analysis when the resolution falls below the minimum (Section 10.2.1.3) to save re-analysis time.

10.3 Ion abundance ratios, minimum levels, and signal-to-noise ratios. Choose an injection volume of either 1 or 2 µL, consistent with the capability of the HRGC/HRMS instrument. Inject a 1 or 2 µL aliquot of the CS-1 calibration solution (Table 5) using the GC conditions in Section 10.1.1.

10.3.1 Measure the SICP areas for each congener or congener group, and compute the ion abundance ratios at the exact m/z's specified in Table 7. Compare the computed ratio to the theoretical ratio given in Table 8.

10.3.1.1 The exact m/z's to be monitored in each descriptor are shown in Table 7. Each group or descriptor must be monitored in succession as a function of GC retention time to ensure that the CBs of interest are detected. Additional m/z's may be monitored in each descriptor, and the m/z's may be divided among more than the descriptors listed in Table 7, provided that the laboratory is able to monitor the m/z's of all CBs that may elute from the GC in a given LOC window. The laboratory must also monitor exact m/z's for congeners at higher levels of chlorination to determine if fragments will compromise measurement of congeners at lower levels of chlorination.

10.3.1.2 The mass spectrometer must be operated in a mass-drift correction mode, using PFK (or other reference substance) to provide lock m/z's. The lock mass for each group of m/z's is shown in Table 7. Each lock mass must be monitored and must not vary by more than ±20% throughout its respective retention time window. Variations of lock mass by more than 20% indicate the presence of co-eluting interferences that raise the source pressure and may significantly reduce the sensitivity of the mass spectrometer. Re-injection of another aliquot of the sample extract may not resolve the problem and additional cleanup of the extract may be required to remove the interference. A lock mass interference or suppression in a retention time region in which CBs and labeled compounds do not elute may be ignored.

10.3.2 All CBs and labeled compounds in the CS-1 standard must be within the QC limits in Table 8 for their respective ion abundance ratios; otherwise, the mass spectrometer must be adjusted and this test repeated until the m/z ratios fall within the limits specified. If the adjustment alters the resolution of the mass spectrometer, resolution must be verified (Section 10.2.1) prior to repeat of the test.

10.3.3 Verify that the HRGC/HRMS instrument meets the estimated minimum levels (EMLs) in Table 2. The peaks representing the CBs and labeled compounds in the CS-1 calibration standard must have signal-to-noise ratios (S/N) ≥ 10; otherwise, the mass spectrometer must be adjusted and this test repeated until the minimum levels in Table 2 are met.

Note: *The EMDLs and EMLs in Table 2 are based on the levels of contamination normally found in laboratories. Lower levels may be readily achievable if segregation and extensive cleaning of glassware is employed. If lower levels are achievable, these levels must be established as described in Section 17.6.1.4.1.*

10.4 Calibration by isotope dilution—Isotope dilution is used for calibration of the Toxics/LOC CBs. The reference compound for each native compound its labeled analog, as listed in Table 2. A 5- or 6-point calibration encompassing the concentration range is prepared for each native congener.

10.4.1 For the Toxics/LOC CBs determined by isotope dilution, the relative response (RR) (labeled to native) vs. concentration in the calibration solutions (Table 5) is computed over the calibration range according to the procedures described below. Five calibration points are employed for less-sensitive HRMS instruments (e.g., VG 70); five or six points may be employed for more-sensitive instruments (e.g., Micromass Autospec Ultima).

10.4.2 The response of each Toxics/LOC CB relative to its labeled analog is determined using the area responses of both the primary and secondary exact m/z's specified in Table 7, for each calibration standard, as follows:

$$RR = \frac{(A1_n + A2_n)\,C_l}{(A1_l + A2_l)\,C_n}$$

Where:

$A1_n$ *and* $A2_n$ = *The areas of the primary and secondary m/z's for the PCB.*

$A1_l$ *and* $A2_l$ = *The areas of the primary and secondary m/z's for the labeled compound.*

C_l = *The concentration of the labeled compound in the calibration standard (Table 5).*

C_n = *The concentration of the native compound in the calibration standard (Table 5).*

10.4.3 To calibrate the analytical system by isotope dilution, inject calibration standards CS-1 through CS-5 (Section 7.10 and Table 5) for a less sensitive instrument or CS-0.2 through CS-5 for a more sensitive instrument. Use a volume identical to the volume chosen in Section 10.3, the procedure in Section 14, and the conditions in Section 10.1.1. Compute and store the relative response (RR) for each Native Toxics/LOC CB at each concentration. Compute the average (mean) RR and the RSD of the 5 (or 6) RRs.

10.4.4 Linearity—If the RR for any Native Toxics/LOC CB is constant (less than 20% RSD), the average RR may be used for that congener, otherwise, the complete calibration curve for that congener must be used over the calibration range.

10.5 Calibration by internal standard—Internal standard calibration is applied to determination of the native CBs for which a labeled compound is not available, to determination of the Labeled Toxics/LOC/window-defining congeners and Labeled cleanup congeners for performance tests and intra-laboratory statistics (Sections 9.4 and 15.5.4), and to determination of the Labeled injection internal standards except for CB 178. The reference compound for each compound is listed in Table 2. For the native congeners (other than the Native Toxics/LOC CBs), calibration is performed at a single point using the CS-3 (VER) standard. For the labeled compounds, calibration is performed using data from the 5 (or 6) points in the calibration for the Native Toxics/LOC CBs (Section 10.4).

10.5.1 Response factors—Internal standard calibration requires the determination of response factors (RF) defined by the following equation:

$$RF = \frac{(A1_x + A2_x)\, C_{is}}{(A1_{is} + A2_{is})\, C_x}$$

Where,

$A1_x$ *and* $A2_x$ = *The areas of the primary and secondary m/z's for the PCB.*

$A1_{is}$ *and* $A2_{is}$ = *The areas of the primary and secondary m/z's for the internal standard.*

C_{is} = *The concentration of the internal standard (Table 5).*

C_x = *The concentration of the compound in the calibration standard (Table 5).*

10.5.2 To single-concentration calibrate the analytical system for native CBs other than the Native Toxics/LOC CBs by internal standard, inject the Diluted combined 209 congener solution (Section 7.10.2.2 and Table 3). Use a volume identical to the volume chosen in Section 10.3, the procedure in Section 14, and the conditions in Section 10.1.1.

10.5.3 Compute and store the response factor (RF) for all native CBs except the Native Toxics/LOC CBs. Use the average (mean) response of the labeled compounds at each level of chlorination (LOC) as the quantitation reference, as shown in Table 2. For the combinations of isomeric congeners that co-elute, compute a

combined RF for the co-eluted group. For example, for congener 122, the areas at the two exact m/z's for 104L, 105L, 114L, 123L, 118L, and 126L are summed and the total area is divided by 6 (because there are 6 congeners in the quantitation reference).

Note: *All labeled congeners at each LOC are used as reference to reduce the effect of an interference if a single congener is used as reference. Other quantitation references and procedures may be used provided that the results produced are as accurate as results produced by the quantitation references and procedures described in this Section.*

10.5.4 Compute and store the response factor (RF) for the labeled compounds, except CB 178. For the Labeled Toxics/LOC/window-defining compounds and the Labeled cleanup standards, use the nearest eluted Labeled injection internal standard as the quantitation reference, as given in Table 2. The Labeled injection internal standards are referenced to CB 178, as shown in Table 2.

11.0 Sample preparation

11.1 Sample preparation involves modifying the physical form of the sample so that the CBs can be extracted efficiently. In general, the samples must be in a liquid form or in the form of finely divided solids in order for efficient extraction to take place. Table 9 lists the phases and suggested quantities for extraction of various sample matrices.

For samples known or expected to contain high levels of the CBs, the smallest sample size representative of the entire sample should be used (see Section 18). For all samples, the blank and IPR/OPR aliquots must be processed through the same steps as the sample to check for contamination and losses in the preparation processes.

11.1.1 For samples that contain particles, percent solids and particle size are determined using the procedures in Sections 11.2 and 11.3, respectively.

11.1.2 Aqueous samples—Because CBs may be bound to suspended particles, the preparation of aqueous samples is dependent on the solids content of the sample.

11.1.2.1 Aqueous samples containing one percent solids or less are prepared per Section 11.4 and extracted directly using one of the extraction techniques in Section 12.2.

11.1.2.2 For aqueous samples containing greater than one percent solids, a sample aliquot sufficient to provide 10 g of dry solids is used, as described in Section 11.5.

11.1.3 Solid samples are prepared using the procedure described in Section 11.5 followed by extraction using the SDS procedure in Section 12.3.

11.1.4 Multi-phase samples—The phase(s) containing the CBs is separated from the non-CB phase using pressure filtration and centrifugation, as described in Section 11.6. The CBs will be in the organic phase in a multi-phase sample in which an organic phase exists.

11.1.5 Procedures for grinding, homogenization, and blending of various sample phases are given in Section 11.7.

11.1.6 Tissue samples—Preparation procedures for fish and other tissues are given in Section 11.8.

11.2 Determination of percent suspended solids

Note: *This aliquot is used for determining the solids content of the sample, not for determination of CBs.*

11.2.1 Aqueous liquids and multi-phase samples consisting of mainly an aqueous phase.

11.2.1.1 Desiccate and weigh a GF/D filter (Section 6.5.3) to three significant figures.

11.2.1.2 Filter 10.0 ± 0.02 mL of well-mixed sample through the filter.

11.2.1.3 Dry the filter a minimum of 12 hours at 110 ± 5 °C and cool in a desiccator.

11.2.1.4 Calculate percent solids as follows:

$$\%\ solids = \frac{weight\ of\ sample\ aliquot\ after\ drying\ (g) - weight\ of\ filter\ (g)}{10\ g} \times 100$$

11.2.2 Non-aqueous liquids, solids, semi-solid samples, and multi-phase samples in which the main phase is not aqueous, but not tissues.

11.2.2.1 Weigh 5 to 10 g of sample to three significant figures in a tared beaker.

11.2.2.2 Dry a minimum of 12 hours at 110 ± 5 °C, and cool in a desiccator.

11.2.2.3 Calculate percent solids as follows.

$$\%\ solids = \frac{weight\ of\ sample\ aliquot\ after\ drying}{weight\ of\ sample\ aliquot\ before\ drying} \times 100$$

11.3 Estimation of particle size.

11.3.1 Spread the dried sample from Section 11.2.2.2 on a piece of filter paper or aluminum foil in a fume hood or glove box.

11.3.2 Estimate the size of the particles in the sample. If the size of the largest particles is greater than 1 mm, the particle size must be reduced to 1 mm or less prior to extraction using the procedures in Section 11.7.

11.4 Preparation of aqueous samples containing one percent suspended solids or less.

11.4.1 Aqueous samples containing one percent suspended solids or less are prepared using the procedure below and extracted using the one of the extraction techniques in Section 12.2.

11.4.2 Preparation of sample and QC aliquots.

11.4.2.1 Mark the original level of the sample on the sample bottle for reference. Weigh the sample plus bottle to ±1 g.

11.4.2.2 Spike 1.0 mL of the Labeled Toxics/LOC/window-defining standard spiking solution (Section 7.12) into the sample bottle. Cap the bottle and mix the sample by careful shaking. Allow the sample to equilibrate for 1 to 2 hours, with occasional shaking.

11.4.2.3 For each sample or sample batch (to a maximum of 20 samples) to be extracted during the same 12-hour shift, place two 1.0-L aliquots of reagent water in clean sample bottles or flasks.

11.4.2.4 Spike 1.0 mL of the Labeled Toxics/LOC/window-defining standard spiking solution (Section 7.12) into both reagent water aliquots. One of these aliquots will serve as the Method blank.

11.4.2.5 Spike 1.0 mL of the Native Toxics/LOC standard spiking solution (Section 7.11) into the remaining reagent water aliquot. This aliquot will serve as the OPR (Section 15.5).

11.4.2.6 For extraction using SPE, add 5 mL of methanol to the sample and QC aliquots. Cap and shake the sample and QC aliquots to mix thoroughly, and proceed to Section 12.2 for extraction.

11.5 Preparation of samples containing greater than one percent solids.

11.5.1 Weigh a well-mixed aliquot of each sample (of the same matrix type) sufficient to provide 10 g of dry solids (based on the solids determination in Section 11.2) into a clean beaker or glass jar.

11.5.2 Spike 1.0 mL of the Labeled Toxics/LOC/window-defining standard spiking solution (Section 7.12) into the sample.

11.5.3 For each sample or sample batch (to a maximum of 20 samples) to be extracted during the same 12 hour shift, weigh two 10-g aliquots of the appropriate reference matrix (Section 7.6) into clean beakers or glass jars.

11.5.4 Spike 1.0 mL of the Labeled Toxics/LOC/window-defining standard spiking solution (Section 7.12) into both reference matrix aliquots. Spike 1.0 mL of the Native Toxics/LOC standard spiking solution (Section 7.11) into one reference matrix aliquot. This aliquot will serve as the OPR (Section 15.5). The other aliquot will serve as the Method blank.

11.5.5 Stir or tumble and equilibrate the aliquots for 1 to 2 hours.

11.5.6 Decant excess water. If necessary to remove water, filter the sample through a glass-fiber filter and discard the aqueous liquid.

11.5.7 If particles >1 mm are present in the sample (as determined in Section 11.3.2), spread the sample on clean aluminum foil in a hood. After the sample is dry, grind to reduce the particle size (Section 11.7).

11.5.8 Extract the sample and QC aliquots using the SDS procedure in Section 12.3.

11.6 Multi-phase samples.

11.6.1 Using the percent solids determined in Section 11.2.1 or 11.2.2, determine the volume of sample that will provide 10 g of solids, up to 1 L of sample.

11.6.2 Spike 1.0 mL of the Labeled Toxics/LOC/window-defining standard spiking solution (Section 7.12) into the amount of sample determined in Section 11.6.1, and into the OPR and blank. Spike 1.0 mL of the Native Toxics/LOC standard spiking solution (Section 7.11) into the OPR. Pressure filter the sample, blank, and OPR through Whatman GF/D glass-fiber filter paper (Section 6.5.3). If necessary to separate the phases and/or settle the solids, centrifuge these aliquots prior to filtration.

11.6.3 Discard any aqueous phase (if present). Remove any non-aqueous liquid present and reserve the maximum amount filtered from the sample (Section 11.6.1) or 10 g, whichever is less, for combination with the solid phase (Section 12.3.5).

11.6.4 If particles >1 mm are present in the sample (as determined in Section 11.3.2) and the sample is capable of being dried, spread the sample and QC aliquots on clean aluminum foil in a hood. Observe the precaution in Section 4.8.

11.6.5 After the aliquots are dry or if the sample cannot be dried, reduce the particle size using the procedures in Section 11.7 and extract the reduced-size particles using the SDS procedure in Section 12.3. If particles >1 mm are not present, extract the particles and filter in the sample and QC aliquots directly using the SDS procedure in Section 12.3.

11.7 Sample grinding, homogenization, or blending. Samples with particle sizes greater than 1 mm (as determined in Section 11.3.2) are subjected to grinding, homogenization, or blending. The method of reducing particle size to less than 1 mm is matrix-dependent. In general, hard particles can be reduced by grinding with a mortar and pestle. Softer particles can be reduced by grinding in a Wiley mill or meat grinder, by homogenization, or in a blender.

11.7.1 Each size-reducing preparation procedure on each matrix must be verified by running the tests in Section 9.2 before the procedure is employed routinely.

11.7.2 The grinding, homogenization, or blending procedures must be carried out in a glove box or fume hood to prevent particles from contaminating the work environment.

11.7.3 Grinding—Certain papers and pulps, slurries, and amorphous solids can be ground in a Wiley mill or heavy duty meat grinder. In some cases, reducing the temperature of the sample to freezing or to dry ice or liquid nitrogen temperatures can aid in the grinding process. Grind the sample aliquots from Sections 11.5.7 or 11.6.5 in a clean grinder. Do not allow the sample temperature to exceed 50 °C. Grind the blank and reference matrix aliquots using a clean grinder.

11.7.4 Homogenization or blending—Particles that are not ground effectively, or particles greater than 1 mm in size after grinding, can often be reduced in size by high speed homogenization or blending. Homogenize and/or blend the particles or filter from Sections 11.5.7 or 11.6.5 for the sample, blank, and OPR aliquots.

11.7.5 Extract the aliquots using the SDS procedure in Section 12.3.

11.8 Fish and other tissues. Prior to processing tissue samples, the laboratory must determine the exact tissue to be analyzed. Common requests for analysis of fish tissue include whole fish-skin on, whole fish-skin removed, edible fish fillets (filleted in the field or by the laboratory), specific organs, and other portions. Once the appropriate tissue has been determined, the sample must be homogenized.

11.8.1 Homogenization

11.8.1.1 Samples are homogenized while still frozen, where practical. If the laboratory must dissect the whole fish to obtain the appropriate tissue for analysis, the unused tissues may be rapidly refrozen and stored in a clean glass jar for subsequent use.

11.8.1.2 Each analysis requires 10 g of tissue (wet weight). Therefore, the laboratory should homogenize at least 20 g of tissue to allow for re-extraction of a second aliquot of the same homogenized sample, if re-analysis is required. When whole fish analysis is necessary, the entire fish is homogenized.

11.8.1.3 Homogenize the sample in a tissue homogenizer (Section 6.3.3) or grind in a meat grinder (Section 6.3.4). Cut tissue too large to feed into the grinder into smaller pieces. To assure homogeneity, grind three times.

11.8.1.4 Transfer approximately 10 g (wet weight) of homogenized tissue to a clean, tared, 400- to 500-mL beaker.

11.8.1.5 Transfer the remaining homogenized tissue to a clean jar with a fluoropolymer-lined lid. Seal the jar and store the tissue at <-10 °C. Return any tissue that was not homogenized to its original container and store at <-10 °C.

11.8.2 QC aliquots

11.8.2.1 Prepare a Method blank by adding approximately 1-2 g of the oily liquid reference matrix (Section 7.6.4) to a 400- to 500-mL beaker.

11.8.2.2 Prepare a precision and recovery aliquot by adding 1-2 g of the oily liquid reference matrix (Section 7.6.4) to a separate 400- to 500-mL beaker. Record the weight to the nearest 10 mg. If the initial precision and recovery test is to be performed, use four aliquots; if the ongoing precision and recovery test is to be performed, use a single aliquot.

11.8.3 Spiking

11.8.3.1 Spike 1.0 mL of the Labeled Toxics/LOC/window-defining standard spiking solution (Section 7.12) into the sample, blank, and OPR aliquot.

11.8.3.2 Spike 1.0 mL of the Native Toxics/LOC standard spiking solution (Section 7.11) into the OPR aliquot

11.8.4 Extract the aliquots using the procedures in Section 12.4.

12.0 Extraction and concentration

12.1 Extraction procedures include solid phase (Section 12.2.1), separatory funnel (Section 12.2.2), and continuous liquid/liquid (Section 12.2.3) for aqueous liquids; Soxhlet/Dean-Stark (Section 12.3) for solids and filters; and Soxhlet extraction (Section 12.4) for tissues. Acid/base back-extraction (Section 12.5) is used for initial cleanup of extracts.

Macro-concentration procedures include rotary evaporation (Section 12.6.1), heating mantle (Section 12.6.2), and Kuderna-Danish (K-D) evaporation (Section 12.6.3). Micro-concentration uses nitrogen blowdown (Section 12.7).

12.2 Extraction of aqueous liquids

12.2.1 SPE of samples containing less than one percent solids.

12.2.1.1 Disk preparation.

12.2.1.1.1 Remove the test tube from the suction flask (Figure 4). Place an SPE disk on the base of the filter holder and wet with methylene chloride. While holding a GMF 150 filter above the SPE disk with tweezers, wet the filter with methylene chloride and lay the filter on the SPE disk, making sure that air is not trapped between the filter and disk. Clamp the filter and SPE disk between the 1-L glass reservoir and the vacuum filtration flask.

12.2.1.1.2 Rinse the sides of the reservoir with approx 15 mL of methylene chloride using a squeeze bottle or pipet. Apply vacuum momentarily until a few drops appear at the drip tip. Release the vacuum and allow the filter/disk to soak for approx one minute. Apply vacuum and draw all of the methylene chloride through the filter/disk. Repeat the wash step with approx 15 mL of acetone and allow the filter/disk to air dry.

12.2.1.2 Sample extraction.

12.2.1.2.1 Pre-wet the disk by adding approx 20 mL of methanol to the reservoir. Pull most of the methanol through the filter/disk, retaining a layer of methanol approx 2 mm

thick on the filter. Do not allow the filter/disk to go dry from this point until the extraction is completed.

12.2.1.2.2 Add approx 20 mL of reagent water to the reservoir and pull most through, leaving a layer approx 2 mm thick on the filter/disk.

12.2.1.2.3 Allow the sample (Section 11.4.2.6) to stand for 1-2 hours, if necessary, to settle the suspended particles. Decant the clear layer of the sample, the blank (Section 11.4.2.4), or IPR/OPR aliquot (Section 11.4.2.5) into its respective reservoir and turn on the vacuum to begin the extraction. Adjust the vacuum to complete the extraction in no less than 10 minutes. For samples containing a high concentration of particles (suspended solids), the extraction time may be an hour or longer.

12.2.1.2.4 Before all of the sample has been pulled through the filter/disk, add approx 50 mL of reagent water to the sample bottle, swirl to suspend the solids (if present), and pour into the reservoir. Pull through the filter/disk. Use additional reagent water rinses until all solids are removed.

12.2.1.2.5 Before all of the sample and rinses have been pulled through the filter/disk, rinse the sides of the reservoir with small portions of reagent water.

12.2.1.2.6 Partially dry the filter/disk under vacuum for approx 3 minutes.

12.2.1.3 Elution of the filter/disk.

12.2.1.3.1 Release the vacuum, remove the entire filter/disk/reservoir assembly from the vacuum flask, and empty the flask. Insert a test tube for eluant collection into the flask. The test tube should have sufficient capacity to contain the total volume of the elution solvent (approx 50 mL) and should fit around the drip tip. The drip tip should protrude into the test tube to preclude loss of sample from spattering when vacuum is applied. Reassemble the filter/disk/reservoir assembly on the vacuum flask.

12.2.1.3.2 Wet the filter/disk with 4-5 mL of acetone. Allow the acetone to spread evenly across the disk and soak for 15-20 seconds. Pull the acetone through the disk, releasing the vacuum when approx 1 mm thickness remains on the filter.

12.2.1.3.3 Rinse the sample bottle with approx 20 mL of methylene chloride and transfer to the reservoir. Pull approx half of the solvent through the filter/disk and release the vacuum. Allow the filter/disk to soak for approx 1 minute. Pull all of the solvent through the disk. Repeat the bottle rinsing and elution step with another 20 mL of methylene chloride. Pull all of the solvent through the disk.

12.2.1.3.4 Release the vacuum, remove the filter/disk/reservoir assembly, and remove the test tube containing the sample solution. Quantitatively transfer the solution to a 250-mL separatory funnel and proceed to Section 12.5 for back-extraction.

12.2.2 Separatory funnel extraction

12.2.2.1 Pour the spiked sample (Section 11.4.2.2) into a 2-L separatory funnel. Rinse the bottle or flask twice with 5 mL of reagent water and add these rinses to the separatory funnel.

12.2.2.2 Add 60 mL methylene chloride to the empty sample bottle. Seal the bottle and shake 60 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel, and extract the sample by shaking the funnel for 2 minutes with periodic venting. Allow the organic layer to separate from the aqueous phase for a minimum of 10 minutes. If an emulsion forms and is more than one-third the volume of the solvent layer, employ mechanical techniques to complete the phase separation (see note below). Drain the methylene chloride extract through a solvent-rinsed glass funnel approximately one-half full of granular anhydrous sodium sulfate (Section 7.2.1) supported on clean glass-fiber paper into a solvent-rinsed concentration device (Section 12.6).

Note: *If an emulsion forms, the laboratory must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, use of phase separation paper, centrifugation, use of an ultrasonic bath with ice, addition of NaCl, or other physical methods. Alternatively, solid-phase (Section 12.2.1), CLLE (Section 12.2.3), or other extraction techniques may be used to prevent emulsion formation. Any alternative technique is acceptable so long as the requirements in Section 9.2 are met.*

12.2.2.3 Extract the water sample two more times with 60-mL portions of methylene chloride. Drain each portion through the sodium sulfate into the concentrator. After the third extraction, rinse the separatory funnel with at least 20 mL of methylene chloride, and drain this rinse through the sodium sulfate into the concentrator. Repeat this rinse at least twice. Set aside the funnel with sodium sulfate if the extract is to be combined with the extract from the particles.

12.2.2.4 Concentrate the extract using one of the macro-concentration procedures in Section 12.6 and proceed to back extraction in Section 12.5.

12.2.3 Continuous liquid/liquid extraction

12.2.3.1 Place 100-150 mL methylene chloride in each continuous extractor and 200-300 mL in each distilling flask.

12.2.3.2 Pour the sample(s), blank, and QC aliquots into the extractors. Rinse the sample containers with 50-100 mL methylene chloride and add to the respective extractors. Include all solids in the extraction process.

12.2.3.3 Begin the extraction by heating the flask until the methylene chloride is boiling. When properly adjusted, 1-2 drops of methylene chloride per second will fall from the condenser tip into the water. Extract for 16-24 hours.

12.2.3.4 Remove the distilling flask, estimate and record the volume of extract (to the nearest 100 mL), and pour the contents through a drying column containing 7 to 10 cm of granular anhydrous sodium sulfate into a 500-mL K-D evaporator flask equipped with a 10-mL concentrator tube. Rinse the distilling flask with 30-50 mL of methylene chloride and pour through the drying column. Concentrate and exchange to hexane per Section 12.6 and back extract per Section 12.5.

12.3 SDS extraction of samples containing particles.

12.3.1 Charge a clean extraction thimble (Section 6.4.2.2) with 5.0 g of 100/200 mesh silica (Section 7.5.1.1) topped with 100 g of quartz sand (Section 7.3.2).

Note: *Do not disturb the silica layer throughout the extraction process.*

12.3.2 Place the thimble in a clean extractor. Place 30 to 40 mL of toluene in the receiver and 200 to 250 mL of toluene in the flask.

12.3.3 Pre-extract the glassware by heating the flask until the toluene is boiling. When properly adjusted, 1 to 2 drops of toluene will fall per second from the condenser tip into the receiver. Extract the apparatus for a minimum of 3 hours.

12.3.4 After pre-extraction, cool and disassemble the apparatus. Rinse the thimble with toluene and allow to air dry.

12.3.5 Load the wet sample and/or filter from Sections 11.5.8, 11.6.5, or 11.7.5 and any nonaqueous liquid from Section 11.6.3 into the thimble and manually mix into the sand layer with a clean metal spatula, carefully breaking up any large lumps of sample.

12.3.6 Reassemble the pre-extracted SDS apparatus, and add a fresh charge of toluene to the receiver and reflux flask. Apply power to the heating mantle to begin refluxing. Adjust the reflux rate to match the rate of percolation through the sand and silica beds until water removal lessens the restriction to toluene flow. Frequently check the apparatus for foaming during the first 2 hours of extraction. If foaming occurs, reduce the reflux rate until foaming subsides.

12.3.7 Drain the water from the receiver at 1-2 hours and 8-9 hours, or sooner if the receiver fills with water. Reflux the sample for a total of 16-24 hours. Cool and disassemble the apparatus. Record the total volume of water collected.

12.3.8 Remove the distilling flask. Drain the water from the Dean-Stark receiver and add any toluene in the receiver to the extract in the flask.

12.3.9 Concentrate the extracts from particles to approximately 10 mL using the rotary evaporator (Section 12.6.1) or heating mantle (Section 12.6.2), transfer to a 250-mL separatory funnel, and proceed with back-extraction (Section 12.5).

12.4 Soxhlet extraction of tissue

12.4.1 Add 30 to 40 g of powdered anhydrous sodium sulfate (Section 7.2.2) to each of the beakers (Section 11.8.4) and mix thoroughly. Cover the beakers with

aluminum foil and allow to equilibrate for 12-24 hours. Remix prior to extraction to prevent clumping.

12.4.2 Assemble and pre-extract the Soxhlet apparatus per Sections 12.3.1-12.3.4, except use the methylene chloride:hexane (1:1) mixture for the pre-extraction and rinsing and omit the quartz sand.

12.4.3 Reassemble the pre-extracted Soxhlet apparatus and add a fresh charge of methylene chloride:hexane to the reflux flask.

12.4.4 Transfer the sample/sodium sulfate mixture (Section 12.4.1) to the Soxhlet thimble, and install the thimble in the Soxhlet apparatus.

12.4.5 Rinse the beaker with several portions of solvent mixture and add to the thimble. Fill the thimble/receiver with solvent. Extract for 18-24 hours.

12.4.6 After extraction, cool and disassemble the apparatus.

12.4.7 Quantitatively transfer the extract to a macro-concentration device (Section 12.6), and concentrate to near dryness. Set aside the concentration apparatus for re-use.

12.4.8 Complete the removal of the solvent using the nitrogen blowdown procedure (Section 12.7) and a water bath temperature of 60 °C. Weigh the receiver, record the weight, and return the receiver to the blowdown apparatus, concentrating the residue until a constant weight is obtained.

12.4.9 Percent lipid determination—The lipid content is determined by extraction of tissue with the same solvent system (methylene chloride:hexane) that was used in EPA's National Dioxin Study (Reference 16) so that lipid contents are consistent with that study.

12.4.9.1 Redissolve the residue in the receiver in hexane and spike 1.0 mL of the Labeled cleanup standard spiking solution (Section 7.13) into the solution.

12.4.9.2 Transfer the residue/hexane to the anthropogenic isolation column (Section 13.6), retaining the boiling chips in the concentration apparatus. Use several rinses to assure that all material is transferred. If necessary, sonicate or heat the receiver slightly to assure that all material is re-dissolved. Allow the receiver to dry. Weigh the receiver and boiling chips.

12.4.9.3 Calculate the lipid content to the nearest three significant figures as follows:

$$Percent\ lipid = \frac{Weight\ of\ residue\ (g)}{Weight\ of\ tissue\ (g)} \times 100$$

12.4.9.4 The laboratory should determine the lipid content of the blank, IPR, and OPR to assure that the extraction system is working effectively.

12.5 Back-extraction with base and acid.

12.5.1 Back-extraction may not be necessary for some samples. For some samples, the presence of color in the extract may indicate that back-extraction is necessary. If back-extraction is not performed, spike 1.0 mL of the Labeled cleanup standard spiking solution (Section 7.13) into the extract and concentrate the extract for cleanup or analysis (Section 12.7). If back-extraction is necessary, spike 1.0 mL of the Labeled cleanup standard spiking solution (Section 7.13) into the separatory funnels containing the sample and QC extracts from Section 12.2.3.4 or 12.3.9.

12.5.2 Partition the extract against 50 mL of potassium hydroxide solution (Section 7.1.1). Shake for 2 minutes with periodic venting into a hood. Remove and discard the aqueous layer. Repeat the base washing until no color is visible in the aqueous layer, to a maximum of four washings. Minimize contact time between the extract and the base to prevent degradation of the CBs. Stronger potassium hydroxide solutions may be employed for back-extraction, provided that the laboratory meets the specifications for labeled compound recovery and demonstrates acceptable performance using the procedure in Section 9.2.

12.5.3 Partition the extract against 50 mL of sodium chloride solution (Section 7.1.4) in the same way as with base. Discard the aqueous layer.

12.5.4 Partition the extract against 50 mL of sulfuric acid (Section 7.1.2) in the same way as with base. Repeat the acid washing until no color is visible in the aqueous layer, to a maximum of four washings.

12.5.5 Repeat the partitioning against sodium chloride solution and discard the aqueous layer.

12.5.6 Pour each extract through a drying column containing 7 to 10 cm of granular anhydrous sodium sulfate (Section 7.2.1). Rinse the separatory funnel with 30 to 50 mL of solvent, and pour through the drying column. Collect each extract in a round-bottom flask. Re-concentrate the sample and QC aliquots per Sections 12.6-12.7, and clean up the samples and QC aliquots per Section 13.

12.6 Macro-concentration. Extracts in toluene are concentrated using a rotary evaporator or a heating mantle; extracts in methylene chloride or hexane are concentrated using a rotary evaporator, heating mantle, or Kuderna-Danish apparatus.

Note: *In the concentration procedures below, the extract must not be allowed to concentrate to dryness because the mono- through tri-chlorobiphenyls may be totally or partially lost.*

12.6.1 Rotary evaporation—Concentrate the extracts in separate round-bottom flasks.

12.6.1.1 Assemble the rotary evaporator according to manufacturer's instructions, and warm the water bath to 45 °C. On a daily basis, pre-clean the rotary evaporator by concentrating 100 mL of clean extraction solvent through the system. Archive both the concentrated solvent and the solvent in the catch flask for a contamination check if necessary. Between samples, three 2- to 3-mL aliquots of solvent should be rinsed down the feed tube into a waste beaker.

12.6.1.2 Attach the round-bottom flask containing the sample extract to the rotary evaporator. Slowly apply vacuum to the system, and begin rotating the sample flask.

12.6.1.3 Lower the flask into the water bath, and adjust the speed of rotation and the temperature as required to complete concentration in 15 to 20 minutes. At the proper rate of concentration, the flow of solvent into the receiving flask will be steady, but no bumping or visible boiling of the extract will occur.

Note: *If the rate of concentration is too fast, analyte loss may occur.*

12.6.1.4 When the liquid in the concentration flask has reached an apparent volume of approximately 2 mL, remove the flask from the water bath and stop the rotation. Slowly and carefully admit air into the system. Be sure not to open the valve so quickly that the sample is blown out of the flask. Rinse the feed tube with approximately 2 mL of solvent.

12.6.1.5 Proceed to Section 12.6.4 for preparation for back-extraction or micro-concentration and solvent exchange.

12.6.2 Heating mantle—Concentrate the extracts in separate round-bottom flasks.

12.6.2.1 Add one or two clean boiling chips to the round-bottom flask, and attach a three-ball macro Snyder column. Prewet the column by adding approximately 1 mL of solvent through the top. Place the round-bottom flask in a heating mantle, and apply heat as required to complete the concentration in 15 to 20 minutes. At the proper rate

of distillation, the balls of the column will actively chatter, but the chambers will not flood.

12.6.2.2 When the liquid has reached an apparent volume of approximately 10 mL, remove the round-bottom flask from the heating mantle and allow the solvent to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the glass joint into the receiver with small portions of solvent.

12.6.2.3 Proceed to Section 12.6.4 for preparation for back-extraction or micro-concentration and solvent exchange.

12.6.3 Kuderna-Danish (K-D) - Concentrate the extracts in separate 500-mL K-D flasks equipped with 10-mL concentrator tubes. The K-D technique is used for solvents such as methylene chloride and hexane. Toluene is difficult to concentrate using the K-D technique unless a water bath fed by a steam generator is used.

12.6.3.1 Add 1 to 2 clean boiling chips to the receiver. Attach a three-ball macro Snyder column. Prewet the column by adding approximately 1 mL of solvent through the top. Place the K-D apparatus in a hot water bath so that the entire lower rounded surface of the flask is bathed with steam.

12.6.3.2 Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood.

12.6.3.3 When the liquid has reached an apparent volume of 1 mL, remove the K-D apparatus from the bath and allow the solvent to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of solvent. A 5-mL syringe is recommended for this operation.

12.6.3.4 Remove the three-ball Snyder column, add a fresh boiling chip, and attach a two ball micro Snyder column to the concentrator tube. Prewet the column by adding approximately 0.5 mL of solvent through the top. Place the apparatus in the hot water bath.

12.6.3.5 Adjust the vertical position and the water temperature as required to complete the concentration in 5 to 10 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood.

12.6.3.6 When the liquid reaches an apparent volume of 0.5 mL, remove the apparatus from the water bath and allow to drain and cool for at least 10 minutes.

12.6.3.7 Proceed to 12.6.4 for preparation for back-extraction or micro-concentration and solvent exchange.

12.6.4 Preparation for back-extraction or micro-concentration and solvent exchange.

12.6.4.1 For back-extraction (Section 12.5), transfer the extract to a 250-mL separatory funnel. Rinse the concentration vessel with small portions of hexane, adjust the hexane volume in the separatory funnel to 10 to 20 mL, and proceed to back-extraction (Section 12.5).

12.6.4.2 For determination of the weight of residue in the extract, or for clean-up procedures other than back-extraction, transfer the extract to a blowdown vial using 2-3 rinses of solvent. Proceed with micro-concentration and solvent exchange (Section 12.7).

12.7 Micro-concentration and solvent exchange.

12.7.1 Extracts to be subjected to GPC cleanup are exchanged into methylene chloride. Extracts to be cleaned up using silica gel, carbon, Florisil, and/or HPLC are exchanged into hexane.

12.7.2 Transfer the vial containing the sample extract to a nitrogen blowdown device. Adjust the flow of nitrogen so that the surface of the solvent is just visibly disturbed.

Note: *A large vortex in the solvent may cause analyte loss.*

12.7.3 Lower the vial into a 45 °C water bath and continue concentrating.

12.7.3.1 If the extract or an aliquot of the extract is to be concentrated to dryness for weight determination (Sections 12.4.8 and 13.6.4), blow dry until a constant weight is obtained.

12.7.3.2 If the extract is to be concentrated for injection into the GC/MS or the solvent is to be exchanged for extract cleanup, proceed as follows:

12.7.4 When the volume of the liquid is approximately 100 µL, add 2 to 3 mL of the desired solvent (methylene chloride for GPC and HPLC, or hexane for the other

cleanups) and continue concentration to approximately 100 µL. Repeat the addition of solvent and concentrate once more.

12.7.5 If the extract is to be cleaned up by GPC, adjust the volume of the extract to 5.0 mL with methylene chloride. If the extract is to be cleaned up by HPLC, concentrate the extract to 1.0 mL. Proceed with GPC or HPLC cleanup (Section 13.2 or 13.5, respectively).

12.7.6 If the extract is to be cleaned up by column chromatography (silica gel, Carbopak/Celite, or Florisil), bring the final volume to 1.0 mL with hexane. Proceed with column cleanup (Sections 13.3, 13.4, or 13.7).

12.7.7 If the extract is to be concentrated for injection into the GC/MS (Section 14), quantitatively transfer the extract to a 0.3-mL conical vial for final concentration, rinsing the larger vial with hexane and adding the rinse to the conical vial. Reduce the volume to approximately 100 µL. Add 20 µL of nonane to the vial, and evaporate the solvent to the level of the nonane. Seal the vial and label with the sample number. Store in the dark at room temperature until ready for GC/MS analysis. If GC/MS analysis will not be performed on the same day, store the vial at <-10 °C.

13.0 Extract cleanup

13.1 Cleanup may not be necessary for relatively clean samples (e.g., treated effluents, groundwater, drinking water). If particular circumstances require the use of a cleanup procedure, the laboratory may use any or all of the procedures below or any other appropriate procedure. Before using a cleanup procedure, the laboratory must demonstrate that the requirements of Section 9.2 can be met using the cleanup procedure.

13.1.1 Gel permeation chromatography (Section 13.2) removes high molecular weight interferences that cause GC column performance to degrade. It should be used for all soil and sediment extracts. It may be used for water extracts that are expected to contain high molecular weight organic compounds (e.g., polymeric materials, humic acids). It should also be used for tissue extracts after initial cleanup on the anthropogenic isolation column (Section 13.6).

13.1.2 Acid, neutral, and basic silica gel (Section 13.3) and Florisil (Section 13.7) are used to remove non-polar and polar interferences.

13.1.3 Carbopak/Celite (Section 13.4) can be used to separate CBs 77, 126, and 169 from the mono- and di- ortho-substituted CBs, if desired.

13.1.4 HPLC (Section 13.5) is used to provide specificity for certain congeners and congener groups.

13.1.5 The anthropogenic isolation column (Section 13.6) is used for removal of lipids from tissue samples.

13.2 Gel permeation chromatography (GPC)

13.2.1 Column packing

13.2.1.1 Place 70 to 75 g of SX-3 Bio-beads (Section 6.7.1.1) in a 400- to 500-mL beaker.

13.2.1.2 Cover the beads with methylene chloride and allow to swell overnight (a minimum of 12 hours).

13.2.1.3 Transfer the swelled beads to the column (Section 6.7.1.1) and pump solvent through the column, from bottom to top, at 4.5 to 5.5 mL/minute prior to connecting the column to the detector.

13.2.1.4 After purging the column with solvent for 1 to 2 hours, adjust the column head pressure to 7 to 10 psig and purge for 4 to 5 hours to remove air. Maintain a head pressure of 7 to 10 psig. Connect the column to the detector (Section 6.7.1.4).

13.2.2 Column calibration

13.2.2.1 Load 5 mL of the GPC calibration solution (Section 7.4) into the sample loop.

13.2.2.2 Inject the GPC calibration solution and record the signal from the detector. The elution pattern will be corn oil, BEHP, methoxychlor, perylene, and sulfur.

13.2.2.3 Set the "dump time" to allow >85% removal of BEHP and >85% collection of methoxychlor.

13.2.2.4 Set the "collect time" to the time of the sulfur peak maximum.

13.2.2.5 Verify calibration with the GPC calibration solution after every 20 extracts. Calibration is verified if the recovery of the methoxychlor is greater than 85%. If calibration is not verified, the system must be recalibrated using the GPC calibration solution, and the previous sample batch must be re-extracted and cleaned up using the calibrated GPC system.

13.2.3 Extract cleanup—GPC requires that the column not be overloaded. The column specified in this Method is designed to handle a maximum of 0.5 g of material

from an aqueous, soil, or mixed-phase sample in a 5-mL extract, and has been shown to handle 1.5 g of lipid from a tissue sample in a 5-mL extract. If the extract is known or expected to contain more than these amounts, the extract is split into aliquots for GPC, and the aliquots are combined after elution from the column. The residue content of the extract may be obtained gravimetrically by evaporating the solvent from a 50-µL aliquot.

13.2.3.1 Filter the extract or load through the filter holder (Section 6.7.1.3) to remove particles. Load the 5.0-mL extract onto the column.

13.2.3.2 Elute the extract using the calibration data determined in Section 13.2.2. Collect the eluate in a clean 400- to 500-mL beaker. Allow the system to rinse for additional 10 minutes before injecting the next sample.

13.2.3.3 Rinse the sample loading tube thoroughly with methylene chloride between extracts to prepare for the next sample.

13.2.3.4 If an extract is encountered that could overload the GPC column to the extent that carry-over could occur, a 5.0-mL methylene chloride blank must be run through the system to check for carry-over.

13.2.3.5 Concentrate the eluate per Sections 12.6 and 12.7 for further cleanup or injection into the GC/MS.

13.3 Silica gel cleanup.

13.3.1 Place a glass-wool plug in a 15-mm ID chromatography column (Section 6.7.4.2). Pack the column bottom to top with: 1 g silica gel (Section 7.5.1.1), 4 g basic silica gel (Section 7.5.1.3), 1 g silica gel, 8 g acid silica gel (Section 7.5.1.2), 2 g silica gel, and 4 g granular anhydrous sodium sulfate (Section 7.2.1). Tap the column to settle the adsorbents.

13.3.2 Pre-elute the column with 50 to 100 mL of hexane. Close the stopcock when the hexane is within 1 mm of the sodium sulfate. Discard the eluate. Check the column for channeling. If channeling is present, discard the column and prepare another.

13.3.3 Apply the concentrated extract to the column. Open the stopcock until the extract is within 1 mm of the sodium sulfate.

13.3.4 Rinse the receiver twice with 1-mL portions of hexane, and apply separately to the column. Elute the CBs with 25 mL of hexane and collect the eluate.

13.3.5 Concentrate the eluate per Section 12.6 and 12.7 for further cleanup or injection into the HPLC or GC/MS.

13.3.6 For extracts of samples known to contain large quantities of other organic compounds, it may be advisable to increase the capacity of the silica gel column. This may be accomplished by increasing the strengths of the acid and basic silica gels. The acid silica gel (Section 7.5.1.2) may be increased in strength to as much as 40% w/w (6.7 g sulfuric acid added to 10 g silica gel). The basic silica gel (Section 7.5.1.3) may be increased in strength to as much as 33% w/w (50 mL 1N NaOH added to 100 g silica gel), or the potassium silicate (Section 7.5.1.4) may be used.

Note: *The use of stronger acid silica gel (44% w/w) may lead to charring of organic compounds in some extracts. The charred material may retain some of the analytes and lead to lower recoveries of the CBs. Increasing the strengths of the acid and basic silica gel may also require different volumes of hexane than those specified above to elute the analytes from the column. The performance of the Method after such modifications must be verified by the procedure in Section 9.2.*

13.4 Carbon column (Reference 17)

13.4.1 Cut both ends from a 50-mL disposable serological pipet (Section 6.7.3.2) to produce a 20-cm column. Fire-polish both ends and flare both ends if desired. Insert a glass-wool plug at one end, and pack the column with 3.6 g of Carbopak/Celite (Section 7.5.2.3) to form an adsorbent bed 20 cm long. Insert a glass-wool plug on top of the bed to hold the adsorbent in place.

13.4.2 Pre-elute the column with 20 mL each in succession of toluene, methylene chloride, and hexane.

13.4.3 When the solvent is within 1 mm of the column packing, apply the n-hexane sample extract to the column. Rinse the sample container twice with 1-mL portions of hexane and apply separately to the column. Apply 2 mL of hexane to complete the transfer.

13.4.4 Elute the column with 25 mL of n-hexane and collect the eluate. This fraction will contain the mono- and di-ortho CBs. If carbon particles are present in the eluate, filter through glass-fiber filter paper.

13.4.5 Elute the column with 15 mL of methanol and discard the eluate. The fraction discarded will contain residual lipids and other potential interferents, if present.

13.4.6 Elute the column with 15 mL of toluene and collect the eluate. This fraction will

contain CBs 77, 126, and 169. If carbon particles are present in the eluate, filter through glass-fiber filter paper.

13.4.7 Concentrate the fractions per Section 12.6 and 12.7 for further cleanup or injection into the HPLC or GC/MS.

13.5 HPLC (References 4 and 18).

13.5.1 Column calibration.

13.5.1.1 Prepare a calibration standard containing the Toxics and other congeners of interest at the concentrations of the stock solution in Table 3, or at a concentration appropriate to the response of the detector.

13.5.1.2 Inject the calibration standard into the HPLC and record the signal from the detector. Collect the eluant for reuse. Elution will be in the order of the di-ortho, mono-ortho, and non-ortho congeners.

13.5.1.3 Establish the collection time for the congeners of interest. Following calibration, flush the injection system with solvent to ensure that residual CBs are removed from the system.

13.5.1.4 Verify the calibration with the calibration solution after every 20 extracts. Calibration is verified if the recovery of the CBs is 75 to 125% compared to the calibration (Section 13.5.1.1). If calibration I s not verified, the system must be recalibrated using the calibration solution, and the previous 20 samples must be re-extracted and cleaned up using the calibrated system.

13.5.2 Extract cleanup—HPLC requires that the column not be overloaded. The column specified in this Method is designed to handle a maximum of 5-50 µg of a given CB, depending on the congener (Reference 18). If the amount of material in the extract will overload the column, split the extract into fractions and combine the fractions after elution from the column.

13.5.2.1 Rinse the sides of the vial containing the sample and adjust to the volume required for the sample loop for injection.

13.5.2.2 Inject the sample extract into the HPLC.

13.5.2.3 Elute the extract using the calibration data determined in Section 13.5.1. Collect the fraction(s) in clean 20-mL concentrator tubes.

13.5.2.4 If an extract containing greater than 500 μg of total CBs is encountered, a blank must be run through the system to check for carry-over.

13.5.2.5 Concentrate the eluate per Section 12.7 for injection into the GC/MS.

13.6 Anthropogenic isolation column (Reference 3)—Used for removal of lipids from tissue extracts.

13.6.1 Prepare the column as given in Section 7.5.3.

13.6.2 Pre-elute the column with 100 mL of hexane. Drain the hexane layer to the top of the column, but do not expose the sodium sulfate.

13.6.3 Load the sample and rinses (Section 12.4.9.2) onto the column by draining each portion to the top of the bed. Elute the CBs from the column into the apparatus used for concentration (Section 12.4.7) using 200 mL of hexane.

13.6.4 Remove a small portion (e.g., 50 μL) of the extract for determination of residue content. Estimate the percent of the total that this portion represents. Concentrate the small portion to constant weight per Section 12.7.3.1. Calculate the total amount of residue in the extract. If more than 500 mg of material remains, repeat the cleanup using a fresh anthropogenic isolation column.

13.6.5 If necessary, exchange the extract to a solvent suitable for the additional cleanups to be used (Section 13.2-13.5 and 13.7).

13.6.6 Clean up the extract using the procedures in Sections 13.2-13.5 and 13.7. GPC (Section 13.2) and Florisil (Section 13.7) are recommended as minimum additional cleanup steps.

13.6.7 Following cleanup, concentrate the extract to 20 μL as described in Section 12.7 and proceed with the analysis in Section 14.

13.7 Florisil cleanup (Reference 19).

13.7.1 Begin to drain the n-hexane from the column (Section 7.5.4.1.2). Adjust the flow rate of eluant to 4.5-5.0 mL/min.

13.7.2 When the n-hexane is within 1 mm of the sodium sulfate, apply the sample extract (in hexane) to the column. Rinse the sample container twice with 1-mL portions of hexane and apply to the column.

13.7.3 Elute the mono-ortho and di-ortho CBs with approx 165 mL of n-hexane and collect the eluate. Elute the non-ortho co-planar CBs with approx 100 mL of 6% ether:hexane and collect the eluate. The exact volumes of solvents will need to be determined for each batch of Florisil. If the mono/di-ortho CBs are not to be separated from the non-ortho co-planar CBs, elute all CBs with 6% ether:hexane.

13.7.4 Concentrate the eluate(s) per Sections 12.6-12.7 for further cleanup or for injection into the HPLC or GC/MS.

14.0 HRGC/HRMS analysis

14.1 Establish the operating conditions given in Section 10.1.

14.2 Add 2 µL of the Labeled injection internal standard spiking solution (Section 7.14) to the 20 µL sample extract immediately prior to injection to minimize the possibility of loss by evaporation, adsorption, or reaction. If an extract is to be reanalyzed and evaporation has occurred, do not add more Labeled injection internal standard spiking solution. Rather, bring the extract back to its previous volume (e.g., 19 µL) with pure nonane (18 µL if 2 µL injections are used).

14.3 Inject 1.0 or 2.0 µL of the concentrated extract containing the Labeled injection internal standards using on-column or splitless injection. The volume injected must be identical to the volume used for calibration (Section 10.3).

14.3.1 Start the GC column initial isothermal hold upon injection. Start MS data collection after the solvent peak elutes.

14.3.2 Monitor the exact m/z's at each LOC throughout the LOC retention time window. Where warranted, monitor m/z's associated with congeners at higher levels of chlorination to assure that fragments are not interfering with the m/z's for congeners at lower levels of chlorination. Also where warranted, monitor m/z's associated with interferents expected to be present.

14.3.3 Stop data collection after $^{13}C_{12}$-DeCB has eluted. Return the column to the initial temperature for analysis of the next extract or standard.

15.0 System and laboratory performance

15.1 At the beginning of each 12-hour shift during which analyses are performed, GC/MS system performance and calibration are verified for all native CBs and labeled compounds. For these tests, analysis of the CS-3 calibration verification (VER) standard (Section 7.10.1 and Table 5) and the Diluted combined 209 congener solution (Section 7.10.2.2 and Table 5) must be used to verify all performance criteria. Adjustment and/or recalibration (Section 10) must be performed until all performance criteria are met. Only after all performance criteria are met may samples, blanks, IPRs, and OPRs be analyzed.

15.2 MS resolution—Static resolving power checks must be performed at the beginning and at the end of each shift per Sections 10.2.1. If analyses are performed on successive shifts, only the beginning of shift static resolving power check is required. If the requirement in Section 10.2.1 cannot be met, the problem must be corrected before analyses can proceed. If any of the samples in the previous shift may be affected by poor resolution, those samples must be re-analyzed.

15.3 Calibration verification

15.3.1 Inject the VER (CS-3) standard using the procedure in Section 14.

15.3.2 The m/z abundance ratios for all CBs must be within the limits in Table 8; otherwise, the mass spectrometer must be adjusted until the m/z abundance ratios fall within the limits specified when the verification test is be repeated. If the adjustment alters the resolution of the mass spectrometer, resolution must be verified (Section 10.2.1) prior to repeat of the verification test.

15.3.3 The GC peak representing each native CB and labeled compound in the VER standard must be present with a S/N of at least 10; otherwise, the mass spectrometer must be adjusted and the verification test repeated.

15.3.4 Compute the concentration of the Toxics/LOC CBs by isotope dilution (Section 17.1). These concentrations are computed based on the calibration data in Section 10.

15.3.5 For each compound, compare the concentration with the calibration verification limit in Table 6. If all compounds meet the acceptance criteria, calibration has been verified and analysis of standards and sample extracts may proceed. If, however, any compound fails its respective limit, the measurement system is not performing properly. In this event, prepare a fresh calibration standard or correct the problem and repeat the resolution (Section 15.2) and verification (Section 15.3) tests, or recalibrate (Section 10). If recalibration is required, recalibration for the 209 congeners (Section 10.5) must also be performed.

15.4 Retention times and GC resolution

15.4.1 Retention times

15.4.1.1 Absolute—The absolute retention times of the Labeled Toxics/LOC/ window defining standard congeners (Section 7.12) in the verification test (Section 15.3) must be within ±15 seconds of the respective retention times in the calibration or, if an alternate column or column system is employed, within ±15 seconds of the respective retention times in the calibration for the alternate column or column system (Section 6.9.1.2).

15.4.1.2 Relative - The relative retention times of native CBs and labeled compounds in the verification test (Section 15.3) must be within their respective RRT limits in Table 2 or, if an alternate column or column system is employed, within their respective RRT limits for the alternate column or column system (Section 6.9.1.2).

15.4.1.3 If the absolute or relative retention time of any compound is not within the limits specified, the GC is not performing properly. In this event, adjust the GC and repeat the verification test (Section 15.3) or recalibrate (Section 10), or replace the GC column and either verify calibration or recalibrate.

15.4.2 GC resolution and minimum analysis time.

15.4.2.1 As a final step in calibration verification, inject the Diluted combined 209 congener solution (Section 7.10.2.2 and Table 5).

15.4.2.2 The resolution and minimum analysis time specifications in Sections 6.9.1.1.2 and 6.9.1.1.1, respectively, must be met for the SPB-octyl column or, if an alternate column or column system is employed, must be met as specified for the alternate column or column system (Section 6.9.1.2). If these specifications are not met, the GC analysis conditions must be adjusted until the specifications are met, or the column must be replaced and the calibration verification tests repeated Sections 15.4.1 through 15.4.2.2), or the system must be recalibrated (Section 10).

15.4.2.3 After the resolution and minimum analysis time specifications are met, update the retention times, relative retention times, and response factors for the all congeners except the Toxics and LOC CBs. For the Toxics and LOC CBs, the multi-point calibration data must be used (see Section 10.4 and 15.3).

15.5 Ongoing precision and recovery.

15.5.1 Analyze the extract of the ongoing precision and recovery (OPR) aliquot (Section 11.4.2.5, 11.5.4, 11.6.2, or 11.8.3.2) prior to analysis of samples from the same batch.

15.5.2 Compute the percent recovery of the Toxics/LOC CBs by isotope dilution (Section 10.4). Compute the percent recovery of each labeled compound by the internal standard method (Section 10.5).

15.5.3 For the Toxics/LOC CBs and labeled compounds, compare the recovery to the OPR limits given in Table 6. If all compounds meet the acceptance criteria,

system performance is acceptable and analysis of blanks and samples may proceed. If, however, any individual concentration falls outside of the range given, the extraction/concentration processes are not being performed properly for that compound. In this event, correct the problem, re-prepare, extract, and clean up the sample batch and repeat the ongoing precision and recovery test (Section 15.5).

15.5.4 If desired, add results that pass the specifications in Section 15.5.3 to initial and previous ongoing data for each compound in each matrix. Update QC charts to form a graphic representation of continued laboratory performance. Develop a statement of laboratory accuracy for each congener in each matrix type by calculating the average percent recovery (R) and the standard deviation of percent recovery (S_R). Express the accuracy as a recovery interval from $R - 2S_R$ to $R + 2S_R$. For example, if R = 95% and S_R = 5%, the accuracy is 85 to 105%.

15.6 Blank. Analyze the Method blank extracted with each sample batch immediately following analysis of the OPR aliquot to demonstrate freedom from contamination and freedom from carryover from the OPR analysis. The results of the analysis of the blank must meet the specifications in Section 9.5.2 before sample analyses may proceed.

16.0 Qualitative determination

A CB or labeled compound is identified in a standard, blank, or sample when all of the criteria in Sections 16.1 through 16.4 are met.

16.1 The signals for the two exact m/z's in Table 7 must be present and must maximize within the same two scans.

16.2 The signal-to-noise ratio (S/N) for the GC peak at each exact m/z must be greater than or equal to 2.5 for each CB detected in a sample extract, and greater than or equal to 10 for all CBs in the calibration and verification standards (Sections 10.3.3 and 15.3.3).

16.3 The ratio of the integrated areas of the two exact m/z's specified in Table 7 must be within the limit in Table 8, or within ±15 percent of the ratio in the midpoint (CS-3) calibration or calibration verification (VER), whichever is most recent.

16.4 The relative retention time of the peak for a CB must be within the RRT QC limits specified in Table 2 or, if an alternate column or column system is employed, within its respective RRT QC limits for the alternate column or column system (Section 6.9.1.2).

Note: *For native CBs determined by internal standard quantitation, a given CB congener may fall within more than RT window and be mis-identified unless the RRT windows are made very narrow, as in Table 2. Therefore, consistency of the RT and RRT with other congeners and the labeled compounds may be required for rigorous congener identification. Retention time regression analysis may aid in this identification.*

16.5 Because of congener overlap and the potential for interfering substances, it is possible that all of the identification criteria (Sections 16.1-16.4) may not be met. It is also possible that loss of one or more chlorines from a highly chlorinated congener may inflate or produce a false concentration for a less-chlorinated congener that elutes at the same retention time. If identification is ambiguous, an experienced spectrometrist (Section 1.4) must determine the presence or absence of the congener.

16.6 If the criteria for identification in Sections 16.1-16.5 are not met, the CB has not been identified and the result for that congener may not be reported or used for permitting or regulatory compliance purposes. If interferences preclude identification, a new aliquot of sample must be extracted, further cleaned up, and analyzed.

17.0 Quantitative determination

17.1 Isotope dilution quantitation.

17.1.1 By adding a known amount of the Labeled Toxics/LOC/window-defining compounds to every sample prior to extraction, correction for recovery of the CB can be made because the native compound and its labeled analog exhibit similar effects upon extraction, concentration, and gas chromatography. Relative responses (RRs) are used in conjunction with the calibration data in Section 10.4 to determine concentrations in the final extract, so long as labeled compound spiking levels are constant.

17.1.2 Compute the concentrations in the extract of the Native Toxics/LOC CBs using the RRs from the calibration data (Section 10.4) and following equation.

$$C_{ex}\ (ng/mL) = \frac{(A1_n + A2_n)\ C_l}{(A1_l + A2_l)\ RR}$$

where:

C_{ex} = *The concentration of the PCB in the extract, and the other terms are as defined in Section 10.5.1*

17.2 Internal standard quantitation and labeled compound recovery.

17.2.1 Compute the concentrations in the extract of the native compounds other than those in the Native Toxics/LOC standard, in the Labeled cleanup standard, and

in the Labeled injection internal standard (except for labeled CB 178) using the response factors determined from the calibration data (Section 10.5) and the following equation:

$$C_{ex}\ (ng/mL) = \frac{(A1_x + A2_x)\ C_{is}}{(A1_{is} + A2_{is})\ RF}$$

where:
C_{ex} = *The concentration of the labeled compound in the extract.*
The other terms are defined in Section 10.6.1

17.2.2 Using the concentration in the extract determined above, compute the percent recovery of the Labeled Toxics/TOC/window-defining CBs and the Labeled cleanup standard CBs using the following equation:

$$Recovery\ (\%) = \frac{Concentration\ found\ (\mu g/mL)}{Concentration\ spiked\ (\mu g/mL)} \times 100$$

17.3 The concentration of a native CB in the solid phase of the sample is computed using the concentration of the compound in the extract and the weight of the solids (Section 11.2.2.3), as follows:

$$Concentration\ in\ solid\ (ng/kg) = \frac{(C_{ex} \times V_{ex})}{W_s}$$

where:
C_{ex} = *The concentration of the compound in the extract.*
V_{ex} = *The extract volume in mL.*
W_s = *The sample weight (dry weight) in kg.*

17.4 The concentration of a native CB in the aqueous phase of the sample is computed using the concentration of the compound in the extract and the volume of water extracted (Section 11.4), as follows:

$$Concentration\ in\ aqueous\ phase\ (pg/L) = \frac{(C_{ex} \times V_{ex})}{V_s}$$

where:
C_{ex} = *The concentration of the compound in the extract.*
V_{ex} = *The extract volume in mL.*
V_s = *The sample volume in liters.*

17.5 If the SICP area at either quantitation m/z for any congener exceeds the calibration range of the system, dilute the sample extract by the factor necessary to bring the concentration within the calibration range, adjust the concentration of the Labeled injection internal standard to 100 pg/μL in the extract, and analyze an aliquot of this diluted extract. If the

CBs cannot be measured reliably by isotope dilution, dilute and analyze an aqueous sample or analyze a smaller portion of a soil, tissue, or mixed-phase sample. Adjust the CB congener concentrations, detection limits, and minimum levels to account for the dilution.

17.6 Results are reported to three significant figures for the CBs and labeled compounds found in all standards, blanks, and samples.

17.6.1 Reporting units and levels

17.6.1.1 Aqueous samples—Report results in pg/L (parts-per-quadrillion).

17.6.1.2 Samples containing greater than 1% solids (soils, sediments, filter cake, compost)—Report results in ng/kg based on the dry weight of the sample. Report the percent solids so that the result may be converted to aqueous units.

17.6.1.3 Tissues—Report results in ng/kg of wet tissue, not on the basis of the lipid content of the tissue. Report the percent lipid content, so that the data user can calculate the concentration on a lipid basis if desired.

17.6.1.4 Reporting level.

17.6.1.4.1 Results above the minimum level of quantitation (ML) are reported for the analysis of blanks, standards, and samples. The estimated minimum levels (EMLs) in Table 2 are based on common laboratory contamination levels. A laboratory may establish an ML for a CB lower than the EMLs in Table 2. MLs may be established as low as the lowest calibration point (Table 5) provided that the concentration of the congener in a minimum of 10 blanks for a sample medium (e.g., water, soil, sludge, tissue) is significantly below the EML in Table 2. Significant means that the ML for the congener is no less than the average (mean) plus 2 standard deviations above the level in the minimum of 10 blanks (Reference 20). The blanks must be analyzed during the same period that the sample is analyzed, ideally over an approximately 1-month period.

17.6.1.4.2 Standards (VER, IPR, OPR) and samples—Report the result for each congener at or above the ML (or EML Table 2) to 3 significant figures. Report results below the ML (or EML) as <ML (where ML is the

concentration at the ML) or as required by the regulatory authority or permit.

17.6.1.4.3 Blanks—Report results above the ML (or EML) to 3 significant figures. Report results below the ML but above the MDL (or EMDL) to 2 significant figures. Report results below the MDL as <MDL (where MDL is the concentration at the MDL) or as required by the regulatory authority or permit.

17.6.1.4.4 Blank correction—Blank-corrected results may be reported in addition to reporting of separate results for samples (Section 17.6.1.4.1) and blanks (Section 17.6.1.4.2). The recommended procedure for blank correction (Reference 20) is that a result is significantly above the blank level, and the level in the blank may be subtracted, if the result is greater than the mean plus 2 standard deviations of results of analyses of 10 or more blanks for a sample medium.

17.6.2 Results for a CB in a sample that has been diluted are reported at the least dilute level at which the area at the quantitation m/z is within the calibration range (Section 17.5).

17.6.3 For a CB having a labeled analog, report results at the least dilute level at which the area at the quantitation m/z is within the calibration range (Section 17.5) and the labeled compound recovery is within the normal range for the Method (Section 9.3 and Table 6).

17.6.4 If requested, the total concentration of all congeners at a given level of chlorination (i.e., total TrCB, total PeCB, total HxCB) may be reported by summing the concentrations of all congeners identified at that LOC, including both the Toxics and other congeners.

18.0 Analysis of complex samples

18.1 Some samples may contain high levels (>10 ng/L; >1000 ng/kg) of the compounds of interest, interfering compounds, and/or polymeric materials. Some extracts may not concentrate to 20 µL (Section 12.7), others may overload the GC column and/or mass spectrometer. Fragment ions from congeners at higher levels of chlorination may interfere with determination of congeners at lower levels of chlorination.

18.2 Analyze a smaller aliquot of the sample (Section 17.5) when the extract will not concentrate to 20 µL after all cleanup procedures have been exhausted. If a smaller aliquot of soils or mixed-phase samples is analyzed, attempt to assure that the sample is

representative.

18.3 Perform integration of peak areas and calculate concentrations manually when interferences preclude computerized calculations.

18.4 Several laboratories have reported that backgrounds of many of the CB congeners are difficult to eliminate, and that these backgrounds can interfere with the determination of the CBs in environmental samples. Backgrounds of Toxics with IUPAC numbers 105, 114, 118, 123, 156, 157, and 167 are common. The effects of contamination on results for these congeners should be understood in order to make a reliable determination.

18.5 Recovery of labeled compounds—In most samples, recoveries of the labeled compounds will be similar to those from reagent water or from the alternate matrix (Section 7.6).

18.5.1 If the recovery of any of the labeled compounds is outside of the normal range (Table 6), a diluted sample must be analyzed (Section 17.5).

18.5.2 If the recovery of any of the labeled compounds in the diluted sample is outside of normal range, the calibration verification standard (Section 7.10.1 and Table 5) must be analyzed and calibration verified (Section 15.3).

18.5.3 If the calibration cannot be verified, a new calibration must be performed and the original sample extract reanalyzed.

18.5.4 If the calibration is verified and the diluted sample does not meet the limits for labeled compound recovery, the Method does not apply to the sample being analyzed and the result may not be reported or used for permitting or regulatory compliance purposes. In this case, alternate extraction and cleanup procedures in this Method or an alternate GC column must be employed to resolve the interference. If all cleanup procedures in this Method and an alternate GC column have been employed and labeled compound recovery remains outside of the normal range, extraction and/or cleanup procedures that are beyond this scope of this Method will be required to analyze the sample.

19.0 Pollution prevention

19.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Many opportunities for pollution prevention exist in laboratory operation. EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address waste generation. When wastes cannot be reduced feasibly at the source, the Agency recommends recycling as the next best option.

19.2 The CBs in this Method are used in extremely small amounts and pose little threat to the

environment when managed properly. Standards should be prepared in volumes consistent with laboratory use to minimize the disposal of excess volumes of expired standards.

19.3 For information about pollution prevention that may be applied to laboratories and research institutions, consult *Less is Better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Governmental Relations and Science Policy, 1155 16th Street NW, Washington DC 20036, 202/872-4477.

20.0 Waste management

20.1 The laboratory is responsible for complying with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations. An overview of requirements can be found in *Environmental Management Guide for Small Laboratories* (EPA 233-B-98-001).

20.2 Samples containing HCl or H_2SO_4 to pH <2 are hazardous and must be neutralized before being poured down a drain or must be handled as hazardous waste.

20.3 The CBs decompose above 800 °C. Low-level waste such as absorbent paper, tissues, animal remains, and plastic gloves may be burned in an appropriate incinerator. Gross quantities (milligrams) should be packaged securely and disposed of through commercial or governmental channels that are capable of handling extremely toxic wastes.

20.4 Liquid or soluble waste should be dissolved in methanol or ethanol and irradiated with ultraviolet light with a wavelength shorter than 290 nm for several days. Use F40 BL or equivalent lamps. Analyze liquid wastes, and dispose of the solutions when the CBs can no longer be detected.

20.5 For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* and *Less is Better-Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

21.0 Method performance

Method 1668A was validated and preliminary data were collected in a single laboratory (Reference 21). The original version of Method 1668 was validated in two single-laboratory studies. Figure 8 is a chromatogram showing method performance at each level of chlorination.

22.0 References

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23.0 Tables and Figures

Table 1. Names, International Union of Pure and Applied Chemistry (IUPAC) numbers, and CAS Registry numbers for native and labeled chlorinated biphenyl (CB) congeners determined by isotope dilution and internal standard HRGC/HRMS.

CB congener[1]	IUPAC number	CAS registry number	Labeled analog	IUPAC analog	CAS registry number
2-MoCB	1	2051-60-7	$^{13}C_{12}$-2-MoCB[2]	1L	234432-85-0
3-MoCB	2	2051-61-8			
4-MoCB	3	2051-62-9	$^{13}C_{12}$-4-MoCB[2]	3L	208263-77-8
2,2'-DiCB	4	13029-08-8	$^{13}C_{12}$-2,2'-DiCB[3]	4L	234432-86-1
2,3-DiCB	5	16605-91-7			
2,3'-DiCB	6	25569-80-6			
2,4-DiCB	7	33284-50-3			
2,4'-DiCB[3]	8	34883-43-7			
2,5-DiCB	9	34883-39-1	$^{13}C_{12}$-2,5-DiCB[4]	9L	250694-89-4
2,6-DiCB	10	33146-45-1			
3,3'-DiCB	11	2050-67-1			
3,4-DiCB	12	2974-92-7			
3,4'-DiCB	13	2974-90-5			
3,5-DiCB	14	34883-41-5			
4,4'-DiCB	15	2050-68-2	$^{13}C_{12}$-4,4'-DiCB[2]	15L	208263-67-6
2,2',3-TrCB	16	38444-78-9			
2,2',4-TrCB	17	37680-66-3			
2,2',5-TrCB[3]	18	37680-65-2			
2,2',6-TrCB	19	38444-73-4	$^{13}C_{12}$-2,2',6-TrCB[3]	19L	234432-87-2
2,3,3'-TrCB	20	38444-84-7			
2,3,4-TrCB	21	55702-46-0			
2,3,4'-TrCB	22	38444-85-8			
2,3,5-TrCB	23	55720-44-0			
2,3,6-TrCB	24	55702-45-9			
2,3',4-TrCB	25	55712-37-3			
2,3',5-TrCB	26	38444-81-4			
2,3',6-TrCB	27	38444-76-7			
2,4,4'-TrCB[3]	28	7012-37-5	$^{13}C_{12}$-2,4,4'-TrCB[3]	28L	208263-76-7
2,4,5-TrCB	29	15862-07-4			
2,4,6-TrCB	30	35693-92-6			
2,4',5-TrCB	31	16606-02-3			
2,4',6-TrCB	32	38444-77-8			
2',3,4-TrCB	33	38444-86-9			
2',3,5-TrCB	34	37680-68-5			
3,3',4-TrCB	35	37680-69-6			
3,3',5-TrCB	36	38444-87-0			
3,4,4'-TrCB	37	38444-90-5	$^{13}C_{12}$-3,4,4'-TrCB[2]	37L	208263-79-0
3,4,5-TrCB	38	53555-66-1			
3,4',5-TrCB	39	38444-88-1			
2,2',3,3'-TeCB	40	38444-93-8			

CB congener[1]	IUPAC number	CAS registry number	Labeled analog	IUPAC analog	CAS registry number
2,2',3,4-TeCB	41	52663-59-9			
2,2',3,4'-TeCB	42	36559-22-5			
2,2',3,5-TeCB	43	70362-46-8			
2,2',3,5'-TeCB[3]	44	41464-39-5			
2,2',3,6-TeCB	45	70362-45-7			
2,2',3,6'-TeCB	46	41464-47-5			
2,2',4,4'-TeCB	47	2437-79-8			
2,2',4,5-TeCB	48	70362-47-9			
2,2',4,5'-TeCB	49	41464-40-8			
2,2',4,6-TeCB	50	62796-65-0			
2,2',4,6'-TeCB	51	68194-04-7			
2,2',5,5'-TeCB[3]	52	35693-99-3	$^{13}C_{12}$-2,2',5,5'-TeCB[4]	52L	208263-80-3
2,2',5,6'-TeCB	53	41464-41-9			
2,2',6,6'-TeCB	54	15968-05-5	$^{13}C_{12}$-2,2',6,6'-TeCB[2]	54L	234432-88-3
2,3,3',4'-TeCB	55	74338-24-2			
2,3,3',4'-TeCB	56	41464-43-1			
2,3,3',5-TeCB	57	70424-67-8			
2,3,3',5'-TeCB	58	41464-49-7			
2,3,3',6-TeCB	59	74472-33-6			
2,3,4,4'-TeCB	60	33025-41-1			
2,3,4,5-TeCB	61	33284-53-6			
2,3,4,6-TeCB	62	54230-22-7			
2,3,4',5-TeCB	63	74472-34-7			
2,3,4',6-TeCB	64	52663-58-8			
2,3,5,6-TeCB	65	33284-54-7			
2,3',4,4'-TeCB[3]	66	32598-10-0			
2,3',4,5-TeCB	67	73575-53-8			
2,3',4,5'-TeCB	68	73575-52-7			
2,3',4,6-TeCB	69	60233-24-1			
2,3',4',5-TeCB	70	32598-11-1			
2,3',4',6-TeCB	71	41464-46-4			
2,3',5,5'-TeCB	72	41464-42-0			
2,3',5',6-TeCB	73	74338-23-1			
2,4,4',5-TeCB	74	32690-93-0			
2,4,4',6-TeCB	75	32598-12-2			
2',3,4,5-TeCB	76	70362-48-0			
3,3',4,4'-TeCB[3,6]	77	32598-13-3	$^{13}C_{12}$-3,3',4,4'-TeCB[2,7]	77L	105600-23-5
3,3',4,5-TeCB	78	70362-49-1			
3,3',4,5'-TeCB	79	41464-48-6			
3,3',5,5'-TeCB	80	33284-52-5			
3,4,4',5-TeCB[6]	81	70362-50-4	$^{13}C_{12}$-3,4,4',5-TeCB[7]	81L	208461-24-9
2,2',3,3',4-PeCB	82	52663-62-4			
2,2',3,3',5-PeCB	83	60145-20-2			
2,2',3,3',6-PeCB	84	52663-60-2			
2,2',3,4,4'-PeCB	85	65510-45-4			
2,2',3,4,5-PeCB	86	55312-69-1			

CB congener[1]	IUPAC number	CAS registry number	Labeled analog	IUPAC analog	CAS registry number
2,2',3,4,5'-PeCB	87	38380-02-8			
2,2',3,4,6-PeCB	88	55215-17-3			
2,2',3,4,6'-PeCB	89	73575-57-2			
2,2',3,4',5-PeCB	90	68194-07-0			
2,2',3,4',6-PeCB	91	68194-05-8			
2,2',3,5,5'-PeCB	92	52663-61-3			
2,2',3,5,6-PeCB	93	73575-56-1			
2,2',3,5,6'-PeCB	94	73575-55-0			
2,2',3,5',6-PeCB	95	38379-99-6			
2,2',3,6,6'-PeCB	96	73575-54-9			
2,2',3',4,5-PeCB	97	41464-51-1			
2,2',3',4,6-PeCB	98	60233-25-2			
2,2',4,4',5-PeCB	99	38380-01-7			
2,2',4,4',6-PeCB	100	39485-83-1			
2,2',4,5,5'-PeCB[3]	101	37680-73-2	$^{13}C_{12}$-2,2',4,5,5'-PeCB[4]	101L	104130-39-4
2,2',4,5,6'-PeCB	102	68194-06-9			
2,2',4,5,'6-PeCB	103	60145-21-3			
2,2',4,6,6'-PeCB	104	56558-16-8	$^{13}C_{12}$-2,2',4,6,6'-PeCB[2]	104L	234432-89-4
2,3,3',4,4'-PeCB[3,6]	105	32598-14-4	$^{13}C_{12}$-2,3,3',4,4'-PeCB[7]	105L	208263-62-1
2,3,3',4,5-PeCB	106	70424-69-0			
2,3,3',4',5-PeCB	107	70424-68-9			
2,3,3',4,5'-PeCB	108	70362-41-3			
2,3,3',4,6-PeCB	109	74472-35-8			
2,3,3',4',6-PeCB	110	38380-03-9			
2,3,3',5,5'-PeCB	111	39635-32-0	$^{13}C_{12}$-2,3,3',5,5'-PeCB[5]	111L	235416-29-2
2,3,3',5,6-PeCB	112	74472-36-9			
2,3,3',5',6-PeCB	113	68194-10-5			
2,3,4,4',5-PeCB[6]	114	74472-37-0	$^{13}C_{12}$-2,3,4,4',5-PeCB[7]	114 L	208263-63-2
2,3,4,4',6-PeCB	115	74472-38-1			
2,3,4,5,6-PeCB	116	18259-05-7			
2,3,4',5,6-PeCB	117	68194-11-6			
2,3',4,4',5-PeCB[3,6]	118	31508-00-6	$^{13}C_{12}$-2,3',4,4',5-PeCB[7]	118 L	104130-40-7
2,3',4,4',6-PeCB	119	56558-17-9			
2,3',4,5,5'-PeCB	120	68194-12-7			
2,3',4,5,'6-PeCB	121	56558-18-0			
2',3,3',4,5-PeCB	122	76842-07-4			
2',3,4,4',5-PeCB[6]	123	65510-44-3	$^{13}C_{12}$-2',3,4,4',5-PeCB[7]	123L	208263-64-3
2',3,4,5,5'-PeCB	124	70424-70-3			
2',3,4,5,6'-PeCB	125	74472-39-2			
3,3',4,4',5-PeCB[3,6]	126	57465-28-8	$^{13}C_{12}$-3,3',4,4',5-PeCB[2,7]	126L	208263-65-4
3,3',4,5,5'-PeCB	127	39635-33-1			
2,2',3,3',4,4'-HxCB[3]	128	38380-07-3			
2,2',3,3',4,5-HxCB	129	55215-18-4			
2,2',3,3',4,5'-HxCB	130	52663-66-8			
2,2',3,3',4,6-HxCB	131	61798-70-7			
2,2',3,3',4,6'-HxCB	132	38380-05-1			

CB congener[1]	IUPAC number	CAS registry number	Labeled analog	IUPAC analog	CAS registry number
2,2',3,3',5,5'-HxCB	133	35694-04-3			
2,2',3,3',5,6-HxCB	134	52704-70-8			
2,2',3,3',5,6'-HxCB	135	52744-13-5			
2,2',3,3',6,6'-HxCB	136	38411-22-2			
2,2',3,4,4',5-HxCB	137	35694-06-5			
2,2',3,4,4',5'-HxCB[3]	138	35065-28-2	$^{13}C_{12}$-2,2',3,4,4',5'-HxCB[4]	138L	208263-66-5
2,2',3,4,4',6-HxCB	139	56030-56-9			
2,2',3,4,4',6'-HxCB	140	59291-64-4			
2,2',3,4,5,5'-HxCB	141	52712-04-6			
2,2',3,4,5,6-HxCB	142	41411-61-4			
2,2',3,4,5,6'-HxCB	143	68194-15-0			
2,2',3,4,5',6-HxCB	144	68194-14-9			
2,2',3,4,6,6'-HxCB	145	74472-40-5			
2,2',3,4',5,5'-HxCB	146	51908-16-8			
2,2',3,4',5,6-HxCB	147	68194-13-8			
2,2',3,4',5,6'-HxCB	148	74472-41-6			
2,2',3,4',5',6-HxCB	149	38380-04-0			
2,2',3,4',6,6'-HxCB	150	68194-08-1			
2,2',3,5,5',6-HxCB	151	52663-63-5			
2,2',3,5,6,6'-HxCB	152	68194-09-2			
2,2',4,4',5,5'-HxCB[3]	153	35065-27-1			
2,2',4,4',5',6-HxCB	154	60145-22-4			
2,2',4,4',6,6'-HxCB	155	33979-03-2	$^{13}C_{12}$-2,2',4,4',6,6'-HxCB[2]	155L	234432-90-7
2,3,3',4,4',5-HxCB[5]	156	38380-08-4	$^{13}C_{12}$-2,3,3',4,4',5-HxCB[7]	156L	208263-68-7
2,3,3',4,4',5'-HxCB[5]	157	69782-90-7	$^{13}C_{12}$-2,3,3',4,4',5'-HxCB[7]	157L	235416-30-5
2,3,3',4,4',6-HxCB	158	74472-42-7			
2,3,3',4,5,5'-HxCB	159	39635-35-3			
2,3,3',4,5,6-HxCB	160	41411-62-5			
2,3,3',4,5',6-HxCB	161	74472-43-8			
2,3,3',4',5,5'-HxCB	162	39635-34-2			
2,3,3',4',5,6-HxCB	163	74472-44-9			
2,3,3',4',5',6-HxCB	164	74472-45-0			
2,3,3',5,5',6-HxCB	165	74472-46-1			
2,3,4,4',5,6-HxCB	166	41411-63-6			
2,3',4,4',5,5'-HxCB[6]	167	52663-72-6	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[7]	167L	208263-69-8
2,3',4,4',5',6-HxCB	168	59291-65-5			
3,3',4,4',5,5'-HxCB[3,6]	169	32774-16-6	$^{13}C_{12}$-3,3',4,4',5,5'-HxCB[2,7]	169L	208263-70-1
2,2',3,3',4,4',5-HpCB[3]	170	35065-30-6			
2,2'3,3',4,4',6-HpCB	171	52663-71-5			
2,2',3,3',4,5,5'-HpCB	172	52663-74-8			
2,2',3,3',4,5,6-HpCB	173	68194-16-1			
2,2',3,3',4,5,6'-HpCB	174	38411-25-5			
2,2',3,3',4,5',6-HpCB	175	40186-70-7			
2,2',3,3',4,6,6'-HpCB	176	52663-65-7			
2,2',3,3',4',5,6-HpCB	177	52663-70-4			
2,2',3,3',5,5',6-HpCB	178	52663-67-9	$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB[5]	178L	232919-67-4

CB congener[1]	IUPAC number	CAS registry number	Labeled analog	IUPAC analog	CAS registry number
2,2',3,3',5,6,6'-HpCB	179	52663-64-6			
2,2',3,4,4',5,5'-HpCB[3]	180	35065-29-3			
2,2',3,4,4',5,6-HpCB	181	74472-47-2			
2,2',3,4,4',5,6'-HpCB	182	60145-23-5			
2,2',3,4,4',5',6-HpCB	183	52663-69-1			
2,2',3,4,4',6,6'-HpCB	184	74472-48-3			
2,2',3,4,5,5',6-HpCB	185	52712-05-7			
2,2',3,4,5,6,6'-HpCB	186	74472-49-4			
2,2',3,4',5,5',6-HpCB[3]	187	52663-68-0			
2,2',3,4',5,6,6'-HpCB	188	74487-85-7	$^{13}C_{12}$-2,2',3,4',5,6,6'-HpCB[2]	188L	234432-91-8
2,3,3',4,4',5,5'-HpCB[3]	189	39635-31-9	$^{13}C_{12}$-2,3,3',4,4',5,5'-HpCB[2,7]	189L	208263-73-4
2,3,3',4,4',5,6-HpCB	190	41411-64-7			
2,3,3',4,4',5',6-HpCB	191	74472-50-7			
2,3,3',4,5,5',6-HpCB	192	74472-51-8			
2,3,3',4',5,5',6-HpCB	193	69782-91-8			
2,2',3,3',4,4',5,5'-OcCB	194	35694-08-7	$^{13}C_{12}$-2,2',3,3',4,4',5,5'-OcCB[4]	194L	208263-74-5
2,2',3,3',4,4',5,6-OcCB[3]	195	52663-78-2			
2,2',3,3',4,4',5,6'-OcCB	196	42740-50-1			
2,2',3,3',4,4',6,6'-OcCB	197	33091-17-7			
2,2',3,3',4,5,5',6-OcCB	198	68194-17-2			
2,2',3,3',4,5,5',6'-OcCB	199	52663-75-9			
2,2',3,3',4,5,6,6'-OcCB	200	52663-73-7			
2,2',3,3',4,5',6,6'-OcCB	201	40186-71-8			
2,2',3,3',5,5',6,6'-OcCB	202	2136-99-4	$^{13}C_{12}$-2,2',3,3',5,5',6,6'-OcCB[2]	202L	105600-26-8
2,2',3,4,4',5,5',6-OcCB	203	52663-76-0			
2,2',3,4,4',5,6,6'-OcCB	204	74472-52-9			
2,3,3',4,4',5,5',6-OcCB	205	74472-53-0	$^{13}C_{12}$-2,3,3',4,4',5,5',6-OcCB[5]	205L	234446-64-1
2,2',3,3',4,4',5,5',6-NoCB[3]	206	40186-72-9	$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-NoCB[5]	206L	208263-75-6
2,2',3,3',4,4',5,6,6'-NoCB	207	52663-79-3			
2,2',3,3',4,5,5',6,6'-NoCB	208	52663-77-1	$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-NoCB[2]	208L	234432-92-9
DeCB[3]	209	2051-24-3	$^{13}C_{12}$-DeCB[2]	209L	105600-27-9

1 Abbreviations for chlorination levels
- MoCB = monochlorobiphenyl
- DiCB = dichlorobiphenyl
- TrCB = trichlorobiphenyl
- TeCB = tetrachlorbiphenyl
- PeCB = pentachlorobiphenyl
- HxCB = hexachlorobiphenyl
- HpCB = heptachlorobiphenyl
- OcCB = octachlorobiphenyl
- NoCB = nonachlorobiphenyl
- DeCB = decachlorobiphenyl

2. Labeled level of chlorination (LOC) window-defining congener
3. National Oceanic and Atmospheric Administration (NOAA) congener of interest
4 Labeled injection internal standard
5 Labeled clean-up standard

6. World Health Organization (WHO) toxic congener
7. Labeled analog of WHO toxic congener

Table 2. Retention times (RT), RT references, relative retention times (RRTs), estimated method detection limits (EMDLs), and estimated minimum levels (EMLs) for the 209 CB congeners on SPB-Octyl.

Cl No.[1]	IUPAC No.[2,3]	RT Ref[4]	RTs[5]	RRT[6]	RRT limits[7]	Window (sec)[8]	Quantitation reference[9]	Detection limits and minimum levels - Matrix and concentration[10]				
								Water (pg/L)		Other (ng/kg)		Extract (pg/μL)
								EMDL	EML	EMDL	EML	EML
Compounds using 9L ($^{13}C_{12}$-2,5-DiCB) as Labeled injection internal standard												
CB congener												
Monochlorobiphenyls												
1	1	1L	13:44	1.0012	0.9951-1.0073	10	1L	82	200	8	20	10
1	2	3L	16:08	0.9878	0.9847-0.9908	6	1L/3L	4	10	0.4	1	0.5
1	3	3L	16:21	1.0010	0.9980-1.0041	6	3L	88	200	9	20	10
Dichlorobiphenyls												
2	4	4L	16:40	1.0010	0.9960-1.0060	10	4L	172	500	17	50	20
2	10	4L	16:53	1.0140	1.0110-1.0170	6	4L/15L	22	50	2	5	2
2	9	4L	18:55	1.1361	1.1331-1.1391	6	4L/15L	20	50	2	5	2
2	7	4L	19:07	1.1481	1.1451-1.1512	6	4L/15L	15	50	2	5	2
2	6	4L	19:26	1.1672	1.1642-1.1702	6	4L/15L	13	50	1	5	2
2	5	4L	19:48	1.1892	1.1862-1.1922	6	4L/15L	11	50	1	5	2
2	8	4L	19:56	1.1972	1.1942-1.2002	6	4L/15L	121	500	12	50	20
2	14	15L	21:42	0.9267	0.9246-0.9288	6	4L/15L	31	100	3	10	5
2	11	15L	22:42	0.9694	0.9673-0.9715	6	4L/15L	105	200	10	20	10
2	13	15L	23:03	0.9843	0.9822-0.9865	6	4L/15L	28	100	3	10	5
2	12	15L	23:06	0.9865	0.9843-0.9886	6	4L/15L					
2	13/12	15L	23:04	0.9851	0.9829-0.9872	6	4L/15L					
2	15	15L	23:26	1.0007	0.9972-1.0043	10	15L	183	500	18	50	20
Trichlorobiphenyls												
3	19	19L	20:19	1.0008	0.9967-1.0049	10	19L	42	100	4	10	5
3	30	19L	22:15	1.0961	1.0936-1.0985	6	19L/37L	175	500	17	50	20
3	18	19L	22:23	1.1026	1.1002-1.1051	6	19L/37L					
3	30/18	19L	22:19	1.0993	1.0969-1.1018	6	19L/37L					
3	17	19L	22:49	1.1240	1.1215-1.1264	6	19L/37L	86	200	9	20	10
3	27	19L	23:06	1.1379	1.1355-1.1404	6	19L/37L	59	200	6	20	10
3	24	19L	23:14	1.1445	1.1420-1.1470	6	19L/37L	53	200	5	20	10
3	16	19L	23:25	1.1535	1.1511-1.1560	6	19L/37L	35	100	4	10	5
3	32	19L	24:57	1.2291	1.2266-1.2315	6	19L/37L	84	200	8	20	10
3	34	19L	25:17	1.2455	1.2430-1.2479	6	19L/37L	74	200	7	20	10
3	23	19L	25:26	1.2529	1.2504-1.2553	6	19L/37L	50	200	5	20	10

Cl No.[1]	IUPAC No.[2,3]	RT Ref[4]	RTs[5]	RRT[6]	RRT limits[7]	Window (sec)[8]	Quantitation reference[9]	Detection limits and minimum levels - Matrix and concentration[10]				
								Water (pg/L)		Other (ng/kg)		Extract (pg/μL)
								EMDL	EML	EMDL	EML	EML
3	29	19L	25:47	1.2701	1.2660-1.2742	10	19L/37L	83	200	8	20	10
3	26	19L	25:48	1.2709	1.2668-1.2750	10	19L/37L					
3	26/29	19L	25:48	1.2709	1.2668-1.2750	10	19L/37L					
3	25	37L	26:04	0.8364	0.8348-0.8380	6	19L/37L	55	200	5	20	10
3	31	37L	26:25	0.8476	0.8460-0.8492	6	19L/37L	152	500	15	50	20
3	28	37L	26:44	0.8578	0.8551-0.8604	10	19L/37L	192	500	19	50	20
3	20	37L	26:49	0.8604	0.8578-0.8631	10	19L/37L					
3	28/20	37L	26:47	0.8594	0.8567-0.8620	10	19L/37L					
3	21	37L	26:58	0.8652	0.8626-0.8679	10	19L/37L	51	200	5	20	10
3	33	37L	27:01	0.8668	0.8642-0.8695	10	19L/37L					
3	21/33	37L	26:59	0.8658	0.8631-0.8684	10	19L/37L					
3	22	37L	27:29	0.8818	0.8802-0.8834	6	19L/37L	90	200	9	20	10
3	36	37L	29:05	0.9332	0.9316-0.9348	6	19L/37L	79	200	8	20	10
3	39	37L	29:30	0.9465	0.9449-0.9481	6	19L/37L	85	200	9	20	10
3	38	37L	30:10	0.9679	0.9663-0.9695	6	19L/37L	83	200	8	20	10
3	35	37L	30:42	0.9850	0.9834-0.9866	6	19L/37L	77	200	8	20	10
3	37	37L	31:11	1.0005	0.9989-1.0021	6	37L	132	500	13	50	20
	Labeled Compounds											
1	1L	9L	13:43	0.7257	0.7125-0.7390	30	9L					
1	3L	9L	16:20	0.8642	0.8510-0.8774	30	9L					
2	4L	9L	16:39	0.8810	0.8677-0.8942	30	9L					
2	15L	9L	23:25	1.2390	1.2302-1.2478	20	9L					
3	19L	9L	20:118	1.0741	1.0608-1.0873	30	9L					
3	37L	52L	31:10	1.0803	1.0716-1.0890	30	52L					
Compounds using 52L ($^{13}C_{12}$-2,2',5,5'-TeCB) as Labeled injection internal standard												
	CB congener											
	Tetrachlorobiphenyls											
4	54	54L	23:51	1.0007	0.9972-1.0042	10	54L	118	500	12	50	20
4	50	54L	26:07	1.0958	1.0923-1.0993	10	54L/81L/77L	58	200	6	20	10
4	53	54L	26:09	1.0972	1.0937-1.1007	10	54L/81L/77L					
4	50/53	54L	26:08	1.0965	1.0930-1.1000	10	54L/81L/77L					
4	45	54L	26:55	1.1294	1.1259-1.1329	10	54L/81L/77L	51	200	5	20	10
4	51	54L	26:58	1.1315	1.1280-1.1350	10	54L/81L/77L					
4	45/51	54L	26:57	1.1308	1.1273-1.1343	10	54L/81L/77L					
4	46	54L	27:18	1.1455	1.1434-1.1476	6	54L/81L/77L	101	200	10	20	10
4	52	54L	28:45	1.2063	1.2042-1.2084	6	54L/81L/77L	191	500	19	50	20

Cl No.[1]	IUPAC No.[2,3]	RT Ref[4]	RTs[5]	RRT[6]	RRT limits[7]	Window (sec)[8]	Quantitation reference[9]	Detection limits and minimum levels - Matrix and concentration[10]				
								Water (pg/L)		Other (ng/kg)		Extract (pg/μL)
								EMDL	EML	EMDL	EML	EML
4	73	54L	28:52	1.2112	1.2091-1.2133	6	54L/81L/77L	160	500	16	50	20
4	43	54L	28:58	1.2154	1.2133-1.2175	6	54L/81L/77L	94	200	9	20	10
4	69	54L	29:08	1.2224	1.2189-1.2259	10	54L/81L/77L	115	500	11	50	20
4	49	54L	29:16	1.2280	1.2245-1.2315	10	54L/81L/77L					
4	69/49	54L	29:12	1.2252	1.2217-1.2287	10	54L/81L/77L					
4	48	54L	29:33	1.2399	1.2378-1.2420	6	54L/81L/77L	76	200	8	20	10
4	65	54L	29:49	1.2510	1.2476-1.2545	10	54L/81L/77L	195	500	19	50	20
4	47	54L	29:50	1.2517	1.2483-1.2552	10	54L/81L/77L					
4	44	54L	29:53	1.2538	1.2503-1.2573	10	54L/81L/77L					
4	44/47/65	54L	29:50	1.2517	1.2483-1.2552	10	54L/81L/77L					
4	62	54L	30:06	1.2629	1.2594-1.2664	10	54L/81L/77L	57	200	6	20	10
4	75	54L	30:08	1.2643	1.2608-1.2678	10	54L/81L/77L					
4	59	54L	30:12	1.2671	1.2636-1.2706	10	54L/81L/77L					
4	59/62/75	54L	30:09	1.2650	1.2615-1.2685	10	54L/81L/77L					
4	42	54L	30:26	1.2769	1.2748-1.2790	6	54L/81L/77L	61	200	6	20	10
4	41	54L	30:52	1.2951	1.2916-1.2986	10	54L/81L/77L	119	500	12	50	20
4	71	54L	30:58	1.2993	1.2958-1.3028	10	54L/81L/77L					
4	40	54L	30:01	1.2594	1.2559-1.2629	10	54L/81L/77L					
4	41/40/71	54L	30:58	1.2993	1.2958-1.3028	10	54L/81L/77L					
4	64	54L	31:12	1.3091	1.3070-1.3112	6	54L/81L/77L	70	200	7	20	10
4	72	81L	31:59	0.8336	0.8323-0.8349	6	54L/81L/77L	158	500	16	50	20
4	68	81L	32:18	0.8419	0.8406-0.8432	6	54L/81L/77L	149	500	15	50	20
4	57	81L	32:46	0.8540	0.8527-0.8553	6	54L/81L/77L	125	500	12	50	20
4	58	81L	33:05	0.8623	0.8610-0.8636	6	54L/81L/77L	127	500	13	50	20
4	67	81L	33:13	0.8658	0.8645-0.8671	6	54L/81L/77L	147	500	15	50	20
4	63	81L	33:30	0.8732	0.8719-0.8745	6	54L/81L/77L	138	500	14	50	20
4	61	81L	33:46	0.8801	0.8775-0.8827	12	54L/81L/77L	171	500	17	50	20
4	70	81L	33:53	0.8831	0.8805-0.8858	12	54L/81L/77L					
4	76	81L	33:55	0.8840	0.8814-0.8866	12	54L/81L/77L					
4	74	54L	33:57	0.8849	0.8827-0.8871	10	54L/81L/77L					
4	61/70/74/76	81L	33:55	0.8840	0.8814-0.8866	12	54L/81L/77L					
4	66	81L	34:15	0.8927	0.8914-0.8940	6	54L/81L/77L	162	500	16	50	20
4	55	81L	34:28	0.8983	0.8970-0.8997	6	54L/81L/77L	120	500	12	50	20
4	56	81L	35:03	0.9136	0.9123-0.9149	6	54L/81L/77L	98	200	10	20	10
4	60	81L	35:16	0.9192	0.9179-0.9205	6	54L/81L/77L	131	500	13	50	20
4	80	81L	35:32	0.9262	0.9248-0.9275	6	54L/81L/77L	175	500	18	50	20

Cl No.[1]	IUPAC No.[2,3]	RT Ref[4]	RT's[5]	RRT[6]	RRT limits[7]	Window (sec)[8]	Quantitation reference[9]	Detection limits and minimum levels - Matrix and concentration[10]				
								Water (pg/L)		Other (ng/kg)		Extract (pg/μL)
								EMDL	EML	EMDL	EML	EML
4	79	81L	37:16	0.9713	0.9700-0.9726	6	54L/81L/77L	173	500	17	50	20
4	78	81L	37:52	0.9870	0.9857-0.9883	6	54L/81L/77L	171	500	17	50	20
4	81	81L	38:23	1.0004	0.9991-1.0017	6	81L	177	500	18	50	20
4	77	77L	39:02	1.0004	0.9991-1.0017	6	77L	169	500	17	50	20
	Labeled compounds											
4	54L	52L	23:50	0.8261	0.8203-0.8319	20	52L					
4	81L	52L	38:22	1.3299	1.3241-1.3356	20	52L					
4	77L	52L	39:01	1.3524	1.3466-1.3582	20	52L					
Compounds using 101L ($^{13}C_{12}$-2,2',4,5,5'-PeCB) as Labeled injection internal standard												
	CB congener											
	Pentachlorobiphenyls											
5	104	104L	29:46	1.0000	0.9972-1.0028	10	104L	228	500	23	50	20
5	96	104L	30:17	1.0174	1.0146-1.0202	10	104L/123L/114L/118L/105L/126L	210	500	21	50	20
5	103	104L	32:11	1.0812	1.0795-1.0829	6	104L/123L/114L/118L/105L/126L	225	500	23	50	20
5	94	104L	32:29	1.0913	1.0896-1.0929	6	104L/123L/114L/118L/105L/126L	121	500	12	50	20
5	95	104L	33:00	1.1086	1.1058-1.1114	10	104L/123L/114L/118L/105L/126L	221	500	22	50	20
5	100	104L	33:06	1.1120	1.1092-1.1148	10	104L/123L/114L/118L/105L/126L					
5	93	104L	33:14	1.1165	1.1137-1.1193	10	104L/123L/114L/118L/105L/126L					
5	102	104L	33:21	1.1204	1.1176-1.1232	10	104L/123L/114L/118L/105L/126L					
5	98	104L	33:26	1.1232	1.1204-1.1260	10	104L/123L/114L/118L/105L/126L					
5	95/100/93/102/98	104L	33:13	1.1159	1.1131-1.1187	15	104L/123L/114L/118L/105L/126L					
5	88	104L	33:48	1.1355	1.1321-1.1389	12	104L/123L/114L/118L/105L/126L	118	500	12	50	20
5	91	104L	33:55	1.1394	1.1366-1.1422	10	104L/123L/114L/118L/105L/126L					
5	88/91	104L	33:52	1.1377	1.1344-1.1411	12	104L/123L/114L/118L/105L/126L					
5	84	104L	34:14	1.1501	1.1484-1.1517	6	104L/123L/114L/118L/105L/126L	124	500	12	50	20
5	89	104L	34:44	1.1669	1.1652-1.1685	6	104L/123L/114L/118L/105L/126L	195	500	19	50	20
5	121	104L	34:57	1.1741	1.1725-1.1758	6	104L/123L/114L/118L/105L/126L	209	500	21	50	20
5	92	123L	35:26	0.8639	0.8627-0.8651	6	104L/123L/114L/118L/105L/126L	115	500	12	50	20
5	113	104L	36:01	0.8781	0.8761-0.8801	10	104L/123L/114L/118L/105L/126L	241	1000	24	100	50
5	90	104L	36:03	0.8789	0.8769-0.8809	10	104L/123L/114L/118L/105L/126L					
5	101	104L	36:04	0.8793	0.8773-0.8813	10	104L/123L/114L/118L/105L/126L					
5	113/90/101	104L	36:03	0.8789	0.8769-0.8809	10	104L/123L/114L/118L/105L/126L					
5	83	104L	36:39	0.8935	0.8911-0.8960	12	104L/123L/114L/118L/105L/126L	217	500	22	50	20
5	99	104L	36:41	0.8944	0.8923-0.8964	10	104L/123L/114L/118L/105L/126L					
5	83/99	104L	36:40	0.8939	0.8915-0.8964	12	104L/123L/114L/118L/105L/126L					

Cl No.[1]	IUPAC No.[2,3]	RT Ref[4]	RTs[5]	RRT[6]	RRT limits[7]	Window (sec)[8]	Quantitation reference[9]	Detection limits and minimum levels - Matrix and concentration[10]				
								Water (pg/L)		Other (ng/kg)		Extract (pg/μL)
								EMDL	EML	EMDL	EML	EML
5	112	104L	36:51	0.8984	0.8972-0.8996	6	104L/123L/114L/118L/105L/126L	245	1000	25	100	50
5	119	104L	37:12	0.9069	0.9037-0.9102	16	104L/123L/114L/118L/105L/126L	149	500	15	50	20
5	108	104L	37:12	0.9069	0.9037-0.9102	16	104L/123L/114L/118L/105L/126L					
5	86	104L	37:17	0.9090	0.9057-0.9122	16	104L/123L/114L/118L/105L/126L					
5	97	104L	37:17	0.9090	0.9057-0.9122	16	104L/123L/114L/118L/105L/126L					
5	125	104L	37:21	0.9106	0.9074-0.9139	16	104L/123L/114L/118L/105L/126L					
5	87	104L	37:25	0.9122	0.9102-0.9143	10	104L/123L/114L/118L/105L/126L					
5	108/119/86/97/125/87	104L	37:19	0.9098	0.9065-0.9130	16	104L/123L/114L/118L/105L/126L					
5	117	104L	37:57	0.9252	0.9228-0.9277	12	104L/123L/114L/118L/105L/126L	104	200	10	20	10
5	116	104L	38:02	0.9273	0.9248-0.9297	12	104L/123L/114L/118L/105L/126L					
5	85	104L	38:05	0.9285	0.9265-0.9305	10	104L/123L/114L/118L/105L/126L					
5	117/116/85	104L	38:00	0.9265	0.9240-0.9289	12	104L/123L/114L/118L/105L/126L					
5	110	104L	38:16	0.9330	0.9309-0.9350	10	104L/123L/114L/118L/105L/126L	243	1000	24	100	50
5	115	104L	38:18	0.9338	0.9317-0.9358	10	104L/123L/114L/118L/105L/126L					
5	110/115	104L	38:17	0.9334	0.9313-0.9354	10	104L/123L/114L/118L/105L/126L					
5	82	104L	38:40	0.9427	0.9415-0.9439	6	104L/123L/114L/118L/105L/126L	133	500	13	50	20
5	111	104L	38:52	0.9476	0.9464-0.9488	6	104L/123L/114L/118L/105L/126L	243	1000	24	100	50
5	120	104L	39:21	0.9594	0.9581-0.9606	6	104L/123L/114L/118L/105L/126L	147	500	15	50	20
5	107	104L	40:39	0.9911	0.9890-0.9931	10	104L/123L/114L/118L/105L/126L	200	1000	27	100	50
5	124	104L	40:40	0.9915	0.9894-0.9935	10	104L/123L/114L/118L/105L/126L					
5	107/124	104L	40:39	0.9911	0.9890-0.9931	10	104L/123L/114L/118L/105L/126L					
5	109	104L	40:54	0.9972	0.9959-0.9984	6	104L/123L/114L/118L/105L/126L	103	200	10	20	10
5	123	123L	41:02	1.0004	0.9992-1.0016	6	123L	150	500	15	50	20
5	106	123L	41:10	1.0037	1.0024-1.0049	6	104L/123L/114L/118L/105L/126L	143	500	14	50	20
5	118	118L	41:22	1.0004	0.9992-1.0016	6	118L	193	500	19	50	20
5	122	118L	41:49	1.0113	1.0101-1.0125	6	104L/123L/114L/118L/105L/126L	117	500	12	50	20
5	114	114L	41:58	1.0004	0.9992-1.0016	6	114L	120	500	12	50	20
5	105	105L	42:43	0.9996	0.9984-1.0008	6	105L	109	200	11	20	10
5	127	105L	44:09	1.0332	1.0320-1.0343	6	104L/123L/114L/118L/105L/126L	278	1000	28	100	50
5	126	126L	45:58	1.0004	0.9993-1.0015	6	126L	136	500	14	50	20
	Labeled compounds											
5	104L	101L	29:46	0.8257	0.8211-0.8303	20	101L					
5	123L	101L	41:01	1.1378	1.1331-1.1424	20	101L					
5	118L	101L	41:21	1.1470	1.1424-1.1516	20	101L					
5	114L	101L	41:57	1.1637	1.1590-1.1683	20	101L					
5	105L	101L	42:44	1.1854	1.1808-1.1900	20	101L					

Cl No.[1]	IUPAC No.[2,3]	RT Ref[4]	RTs[5]	RRT[6]	RRT limits[7]	Window (sec)[8]	Quantitation reference[9]	Detection limits and minimum levels - Matrix and concentration[10]				
								Water (pg/L)		Other (ng/kg)		Extract (pg/μL)
								EMDL	EML	EMDL	EML	EML
5	126L	101L	45:57	1.2746	1.2700-1.2792	20	101L					
Compounds using 138L ($^{13}C_{12}$-2,2',3,4,4',5'-HxCB) as Labeled injection internal standard												
CB congener												
Hexachlorobiphenyls												
6	155	155L	35:44	1.0000	0.9977-1.0023	10	155L	339	1000	34	100	50
6	152	155L	36:07	1.0107	1.0093-1.0121	6	155L/156L/157L/167L	238	1000	24	100	50
6	150	155L	36:15	1.0145	1.0131-1.0159	6	155L/156L/157L/167L	328	1000	33	100	50
6	136	155L	36:44	1.0280	1.0266-1.0294	6	155L/156L/157L/167L	91	200	9	20	10
6	145	155L	37:00	1.0354	1.0340-1.0368	6	155L/156L/157L/167L	317	1000	32	100	50
6	148	155L	34:26	1.0756	1.0742-1.0770	6	155L/156L/157L/167L	324	1000	32	100	50
6	151	155L	39:10	1.0961	1.0938-1.0984	10	155L/156L/157L/167L					
6	135	155L	39:17	1.0993	1.0970-1.1017	10	155L/156L/157L/167L	112	500	11	50	20
6	154	155L	39:21	1.1012	1.0989-1.1035	10	155L/156L/157L/167L					
6	151/135/154	155L	39:15	1.0984	1.0961-1.1007	10	155L/156L/157L/167L					
6	144	155L	39:47	1.1133	1.1119-1.1147	6	155L/156L/157L/167L	167	500	17	50	20
6	147	155L	40:09	1.1236	1.1213-1.1259	10	155L/156L/157L/167L					
6	149	155L	40:12	1.1250	1.1227-1.1273	10	155L/156L/157L/167L	179	500	18	50	20
6	147/149	155L	40:10	1.1241	1.1217-1.1264	10	155L/156L/157L/167L					
6	134	155L	40:27	1.1320	1.1297-1.1343	10	155L/156L/157L/167L					
6	143	155L	40:30	1.1334	1.1311-1.1357	10	155L/156L/157L/167L	134	500	13	50	20
6	134/143	155L	40:29	1.1329	1.1306-1.1353	10	155L/156L/157L/167L					
6	139	155L	40:47	1.1413	1.1390-1.1437	10	155L/156L/157L/167L					
6	140	155L	40:48	1.1418	1.1395-1.1441	10	155L/156L/157L/167L	196	500	20	50	20
6	139/140	155L	40:47	1.1413	1.1390-1.1437	10	155L/156L/157L/167L					
6	131	155L	41:03	1.1488	1.1474-1.1502	6	155L/156L/157L/167L	121	500	12	50	20
6	142	155L	41:13	1.1535	1.1521-1.1549	6	155L/156L/157L/167L	311	1000	31	100	50
6	132	155L	41:36	1.1642	1.1618-1.1665	10	155L/156L/157L/167L	125	500	12	50	20
6	133	155L	41:57	1.1740	1.1726-1.1754	6	155L/156L/157L/167L	169	500	17	50	20
6	165	167L	42:23	0.8864	0.8853-0.8874	6	155L/156L/157L/167L	361	1000	36	100	50
6	146	167L	42:38	0.8916	0.8906-0.8926	6	155L/156L/157L/167L	182	500	18	50	20
6	161	167L	42:47	0.8947	0.8937-0.8958	6	155L/156L/157L/167L	352	1000	35	100	50
6	153	167L	43:17	0.9052	0.9035-0.9069	10	155L/156L/157L/167L					
6	168	167L	43:21	0.9066	0.9048-0.9083	10	155L/156L/157L/167L	130	500	13	50	20
6	153/168	167L	43:19	0.9059	0.9041-0.9076	10	155L/156L/157L/167L					
6	141	167L	43:34	0.9111	0.9101-0.9122	6	155L/156L/157L/167L	93	200	9	20	10
6	130	167L	44:01	0.9205	0.9195-0.9216	6	155L/156L/157L/167L	136	500	14	50	20

Cl No.[1]	IUPAC No.[2,3]	RT Ref[4]	RTs[5]	RRT[6]	RRT limits[7]	Window (sec)[8]	Quantitation reference[9]	Detection limits and minimum levels - Matrix and concentration[10]				
								Water (pg/L)		Other (ng/kg)		Extract (pg/μL)
								EMDL	EML	EMDL	EML	EML
6	137	167L	44:14	0.9251	0.9240-0.9261	6	155L/156L/157L/167L	300	1000	30	100	50
6	164	167L	44:22	0.9278	0.9268-0.9289	6	155L/156L/157L/167L	136	500	14	50	20
6	138	167L	44:42	0.9348	0.9324-0.9373	14	155L/156L/157L/167L	211	500	21	50	20
6	163	167L	44:42	0.9348	0.9324-0.9373	14	155L/156L/157L/167L					
6	129	167L	44:47	0.9366	0.9341-0.9390	14	155L/156L/157L/167L					
6	160	167L	44:53	0.9387	0.9369-0.9404	10	155L/156L/157L/167L					
6	138/163/129/160	167L	44:47	0.9366	0.9341-0.9390	14	155L/156L/157L/167L					
6	158	167L	45:05	0.9428	0.9418-0.9439	6	155L/156L/157L/167L	96	200	10	20	10
6	166	167L	45:59	0.9617	0.9599-0.9634	10	155L/156L/157L/167L	124	500	12	50	20
6	128	167L	46:46	0.9651	0.9634-0.9669	10	155L/156L/157L/167L					
6	128/166	167L	46:04	0.9634	0.9617-0.9651	10	155L/156L/157L/167L					
6	159	167L	46:59	0.9826	0.9815-0.9836	6	155L/156L/157L/167L	348	1000	35	100	50
6	162	167L	47:18	0.9892	0.9881-0.9902	6	155L/156L/157L/167L	355	1000	35	100	50
6	167	167L	47:49	1.0000	0.9990-1.0010	6	155L/156L/157L/167L	115	500	11	50	20
6	156	156L/157L	49:05	0.9993	0.9983-1.0003	6	156L/157L	132	500	13	50	20
6	157	156L/157L	49:09	1.0007	0.9990-1.0024	10	156L/157L					
6	156/157	156L/157L	45:07	1.0000	0.9990-1.0010	6	156L/157L					
6	169	169L	52:31	0.9949	0.9940-0.9959	6	169L	161	500	16	50	20
	Labeled compounds											
6	155L	138L	35:44	0.7997	0.7960-0.8034	20	138L					
6	167L	138L	47:49	1.0701	1.0664-1.0739	20	138L					
6	156L	138L	49:05	1.0985	1.0974-1.0996	6	138L					
6	157L	138L	49:08	1.0996	1.0959-1.1033	20	138L					
6	156L/157L	138L	49:07	1.0992	1.0981-1.1003	6	138L					
6	169L	138L	52:30	1.1749	1.1738-1.1761	6	138L					
Compounds using 194L($^{13}C_{12}$-2,2',3,3',4,4',5,5'-OcCB) as Labeled injection internal standard												
	CB congener											
	Heptachlorobiphenyls											
7	188	188L	41:51	1.0000	0.9988-1.0012	6	188L	235	500	23	50	20
7	179	188L	42:19	1.0112	1.0100-1.0123	6	188L/189L	229	500	23	50	20
7	184	188L	42:45	1.0215	1.0203-1.0227	6	188L/189L	403	1000	40	100	50
7	176	188L	43:15	1.0335	1.0323-1.0346	6	188L/189L	385	1000	39	100	50
7	186	188L	43:45	1.0454	1.0442-1.0466	6	188L/189L	407	1000	41	100	50
7	178	188L	45:06	1.0777	1.0765-1.0789	6	188L/189L	221	500	22	50	20
7	175	188L	45:46	1.0936	1.0924-1.0948	6	188L/189L	383	1000	38	100	50
7	187	188L	46:02	1.1000	1.0988-1.1012	6	188L/189L	191	500	19	50	20

Cl No.[1]	IUPAC No.[2,3]	RT Ref[4]	RTs[5]	RRT[6]	RRT limits[7]	Window (sec)[8]	Quantitation reference[9]	Detection limits and minimum levels - Matrix and concentration[10]				
								Water (pg/L)		Other (ng/kg)		Extract (pg/μL)
								EMDL	EML	EMDL	EML	EML
7	182	188L	46:14	1.1047	1.1035-1.1059	6	188L/189L	398	1000	40	100	50
7	183	188L	46:42	1.1159	1.1147-1.1171	6	188L/189L	401	1000	40	100	50
7	185	188L	46:53	1.1203	1.1191-1.1215	6	188L/189L					
7	183/185	188L	46:47	1.1179	1.1167-1.1191	6	188L/189L					
7	174	188L	47:02	1.1239	1.1227-1.1251	6	188L/189L	186	500	19	50	20
7	177	188L	47:30	1.1350	1.1338-1.1362	6	188L/189L	141	500	14	50	20
7	181	188L	47:52	1.1438	1.1426-1.1450	6	188L/189L	396	1000	40	100	50
7	171	188L	48:10	1.1509	1.1489-1.1529	10	188L/189L	374	1000	37	100	50
7	173	188L	48:11	1.1513	1.1501-1.1525	6	188L/189L					
7	171/173	188L	48:10	1.1509	1.1489-1.1529	10	188L/189L					
7	172	189L	49:47	0.9035	0.9026-0.9044	6	188L/189L	377	1000	38	100	50
7	192	189L	50:06	0.9093	0.9083-0.9102	6	188L/189L	420	1000	42	100	50
7	193	189L	50:26	0.9153	0.9144-0.9162	6	188L/189L	136	500	14	50	20
7	180	189L	50:27	0.9156	0.9147-0.9165	6	188L/189L					
7	180/193	189L	50:26	0.9153	0.9144-0.9162	6	188L/189L					
7	191	189L	50:51	0.9229	0.9220-0.9238	6	188L/189L	418	1000	42	100	50
7	170	189L	51:54	0.9419	0.9410-0.9428	6	188L/189L	162	500	16	50	20
7	190	189L	52:26	0.9516	0.9507-0.9525	6	188L/189L	234	500	23	50	20
7	189	189L	55:07	1.0003	0.9994-1.0012	6	189L	177	500	18	50	20
Octachlorobiphenyls												
8	202	202L	47:32	1.0004	0.9986-1.0021	10	202L	442	1000	44	100	50
8	201	202L	48:31	1.0210	1.0193-1.0228	10	202L/205L	440	1000	44	100	50
8	204	202L	49:11	1.0351	1.0340-1.0361	6	202L/205L	447	1000	45	100	50
8	197	202L	49:27	1.0407	1.0396-1.0417	6	202L/205L	245	1000	25	100	50
8	200	202L	49:40	1.0452	1.0442-1.0463	6	202L/205L					
8	197/200	202L	49:33	1.0428	1.0417-1.0438	6	202L/205L					
8	198	202L	52:30	1.1049	1.1031-1.1066	10	202L/205L	203	500	20	50	25
8	199	202L	52:32	1.1056	1.1045-1.1066	6	202L/205L					
8	198/199	202L	52:31	1.1052	1.1035-1.1070	10	202L/205L					
8	196	205L	53:13	0.9207	0.9198-0.9216	6	202L/205L	429	1000	43	100	50
8	203	205L	53:26	0.9245	0.9236-0.9253	6	202L/205L	444	1000	44	100	50
8	195	205L	54:55	0.9501	0.9493-0.9510	6	202L/205L	427	1000	43	100	50
8	194	205L	57:19	0.9916	0.9908-0.9925	6	202L/205L	170	500	17	50	20
8	205	205L	57:49	1.0003	0.9994-1.0012	6	205L	449	1000	45	100	50
Nonachlorobiphenyls												
9	208	208L	54:33	1.0003	0.9994-1.0012	6	208L	455	1000	46	100	50

Cl No.[1]	IUPAC No.[2,3]	RT Ref[4]	RTs[5]	RRT[6]	RRT limits[7]	Window (sec)[8]	Quantitation reference[9]	Detection limits and minimum levels – Matrix and concentration[10]				
								Water (pg/L)		Other (ng/kg)		Extract (pg/μL)
								EMDL	EML	EMDL	EML	EML
9	207	208L	55:32	1.0183	1.0174-1.0193	6	208L/206L	453	1000	45	100	50
9	206	206L	59:37	1.0003	0.9994-1.0011	6	206L	451	1000	45	100	50
Decachlorobiphenyl												
10	209	209L	61:15	1.0003	0.9995-1.0011	6	209L	153	500	15	50	20
Labeled compounds												
7	188L	194L	41:51	0.7304	0.7275-0.7333	20	194L					
7	180L	194L	50:27	0.8805	0.8775-0.8834	20	194L					
7	170L	194L	51:53	0.9055	0.9026-0.9084	20	194L					
7	189L	194L	55:06	0.9616	0.9587-0.9645	20	194L					
8	202L	194L	47:31	0.8293	0.8264-0.8322	20	194L					
8	205L	194L	57:48	1.0087	1.0044-1.0131	30	194L					
9	208L	194L	54:32	0.9517	0.9488-0.9546	20	194L					
9	206L	194L	59:36	1.0401	1.0358-1.0445	30	194L					
10	209L	194L	61:14	1.0686	1.0643-1.0730	30	194L					
Labeled clean-up standards												
3	28L	52L	26:44	0.9266	0.9209-0.9324	20	52L					
5	111L	101L	38:51	1.0777	1.0730-1.0823	20	101L					
7	178L	138L	45:05	1.0090	1.0052-1.0127	20	138L					
Labeled injection internal standards												
2	9L	138L	18:54	0.4648	0.4596-0.4699	25	178L					
4	52L	138L	28:51	0.7094	0.7043-0.7145	25	178L					
5	101L	138L	36:03	0.8865	0.8814-0.8916	25	178L					
6	138L	138L	44:41	1.0988	1.0783-1.1193	100	178L					
8	194L	138L	57:18	1.4090	1.4039-1.4141	25	178L					

1. Number of chlorines on congener.
2. Suffix "L" indicates labeled compound.
3. Multiple congeners in a box indicates a group of congeners that co-elute or may not be adequately resolved on a 30-m SPB-Octyl column. Congeners included in the group are listed as the last entry in the box.
4. Retention time reference that is used to locate target congener.
5. Retention time of target congener.
6. RRT between the RT for the congener and RT for the reference.
7. Nominal limits based on an ± 0.5% of the RRT, adjusted for the nearest eluted isomer.
8. RT window width for congener or group of two or more congeners.

9. Labeled congeners that form the quantitation reference. Areas from the exact m/z's of the congeners listed in the quantitation reference are summed, and divided by the number of congeners in the quantitation reference. For example, for congener 10, the areas at the exact m/z's for 4L and 15L are summed and the sum is divided by 2 (because there are 2 congeners in the quantitation reference).
10. EMDLs and EMLs with common laboratory interferences present. Without interferences, EMDLs and EMLs will be, respectively, 5 and 10 pg/L for aqueous samples, 0.5 and 1.0 ng/kg for soil, tissue, and mixed-phase samples, and EMLs for extracts will be 0.5 pg/uL.

Table 3. Concentrations of native and labeled chlorinated biphenyls in stock solutions, spiking solutions, and final extracts

	Solution concentrations		
CB congener	**Stock (μg/mL)**	**Spiking (ng/mL)**	**Extract (ng/mL)**
Native Toxics/LOC[1]			
1	20	1.0	50
3	20	1.0	50
4	20	1.0	50
15	20	1.0	50
19	20	1.0	50
37	20	1.0	50
54	20	1.0	50
77	20	1.0	50
81	20	1.0	50
104	20	1.0	50
105	20	1.0	50
114	20	1.0	50
118	20	1.0	50
123	20	1.0	50
126	20	1.0	50
155	20	1.0	50
156	20	1.0	50
157	20	1.0	50
167	20	1.0	50
169	20	1.0	50
188	20	1.0	50
189	20	1.0	50
202	20	1.0	50
205	20	1.0	50
206	20	1.0	50
208	20	1.0	50
209	20	1.0	50
Native congener mix stock solutions[2]			
MoCB thru TrCB	2.5		
TeCB thru HpCB	5.0		
OcCB thru DeCB	7.5		
Labeled Toxics/LOC/window-defining[3]			
1L	1.0	2.0	100
3L	1.0	2.0	100
4L	1.0	2.0	100

	Solution concentrations		
CB congener	Stock (µg/mL)	Spiking (ng/mL)	Extract (ng/mL)
15L	1.0	2.0	100
19L	1.0	2.0	100
37L	1.0	2.0	100
54L	1.0	2.0	100
77L	1.0	2.0	100
81L	1.0	2.0	100
104L	1.0	2.0	100
105L	1.0	2.0	100
114L	1.0	2.0	100
118L	1.0	2.0	100
123L	1.0	2.0	100
126L	1.0	2.0	100
155L	1.0	2.0	100
156L	1.0	2.0	100
157L	1.0	2.0	100
167L	1.0	2.0	100
169L	1.0	2.0	100
188L	1.0	2.0	100
189L	1.0	2.0	100
202L	1.0	2.0	100
205L	1.0	2.0	100
206L	1.0	2.0	100
208L	1.0	2.0	100
209L	1.0	2.0	100
Labeled clean-up[4]			
28L	1.0	2.0	100
111L	1.0	2.0	100
178L	1.0	2.0	100
Labeled injection internal[5]			
9L	5.0	1000	100
52L	5.0	1000	100
101L	5.0	1000	100
138L	5.0	1000	100
194L	5.0	1000	100

Diluted combined 209 congener[b]		
	Solution concentration (μg/mL)	
Standard	Native	Labeled
Native congeners		
MoCB thru TrCB	50	
TeCB thru HpCB	100	
OcCB thru DeCB	150	
Labeled Toxics/LOC/window-defining		100
Labeled Cleanup		100
Labeled Injection internal		100

1. Stock solution: Section 7.8.1; Spiking solution: Section 7.11
2. Section 7.8.1.2
3. Stock solution: Section 7.9.1; Spiking solution: Section 7.12
4. Stock solution: Section 7.9.2; Spiking solution: Section 7.13
5. Stock solution: Section 7.9.3; Spiking solution: Section 7.14
6. Section 7.10.2.2.2

Table 4. Composition of individual native CB congener solutions[1]

Solution identifier				
A2	**B2**	**C2**	**D2**	**E2**
Accu-Standard part number				
M-1668A-1	M-1668A-2	M-1668A-3	M-1668A-4	M-1668A-5
2	7	13	25	1
10	5	17	21	3
9	12	29	69	4
6	18	20	47	15
8	24	46	42	19
14	23	65	64	16
11	28	59	70	37
30	22	40	102	54
27	39	67	97	43
32	53	76	115	44
34	51	80	123	74
26	73	93	134	56
31	48	84	131	77
33	62	101	163	104
36	71	112	180	98
38	68	86		125
35	58	116		110
50	61	109/107		126
45	55	154		155
52	60	147		138
49	94	140		169
75	100	146		188
41	91	141		189
72	121	164		202
57	90	158		205
63	99	182		208
66	108/109	174		206
79	117	173		209
78	111	193		
81	107/108			
96	118			
103	114			
95	150			
88	145			
89	135			
92	149			
113	139			
83	132			
119	165			
87	168			

Solution identifier				
A2	**B2**	**C2**	**D2**	**E2**
Accu-Standard part number				
M-1668A-1	M-1668A-2	M-1668A-3	M-1668A-4	M-1668A-5
85	137			
82	160			
120	128			
124	162			
106	157			
122	184			
105	186			
127	187			
152	185			
136	181			
148	192			
151	197			
144	199/201			
143	203			
142				
133				
161				
153				
130				
129				
166				
159				
167				
156				
179				
176				
178				
175				
183				
177				
171				
172				
191				
170				
190				
201/200				
204				
200/199				
198				
196				
195				
194				

Solution identifier				
A2	**B2**	**C2**	**D2**	**E2**
Accu-Standard part number				
M-1668A-1	M-1668A-2	M-1668A-3	M-1668A-4	M-1668A-5
207				
Totals				
83	**54**	**29**	**15**	**28**

1 Congeners present in each standard listed in elution order for each level of chlorination. IUPAC number listed first; BZ number listed second where ambiguous. See Table 3 for concentrations of congeners in stock solutions and Table 5 for concentrations in calibration standard.

Table 5. Concentration of CB congeners in calibration and calibration verification standards

		Solution concentration (ng/mL)					
CB congener	**IUPAC[1]**	**CS-0.2 (Hi sens)[2]**	**CS-1**	**CS-2**	**CS-3 (VER)**	**CS-4**	**CS-5**
Native Toxics/LOC							
2-MoCB	1	0.2	1.0	5.0	50	400	2000
4-MoCB	3	0.2	1.0	5.0	50	400	2000
2,2'-DiCB	4	0.2	1.0	5.0	50	400	2000
4,4'-DiCB	15	0.2	1.0	5.0	50	400	2000
2,2',6'-TrCB	19	0.2	1.0	5.0	50	400	2000
3,4,4'-TrCB	37	0.2	1.0	5.0	50	400	2000
2,2',6,6'-TeCB	54	0.2	1.0	5.0	50	400	2000
3,3',4,4'-TeCB	77	0.2	1.0	5.0	50	400	2000
3,4,4',5-TeCB	81	0.2	1.0	5.0	50	400	2000
2,2',4,6,6'-PeCB	104	0.2	1.0	5.0	50	400	2000
2,3,3',4,4'-PeCB	105	0.2	1.0	5.0	50	400	2000
2,3,4,4',5-PeCB	114	0.2	1.0	5.0	50	400	2000
2,3',4,4',5-PeCB	118	0.2	1.0	5.0	50	400	2000
2',3,4,4',5-PeCB	123	0.2	1.0	5.0	50	400	2000
3,3',4,4',5-PeCB	126	0.2	1.0	5.0	50	400	2000
2,2',4,4',6,6'-HxCB	155	0.2	1.0	5.0	50	400	2000
2,3,3',4,4',5-HxCB	156	0.2	1.0	5.0	50	400	2000
2,3,3',4,4',5'-HxCB	157	0.2	1.0	5.0	50	400	2000
2,3',4,4',5,5'-HxCB	167	0.2	1.0	5.0	50	400	2000
3,3',4,4',5,5'-HxCB	169	0.2	1.0	5.0	50	400	2000
2,2',3,4',5,6,6'-HpCB	188	0.2	1.0	5.0	50	400	2000
2,3,3',4,4',5,5'-HpCB	189	0.2	1.0	5.0	50	400	2000
2,2',3,3',5,5',6,6'-OcCB	202	0.2	1.0	5.0	50	400	2000
2,3,3',4,4',5,5',6-OcCB	205	0.2	1.0	5.0	50	400	2000
2,2',3,3',4,4',5,5',6-NoCB	206	0.2	1.0	5.0	50	400	2000
2,2',3,3',4',5,5',6,6'-NoCB	208	0.2	1.0	5.0	50	400	2000
DeCB	209	0.2	1.0	5.0	50	400	2000
Labeled Toxics/LOC/window-defining							
$^{13}C_{12}$-2-MoCB	1L	100	100	100	100	100	100
$^{13}C_{12}$-4-MoCB	3L	100	100	100	100	100	100
$^{13}C_{12}$-2,2'-DiCB	4L	100	100	100	100	100	100
$^{13}C_{12}$-4,4'-DiCB	15L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',6'-TrCB	19L	100	100	100	100	100	100
$^{13}C_{12}$-3,4,4'-TrCB	37L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',6,6'-TeCB	54L	100	100	100	100	100	100
$^{13}C_{12}$-3,3',4,4'-TeCB	77L	100	100	100	100	100	100
$^{13}C_{12}$-3,4,4',5-TeCB	81L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',4,6,6'-PeCB	104L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4'-PeCB	105L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,4,4',5-PeCB	114L	100	100	100	100	100	100
$^{13}C_{12}$-2,3',4,4',5-PeCB	118L	100	100	100	100	100	100
$^{13}C_{12}$-2',3,4,4',5-PeCB	123L	100	100	100	100	100	100
$^{13}C_{12}$-3,3',4,4',5-PeCB	126L	100	100	100	100	100	100

CB congener	IUPAC[1]	Solution concentration (ng/mL)					
		CS-0.2 (Hi sens)[2]	CS-1	CS-2	CS-3 (VER)	CS-4	CS-5
$^{13}C_{12}$-2,2',4,4',6,6'-HxCB	155L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4',5-HxCB	156L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4',5'-HxCB	157L	100	100	100	100	100	100
$^{13}C_{12}$-2,3',4,4',5,5'-HxCB	167L	100	100	100	100	100	100
$^{13}C_{12}$-3,3',4,4',5,5'-HxCB	169L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,4',5,6,6'-HpCB	188L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4',5,5'-HpCB	189L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-OcCB	202L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4',5,5',6-OcCB	205L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-NoCB	206L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4',5,5',6,6'-NoCB	208L	100	100	100	100	100	100
$^{13}C_{12}$-DeCB	209L	100	100	100	100	100	100
Labeled clean-up							
$^{13}C_{12}$-2,4,4'-TrCB	28L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',5,5'-PeCB	111L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB	178L	100	100	100	100	100	100
Labeled injection internal							
$^{13}C_{12}$-2,5-DiCB	9L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',5,5'-TeCB	52L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',4,5,5'-PeCB	101L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3',4,4',5'-HxCB	138L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4,4',5,5'-OcCB	194L	100	100	100	100	100	100

1. Suffix "L" indicates labeled compound
2. Additional concentration used for calibration of high sensitivity HRGC/HRMS systems

Table 6. QC acceptance criteria for chlorinated biphenyls in VER, IPR, OPR, and samples[1]

Congener	IUPAC number[2]	Test conc (ng/mL)[3]	VER[4] (%)	IPR		OPR (%)	Labeled compound recovery in samples (%)
				RSD (%)	X (%)		
2-MoCB	1	50	70-130	40	60-140	50-150	
4-MoCB	3	50	70-130	40	60-140	50-150	
2,2'-DiCB	4	50	70-130	40	60-140	50-150	
4,4'-DiCB	15	50	70-130	40	60-140	50-150	
2,2'6-TrCB	19	50	70-130	40	60-140	50-150	
3,4,4'-TrCB	37	50	70-130	40	60-140	50-150	
2,2'6,6'TeCB	54	50	70-130	40	60-140	50-150	
3,3',4,4'-TeCB	77	50	70-130	40	60-140	50-150	
3,4,4',5-TeCB	81	50	70-130	40	60-140	50-150	
2,2',4,6,6'-PeCB	104	50	70-130	40	60-140	50-150	
2,3,3',4,4'-PeCB	105	50	70-130	40	60-140	50-150	
2,3,4,4',5-PeCB	114	50	70-130	40	60-140	50-150	
2,3',4,4',5-PeCB	118	50	70-130	40	60-140	50-150	
2',3,4,4',5-PeCB	123	50	70-130	40	60-140	50-150	
3,3',4,4',5-PeCB	126	50	70-130	40	60-140	50-150	
2,2',4,4',6,6'-HxCB	155	50	70-130	40	60-140	50-150	
2,3,3',4,4',5-HxCB[5]	156	50	70-130	40	60-140	50-150	
2,3,3',4,4',5'-HxCB[5]	157	50	70-130	40	60-140	50-150	
2,3',4,4',5,5'-HxCB	167	50	70-130	40	60-140	50-150	
3,3',4,4',5,5'-HxCB	169	50	70-130	40	60-140	50-150	
2,2',3,4',5,6,6'-HpCB	188	50	70-130	40	60-140	50-150	
2,3,3',4,4',5,5'-HpCB	189	50	70-130	40	60-140	50-150	
2,2',3,3',5,5',6,6'-OcCB	202	50	70-130	40	60-140	50-150	
2,3,3',4,4',5,5',6-OcCB	205	50	70-130	40	60-140	50-150	
2,2',3,3',4,4',5,5',6-NoCB	206	50	70-130	40	60-140	50-150	
2,2',3,3'4,5,5',6,6'-NoCB	208	50	70-130	40	60-140	50-150	
DeCB	209	50	70-130	40	60-140	50-150	
$^{13}C_{12}$-2-MoCB	1L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-4-MoCB	3L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,2'-DiCB	4L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-4,4'-DiCB	15L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,2',6-TrCB	19L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-3,4,4'-TrCB	37L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,2',6,6'-TeCB	54L	100	50-150	50	35-135	30-140	25-150
13C12-3,3',4,4'-TCB	77L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-3,4,4',5-TeCB	81L	100	50-150	50	35-135	30-140	25-150

Congener	IUPAC number[2]	Test conc (ng/mL)[3]	VER[4] (%)	IPR		OPR (%)	Labeled compound recovery in samples (%)
				RSD (%)	X (%)		
$^{13}C_{12}$-2,2',4,6,6'-PeCB	104L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,3,3',4,4'-PeCB	105L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,3,4,4',5-PeCB	114L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,3',4,4',5-PeCB	118L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2',3,4,4',5-PeCB	123L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-3,3',4,4',5-PeCB	126L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,2',4,4',6,6'-HxCB	155L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,3,3',4,4',5 -HxCB[5]	156L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,3,3',4,4',5'-HxCB[5]	157L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,3',4,4',5,5'-HxCB	167L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-3,3',4,4',5,5'-HxCB	169L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,2',3,4',5,6,6'-HpCB	188L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB	189L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-OcCB	202L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,3,3',4,4',5,5',6-OcCB	205L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-NoCB	206L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-NoCB	208L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6,6'-DeCB	209L	100	50-150	50	35-135	30-140	25-150
Cleanup standard							
$^{13}C_{12}$-2,4,4'-TrCB	28L	100	60-130	45	45-120	40-125	30-135
$^{13}C_{12}$-2,3,3',5,5'-PeCB	111L	100	60-130	45	45-120	40-125	30-135
$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB	178L	100	60-130	45	45-120	40-125	30-135

1. QC acceptance criteria for IPR, OPR, and samples based on a 20 μL extract final volume
2. Suffix "L" indicates labeled compound.
3. See Table 5.
4. Section 15.3
5. PCBs 156 and 157 are tested as the sum of two concentrations

Table 7. Scan descriptors, levels of chlorination, m/z information, and substances monitored by HRGC/HRMS

Function and chlorine level	m/z	m/z type	m/z formula	Substance
Fn-1; Cl-1	188.0393	M	$^{12}C_{12}H_9{}^{35}Cl$	Cl-1 CB
	190.0363	M+2	$^{12}C_{12}H_9{}^{37}Cl$	Cl-1 CB
	200.0795	M	$^{13}C_{12}H_9{}^{35}Cl$	$^{13}C_{12}$ Cl-1 CB
	202.0766	M+2	$^{13}C_{12}H_9{}^{37}Cl$	$^{13}C_{12}$ Cl-1 CB
	218.9856	lock	C_4F_9	PFK
Fn-2; Cl-2,3	222.0003	M	$^{12}C_{12}H_8{}^{35}Cl_2$	Cl-2 PCB
	223.9974	M+2	$^{12}C_{12}H_8{}^{35}Cl{}^{37}Cl$	Cl-2 PCB
	225.9944	M+4	$^{12}C_{12}H_8{}^{37}Cl_2$	Cl-2 PCB
	234.0406	M	$^{13}C_{12}H_8{}^{35}Cl_2$	$^{13}C_{12}$ Cl-2 PCB
	236.0376	M+2	$^{13}C_{12}H_8{}^{35}Cl{}^{37}Cl$	$^{13}C_{12}$ Cl-2 PCB
	242.9856	lock	C_6F_9	PFK
	255.9613	M	$^{12}C_{12}H_7{}^{35}Cl_3$	Cl-3 PCB
	257.9584	M+2	$^{12}C_{12}H_7{}^{35}Cl_2{}^{37}Cl$	Cl-3 PCB
Fn-3	255.9613	M	$^{12}C_{12}H_7{}^{35}Cl_3$	Cl-3 PCB
Cl-3,4,5	257.9584	M+2	$^{12}C_{12}H_7{}^{35}Cl_2{}^{37}Cl$	Cl-3 PCB
	259.9554	M+4	$^{12}C_{12}H_7{}^{35}Cl{}^{37}Cl_2$	Cl-3 PCB
	268.0016	M	$^{13}C_{12}H_7{}^{35}Cl_3$	$^{13}C_{12}$ Cl-3 PCB
	269.9986	M+2	$^{13}C_{12}H_7{}^{35}Cl_2{}^{37}Cl$	$^{13}C_{12}$ Cl-3 PCB
	280.9825	lock	C_6F_{11}	PFK
	289.9224	M	$^{12}C_{12}H_6{}^{35}Cl_4$	Cl-4 PCB
	291.9194	M+2	$^{12}C_{12}H_6{}^{35}Cl_3{}^{37}Cl$	Cl-4 PCB
	293.9165	M+4	$^{12}C_{12}H_6{}^{35}Cl_2{}^{37}Cl_2$	Cl-4 PCB

Function and chlorine level	m/z	m/z type	m/z formula	Substance
	301.9626	M	$^{13}C_{12}H_6{}^{35}Cl_4$	$^{13}C_{12}$ Cl-4 PCB
	303.9597	M+2	$^{13}C_{12}H_6{}^{35}Cl_3{}^{37}Cl$	$^{13}C_{12}$ Cl-4 PCB
	323.8834	M	$^{12}C_{12}H5{}^{35}Cl_5$	Cl-5 PCB
	325.8804	M+2	$^{12}C_{12}H5{}^{35}Cl_4{}^{37}Cl$	Cl-5 PCB
	327.8775	M+4	$^{12}C_{12}H5{}^{35}Cl_3{}^{37}Cl_2$	Cl-5 PCB
	337.9207	M+2	$^{13}C_{12}H5{}^{35}Cl_4{}^{37}Cl$	$^{13}C_{12}$ Cl-5 PCB
	339.9178	M+4	$^{13}C_{12}H5{}^{35}Cl_3{}^{37}Cl_2$	$^{13}C_{12}$ Cl-5 PCB
Fn-4	289.9224	M	$^{12}C_{12}H_6{}^{35}Cl_4$	Cl-4 PCB
Cl-4,5,6	291.9194	M+2	$^{12}C_{12}H_6{}^{35}Cl_3{}^{37}Cl$	Cl-4 PCB
	293.9165	M+4	$^{12}C_{12}H_6{}^{35}Cl_2{}^{37}Cl_2$	Cl-4 PCB
	301.9626	M+2	$^{13}C_{12}H_6{}^{35}Cl_3{}^{37}Cl$	$^{13}C_{12}$ Cl-4 PCB
	303.9597	M+4	$^{13}C_{12}H_6{}^{35}Cl_2{}^{37}Cl_2$	$^{13}C_{12}$ Cl-4 PCB
	323.8834	M	$^{12}C_{12}H_5{}^{35}Cl_5$	Cl-5 PCB
	325.8804	M+2	$^{12}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	Cl-5 PCB
	327.8775	M+4	$^{12}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	Cl-5 PCB
	330.9792	lock	C_7F_{15}	PFK
	337.9207	M+2	$^{13}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	$^{13}C_{12}$ Cl-5 PCB
	339.9178	M+4	$^{13}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	$^{13}C_{12}$ Cl-5 PCB
	359.8415	M+2	$^{13}C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	Cl-6 PCB
	361.8385	M+4	$^{13}C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	Cl-6 PCB
	363.8356	M+6	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}Cl_2$	Cl-6 PCB
	371.8817	M+2	$^{13}C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	$^{13}C_{12}$ Cl-6 PCB
	373.8788	M+4	$^{13}C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	$^{13}C_{12}$ Cl-6 PCB
Fn-5	323.8834	M	$^{12}C_{12}H_5{}^{35}Cl_5$	Cl-5 PCB

Function and chlorine level	m/z	m/z type	m/z formula	Substance
Cl-5,6,7	325.8804	M+2	$^{12}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	Cl-5 PCB
	327.8775	M+4	$^{12}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	Cl-5 PCB
	337.9207	M+2	$^{13}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	$^{13}C_{12}$ Cl-5 PCB
	339.9178	M+4	$^{13}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	$^{13}C_{12}$ Cl-5 PCB
	354.9792	lock	C_9F_{13}	PFK
	359.8415	M+2	$^{12}C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	Cl-6 PCB
	361.8385	M+4	$^{12}C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	Cl-6 PCB
	363.8356	M+6	$^{12}C_{12}H_4{}^{35}Cl_3{}^{37}Cl_3$	Cl-6 PCB
	371.8817	M+2	$^{13}C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	$^{13}C_{12}$ Cl-6 PCB
	373.8788	M+4	$^{13}C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	$^{13}C_{12}$ Cl-6 PCB
	393.8025	M+2	$^{12}C_{12}H_3{}^{35}Cl_6{}^{37}Cl$	Cl-7 PCB
	395.7995	M+4	$^{12}C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$	Cl-7 PCB
	397.7966	M+6	$^{12}C_{12}H_3{}^{35}Cl_4{}^{37}Cl_3$	Cl-7 PCB
	405.8428	M+2	$^{13}C_{12}H_3{}^{35}Cl_6{}^{37}Cl$	$^{13}C_{12}$ Cl-7 PCB
	407.8398	M+4	$^{13}C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$	$^{13}C_{12}$ Cl-7 PCB
	454.9728	QC	$C_{11}F_{17}$	PFK
Fn-6	393.8025	M+2	$^{12}C_{12}H_3{}^{35}Cl_6{}^{37}Cl$	Cl-7 PCB
Cl-7,8,9,10	395.7995	M+4	$^{12}C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$	Cl-7 PCB
	397.7966	M+6	$^{12}C_{12}H_3{}^{35}Cl_4{}^{37}Cl_3$	Cl-7 PCB
	405.8428	M+2	$^{13}C_{12}H_3{}^{35}Cl_6{}^{37}Cl$	$^{13}C_{12}$ Cl-7 PCB
	407.8398	M+4	$^{13}C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$	$^{13}C_{12}$ Cl-7 PCB
	427.7635	M+2	$^{12}C_{12}H_2{}^{35}Cl_7{}^{37}Cl$	Cl-8 PCB
	429.7606	M+4	$^{12}C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$	Cl-8 PCB
	431.7576	M+6	$^{12}C_{12}H_2{}^{35}Cl_5{}^{37}Cl_3$	Cl-8 PCB

Function and chlorine level	m/z	m/z type	m/z formula	Substance
	439.8038	M+2	$^{13}C_{12}H_2{}^{35}Cl_7{}^{37}Cl$	$^{13}C_{12}$ Cl-8 PCB
	441.8008	M+4	$^{13}C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$	$^{13}C_{12}$ Cl-8 PCB
	442.9728	QC	$C_{10}F_{13}$	PFK
	454.9728	lock	$C_{11}F_{13}$	PFK
	461.7246	M+2	$^{12}C_{12}H_1{}^{35}Cl_8{}^{37}Cl$	Cl-9 PCB
	463.7216	M+4	$^{12}C_{12}H_1{}^{35}Cl_7{}^{37}Cl_2$	Cl-9 PCB
	465.7187	M+6	$^{12}C_{12}H_1{}^{35}Cl_6{}^{37}Cl_3$	Cl-9 PCB
	473.7648	M+2	$^{13}C_{12}H_1{}^{35}Cl_8{}^{37}Cl$	$^{13}C_{12}$ Cl-9 PCB
	475.7619	M+4	$^{13}C_{12}H_1{}^{35}Cl_7{}^{37}Cl_2$	$^{13}C_{12}$ Cl-9 PCB
	495.6856	M+2	$^{13}C_{12}H_4{}^{35}Cl_9{}^{37}Cl$	Cl-10 PCB
	497.6826	M+4	$^{12}C_{12}{}^{35}Cl_8{}^{37}Cl_2$	Cl-10 PCB
	499.6797	M+6	$^{12}C_{12}{}^{35}Cl_7{}^{37}Cl_3$	Cl-10 PCB
	507.7258	M+2	$^{13}C_{12}H_3{}^{35}Cl_9{}^{37}Cl$	$^{13}C_{12}$ Cl-10 PCB
	509.7229	M+4	$^{13}C_{12}H_1{}^{35}Cl_8{}^{37}Cl_2$	$^{13}C_{12}$ Cl-10 PCB
	511.7199	M+6	$^{13}C_{12}H_4{}^{35}Cl_8{}^{37}Cl_4$	$^{13}C_{12}$ Cl-10 PCB

1. Isotopic masses used for accurate mass calculation

^{1}H	1.0078
^{12}C	12.0000
^{13}C	13.0034
^{35}Cl	34.9689
^{37}Cl	36.9659
^{19}F	18.9984

Table 8. Theoretical ion abundance ratios and QC limits

Chlorine atoms	m/z's forming ratio	Theoretical ratio	Lower QC limit	Upper QC limit
1	m/m+2	3.13	2.66	3.60
2	m/(m+2)	1.56	1.33	1.79
3	m/(m+2)	1.04	0.88	1.20
4	m/(m+2)	0.77	0.65	0.89
5	(m+2)/(m+4)	1.55	1.32	1.78
6	(m+2)/(m+4)	1.24	1.05	1.43
7	(m+2)/(m+4)	1.05	0.89	1.21
8	(m+2)/(m+4)	0.89	0.76	1.02
9	(m+2)/(m+4)	0.77	0.65	0.89
10	(m+2)/(m+4)	0.69	0.59	0.79

Table 9. Suggested Sample Quantities to be Extracted for Various Matrices[1]

Sample matrix[2]	Example	Percent solids	Phase	Quantity extracted
Single-phase				
Aqueous	Drinking water	<1	[3]	1000 mL
	Groundwater			
	Treated wastewater			
Solid	Dry soil	>20	Solid	10 g
	Compost			
	Ash			
Organic	Waste solvent	<1	Organic	10 g
	Waste oil			
	Organic polymer			
Tissue	Fish	—	Organic	10 g
	Human adipose			
Multi-phase				
Liquid/Solid				
Aqueous/Solid	Wet soil	1-30	Solid	10 g
	Untreated effluent			
	Digested municipal sludge			
	Filter cake			
	Paper pulp			
Organic/solid	Industrial sludge	1-100	Both	10 g
	Oily waste			
Liquid/Liquid				
Aqueous/organic	In-process effluent	<1	Organic	10 g
	Untreated effluent			
	Drum waste			
Aqueous/organic/solid	Untreated effluent	>1	Organic & solid	10 g
	Drum waste			

1. The quantity of sample to be extracted is adjusted to provide 10 g of solids (dry weight). One liter of aqueous samples containing one percent solids will contain 10 grams of solids. For aqueous samples containing greater than one percent solids, a lesser volume is used so that 10 grams of solids (dry weight) will be extracted.
2. The sample matrix may be amorphous for some samples. In general, when the CBs are in contact with a multi-phase system in which one of the phases is water, they will be preferentially dispersed in or adsorbed on the alternate phase because of their low solubility in water.
3. Aqueous samples are filtered after spiking with the labeled compounds. The filtrate and the materials trapped on the filter are extracted separately, and the extracts are combined for cleanup and analysis.

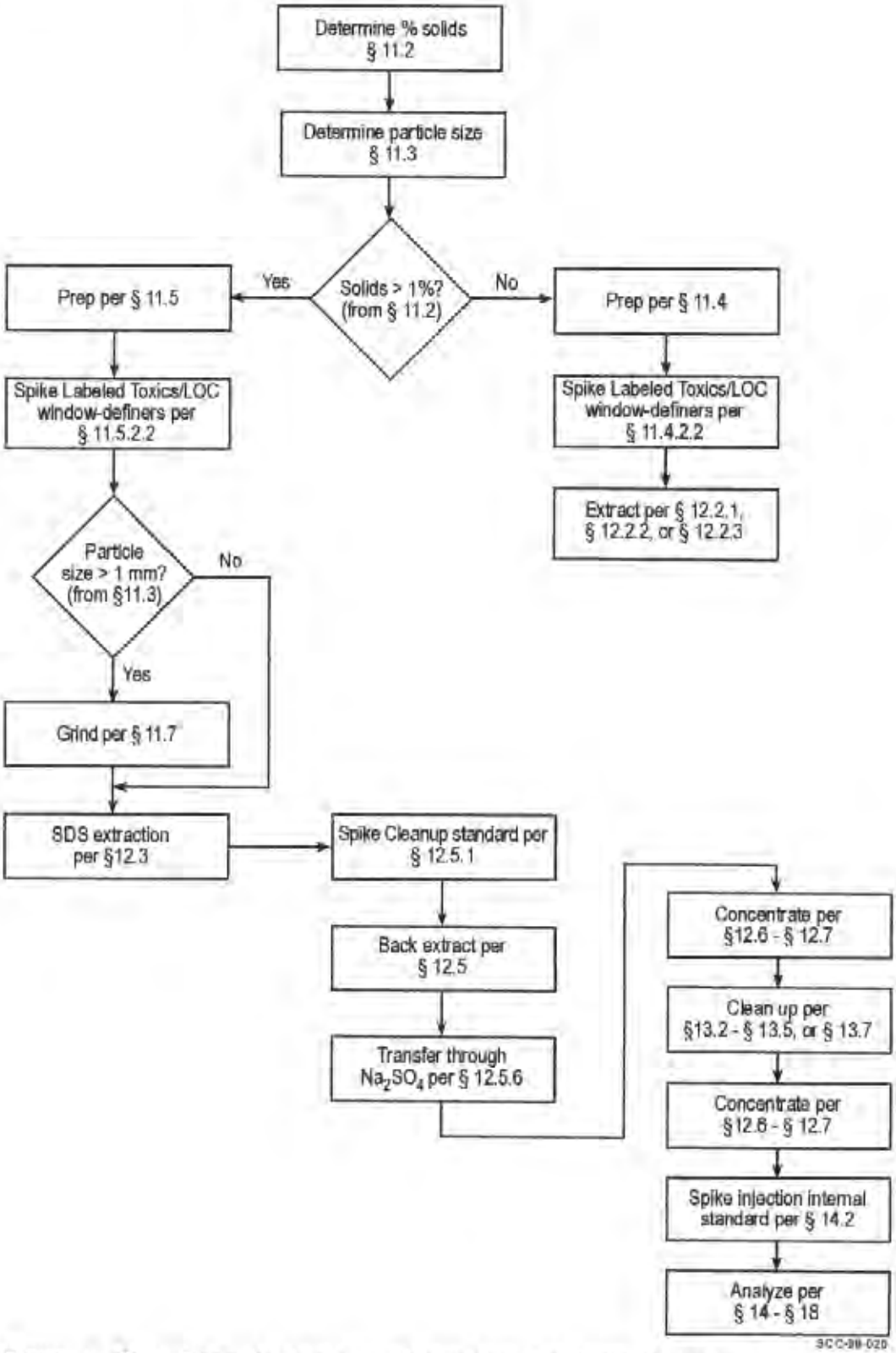


Figure 1 Flow Chart for Analysis of Aqueous and Solid Samples

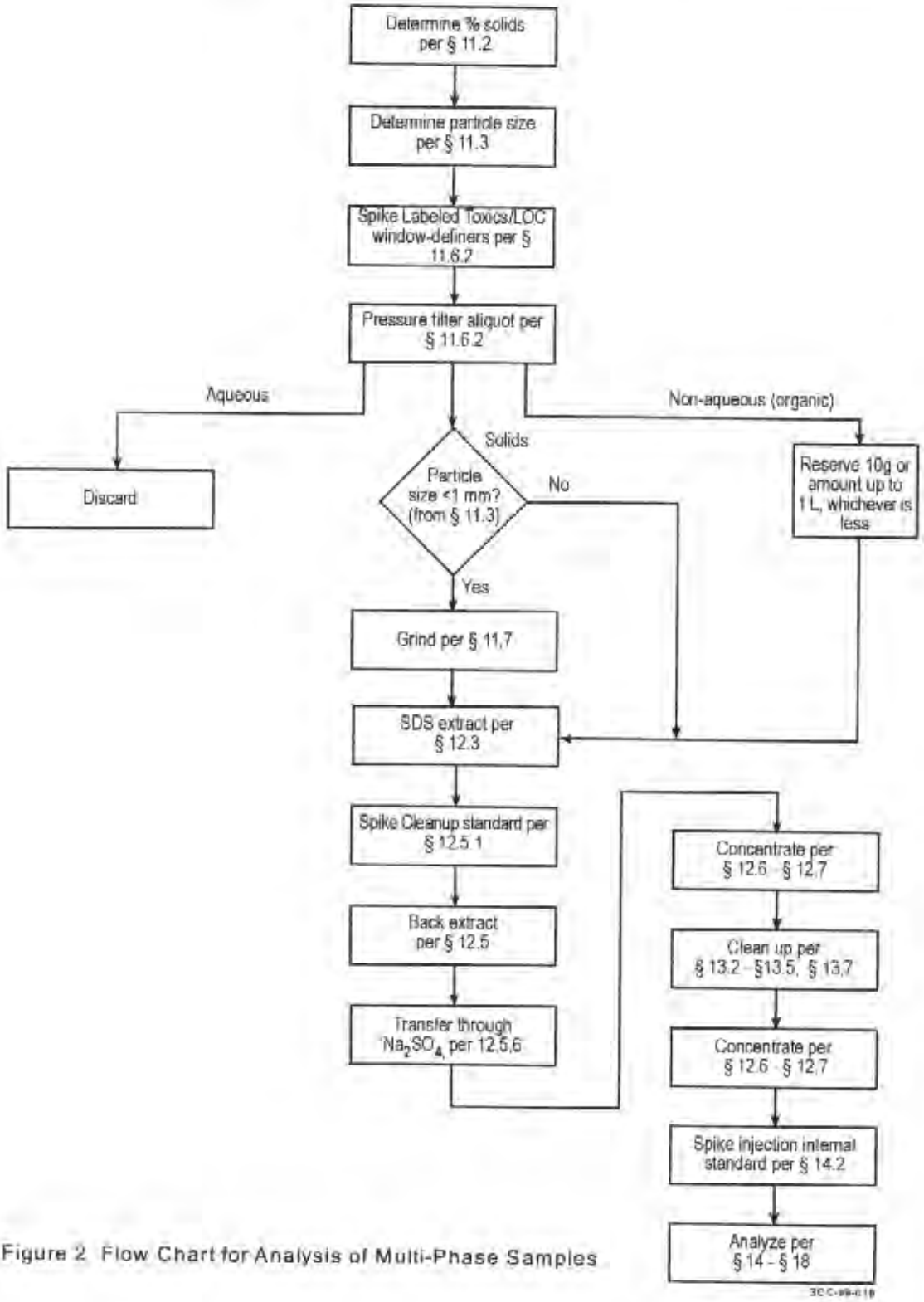


Figure 2. Flow Chart for Analysis of Multi-Phase Samples

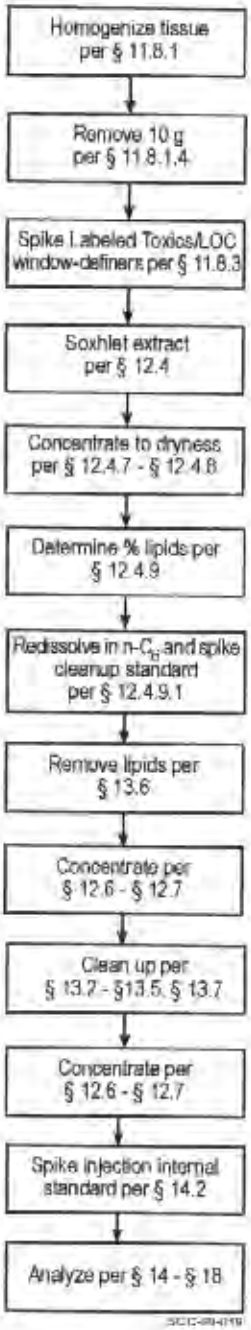


Figure 3 Flow Chart for Analysis of Tissue Samples

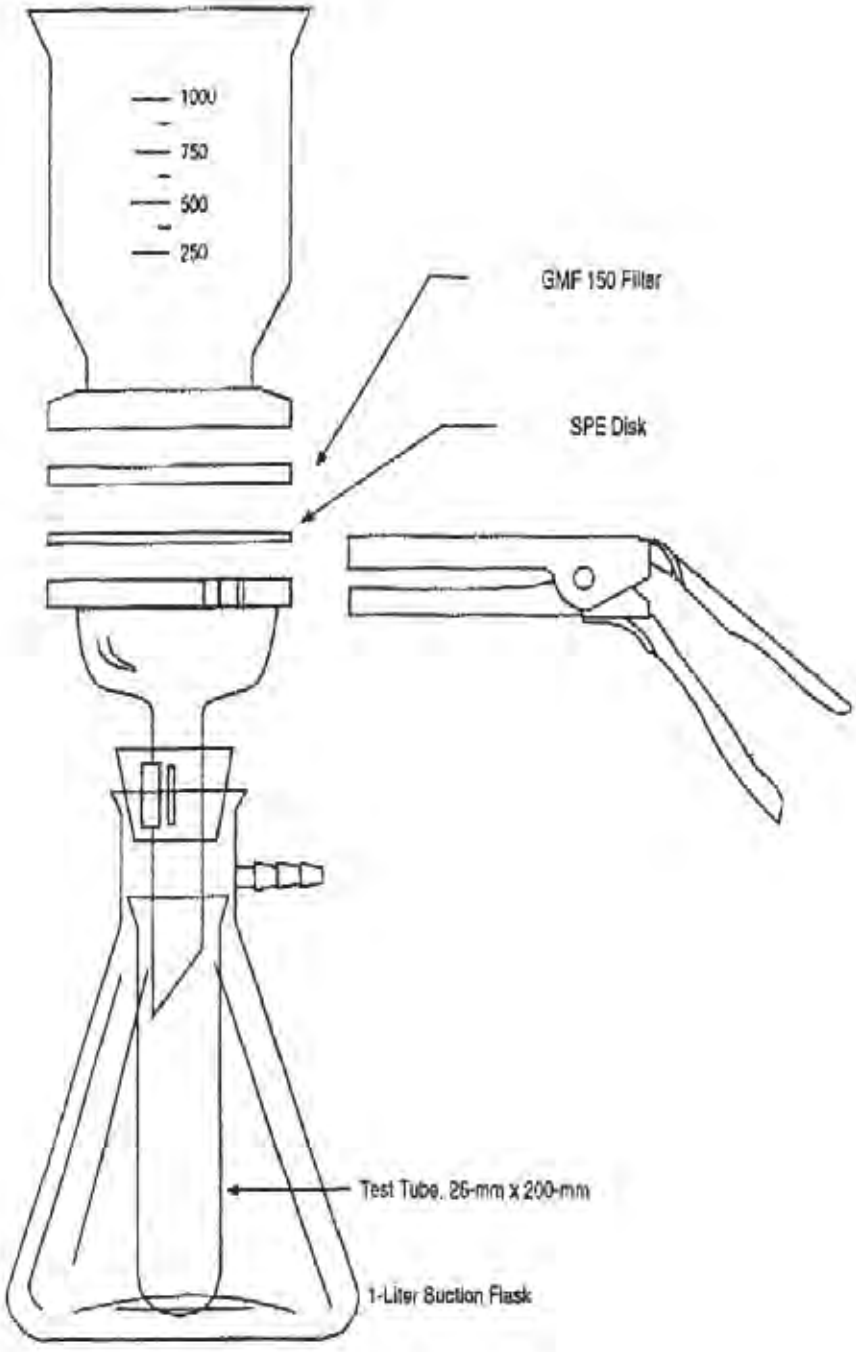


Figure 4 Solid-phase Extraction Apparatus

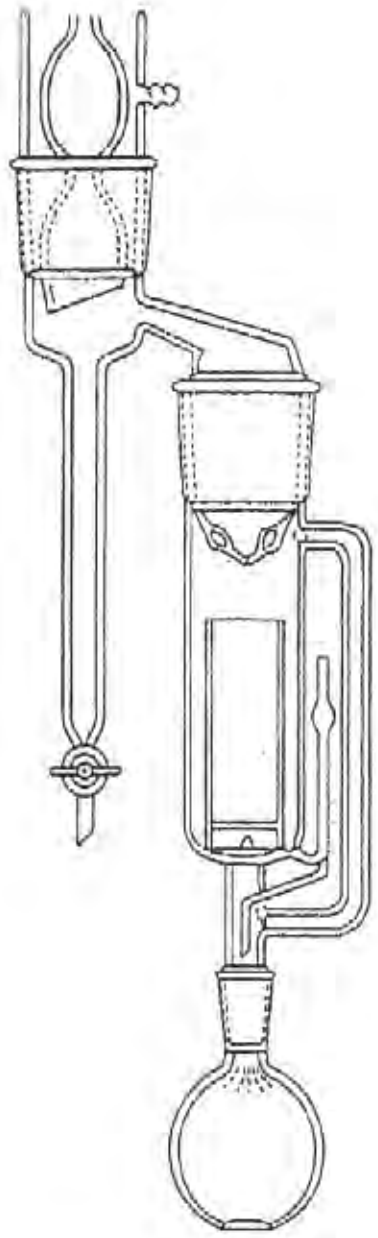


Figure 5 Soxhlet/Dean-Stark Extractor

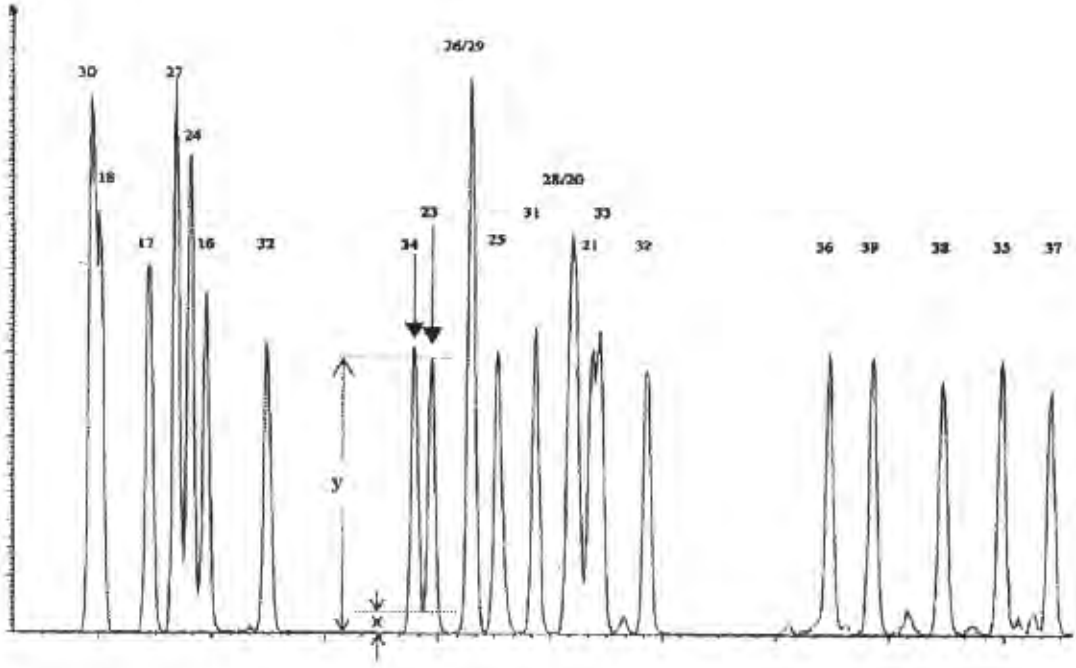


Figure 6 Octyl column resolution test #1: Separation of Cl-3 congeners 34 and 23 with valley <40% (i.e. 100x/y < 40%)

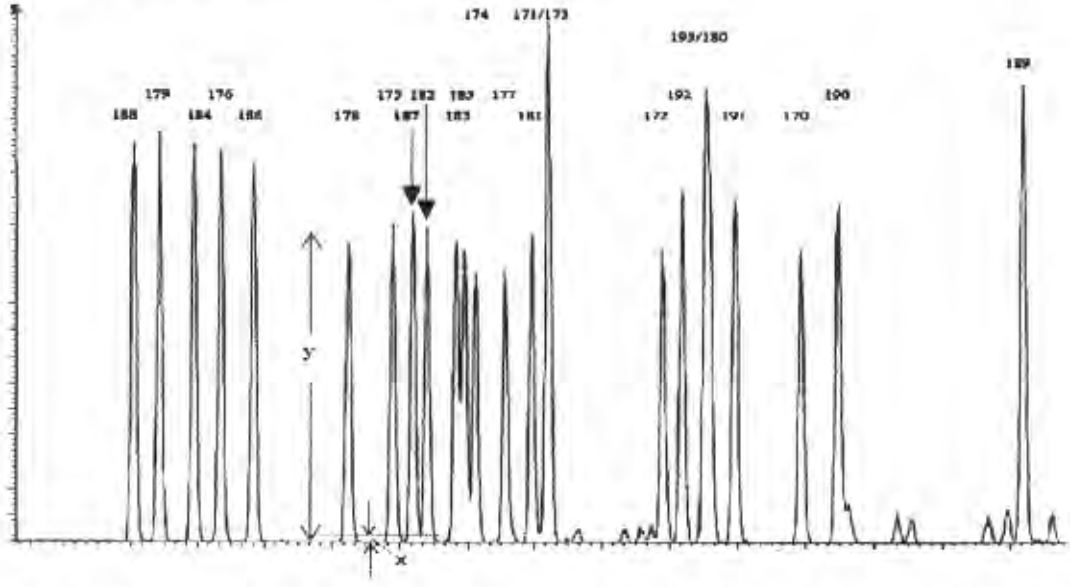


Figure 7 Octyl column resolution test #2: Separation of Cl-7 congeners 187 and 182 with valley < 40% (i.e. 100 x/y < 40%)

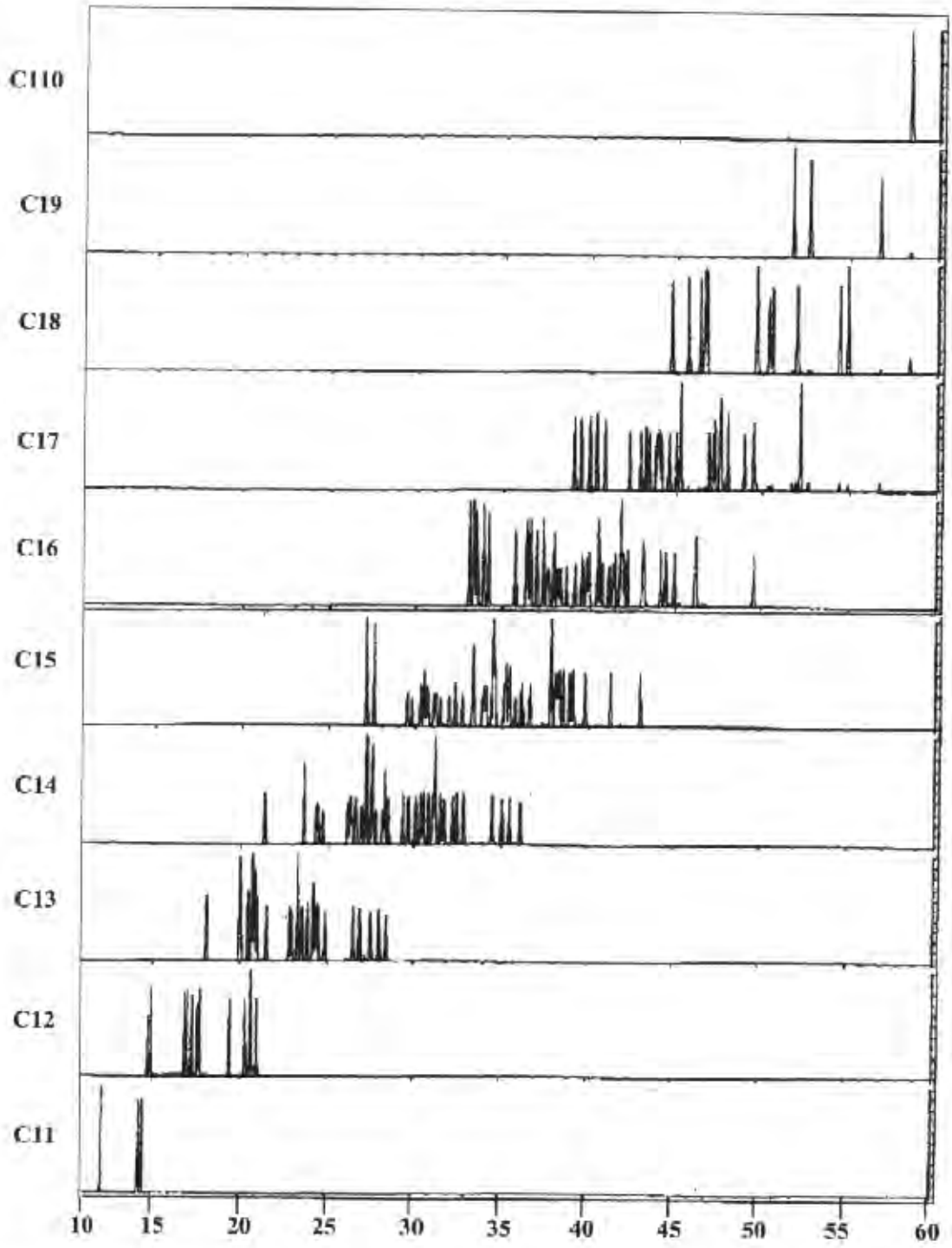


Figure 8 CB congeners at each level of chlorination on the SPB-octyl column

24.0 Glossary

These definitions and purposes are specific to this Method but have been conformed to common usage to the extent possible.

24.1 Units of weight and measure and their abbreviations

24.1.1 Symbols

°C	degrees Celsius
µL	microliter
µm	micrometer
<	less than
>	greater than
%	percent

24.1.2 Alphabetical abbreviations

cm	centimeter
g	gram
h	hour
ID	inside diameter
in	inch
L	liter
M	Molecular ion
m	meter
mg	milligram
min	minute
mL	milliliter
mm	millimeter
m/z	mass-to-charge ratio
N	normal; gram molecular weight of solute divided by hydrogen equivalent of solute, per liter of solution
OD	outside diameter
pg	picogram
ppb	part-per-billion
ppm	part-per-million
ppq	part-per-quadrillion
ppt	part-per-trillion
psig	pounds-per-square inch gauge
v/v	volume per unit volume
w/v	weight per unit volume

24.2 Definitions and acronyms (in alphabetical order).

Analyte—A CB tested for by this Method. The analytes are listed in Table 1.

Calibration standard (CAL)—A solution prepared from a secondary standard and/or stock solutions and used to calibrate the response of the HRGC/HRMS instrument.

Calibration verification standard (VER)—The mid-point calibration standard (CS-3) that is used to verify calibration. See Table 5.

CB—chlorinated biphenyl congener. One of the 209 individual chlorinated biphenyl congeners determined using this Method. The 209 CBs are listed in Table 1.

CS-0.2, CS-1, CS-2, CS-3, CS-4, CS-5. See Calibration standards and Table 5.

DeCB—decachlorobiphenyl (PCB 209)

DiCB—dichlorobiphenyl

Estimated method detection limit (EMDL)—The lowest concentration at which a CB can be detected with common laboratory interferences present. EMDLs are listed in Table 2.

Estimated minimum level (EML)—The lowest concentration at which a CB can be measured reliably with common laboratory interferences present. EMLs are listed in Table 2.

Field blank—An aliquot of reagent water or other reference matrix that is placed in a sample container in the laboratory or the field, and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.

GC—Gas chromatograph or gas chromatography

GPC—Gel permeation chromatograph or gel permeation chromatography

HpCB—heptachlorobiphenyl

HPLC—High performance liquid chromatograph or high performance liquid chromatography

HRGC—High resolution GC

HRMS—High resolution MS

HxCB—hexachlorobiphenyl

Labeled injection internal standard—All five, or any one of the five, $^{13}C_{12}$-labeled CB congeners spiked into the concentrated extract immediately prior to injection of an aliquot of the extract into the HRGC/HRMS. The five Labeled injection internal standards in this Method are CBs with IUPAC numbers 9, 52, 101, 138, and 194.

Internal standard—a labeled compound used as a reference for quantitation of other labeled compounds and for quantitation of native CB congeners other than the congener of which it is a labeled analog. See Internal standard quantitation.

Internal standard quantitation—A means of determining the concentration of (1) a naturally occurring (native) compound by reference to a compound other than its labeled analog and (2) a labeled compound by reference to another labeled compound.

IPR—Initial precision and recovery; four aliquots of a reference matrix spiked with the analytes of interest and labeled compounds and analyzed to establish the ability of the laboratory to generate acceptable precision and recovery. An IPR is performed prior to the first time this Method is used and any time the Method or instrumentation is modified.

Isotope dilution quantitation—A means of determining a naturally occurring (native) compound by reference to the same compound in which one or more atoms has been isotopically enriched. In this Method, all 12 carbon atoms in the biphenyl molecule are enriched with carbon-13 to produce $^{13}C_{12}$-labeled analogs of the chlorinated biphenyls. The $^{13}C_{12}$-labeled CBs are spiked into each sample and allow identification and correction of the concentration of the native compounds in the analytical process.

K-D—Kuderna-Danish concentrator; a device used to concentrate the analytes in a solvent.

Laboratory blank—See Method blank.

Laboratory control sample (LCS)—See Ongoing precision and recovery standard (OPR).

Laboratory reagent blank—See Method blank.

May—This action, activity, or procedural step is neither required nor prohibited.

May not—This action, activity, or procedural step is prohibited.

Method blank—An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The Method blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

Minimum level of quantitation (ML)—The level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all Method-specified sample weights, volumes, and cleanup procedures have been employed.

MoCB—monochlorobiphenyl.

MS—Mass spectrometer or mass spectrometry.

Must—This action, activity, or procedural step is required.

NoCB-nonachlorobiphenyl.

OcCB—octachlorobiphenyl.

OPR—Ongoing precision and recovery standard (OPR); a method blank spiked with known quantities of analytes. The OPR is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this Method for precision and recovery.

Perfluorokerosene (PFK)—A mixture of compounds used to calibrate the exact m/z scale in the HRMS.

Preparation blank—See Method blank.

Quality control check sample (QCS)—A sample containing all or a subset of the analytes at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from a source of standards different from the source of calibration standards. It is used to check laboratory performance with test materials prepared external to the normal preparation process.

PeCB—pentachlorobiphenyl.

PCB—polychlorinated biphenyl.

Reagent water—water demonstrated to be free from the analytes of interest and potentially interfering substances at the method detection limit for the analyte.

Relative standard deviation (RSD)—The standard deviation times 100 divided by the mean. Also termed "coefficient of variation."

RF—Response factor. See Section 10.5.

RR—Relative response. See Section 10.4.

RSD—See Relative standard deviation.

SDS—Soxhlet/Dean-Stark extractor, an extraction device applied to the extraction of solid and semi-solid materials (Reference 11 and Figure 5).

Signal-to-noise ratio (S/N)—The height of the signal as measured from the mean (average) of the noise to the peak maximum divided by the width of the noise.

Should—This action, activity, or procedural step is suggested but not required.

SICP—Selected ion current profile; the line described by the signal at an exact m/z.

SPE—Solid-phase extraction; an extraction technique in which an analyte is extracted from an aqueous sample by passage over or through a material capable of reversibly adsorbing the analyte. Also termed liquid-solid extraction.

Stock solution—A solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

TeCB—tetrachlorobiphenyl.

TEF-Toxicity equivalency factor; an estimate of the toxicity of a specific congener relative to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin.

TEQ—the toxicity equivalent concentration in an environmental sample. It is the sum of the concentrations of each individual toxic PCB and each individual 2,3,7,8-substituted, tetra-through octachlorinated, dibenzo-p-dioxin and dibenzofuran multiplied by their respective TEFs (Reference 1).

TEQ_{PCB}—the portion of the TEQ attributable to the toxic PCBs.

TrCB—trichlorobiphenyl

Unique GC resolution or uniquely resolved—Two adjacent chromatographic peaks in which the height of the valley is less than 40 percent of the height of the shorter peak (See section 6.9.1.1.2 and Figures 6 and 7 for unique resolution specific to the SPB-octyl column).

VER—See Calibration verification.

Annex A - Preliminary information for determination of 209 CBs on the DB-1 column

1 Column and Conditions

1.1 Column—30±5-m long x 0.25±0.02-mm ID; 0.25-μm film DB-1 (J&W, or equivalent).

1.2 Suggested GC operating conditions:

Injector temperature:	270 °C
Interface temperature:	290 °C
Initial temperature:	75 °C
Initial time:	2 minutes
Temperature program:	75-150 °C @ 15 °C/minute
	150-270 °C @ 2.5 °C/minute
Final time:	7 minutes
Carrier gas velocity	40 cm/sec @ 200 °C

Note: *The GC conditions may be optimized for compound separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, blanks, IPR and OPR aliquots, and samples.*

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2 Operating information

2.1 Congener solutions—Mixes of individual congeners that will allow separation of all 209 congeners on the DB-1 column had not been developed at the date of writing of Revision A to Method 1668.

2.2 Elution order data—The congener mixes developed for the SPB-octyl column (Table 4 of Method 1668) were run on the DB-1 column. Although some congeners in these mixes co-elute on the DB-1 column, the mixes allow determination of retention times the DB-1 column. These retention times are shown in Annex Table A-1

2.2 Window-defining congeners—The beginning and ending congeners at each level of chlorination are the same as those for the SPB-octyl column. See Table 2 in Method 1668.

2.3 Scan descriptors—The 6-function scan descriptors are shown in Annex Table A-2

Table A-1 Retention time (RT) references, quantitation references, relative retention times (RRTs), estimated detection limits (EMDLs), and estimated minimum levels (EMLs) for CB congeners using a DB-1 column.

Labeled or native CB[1]	IUPAC number[2]	Retention time and quantitation references	IUPAC number	RT	RRT	RRT QC limits[3]
$^{13}C_{12}$-2-MoCB[4]	1L	$^{13}C_{12}$-4-MoCB[4,5]	3L	09:17	0.8855	0.8776-0.8935
2-MoCB	1	$^{13}C_{12}$-2-MoCB[4]	1L	09:17	1.0000	0.9964-1.0072
3-MoCB	2	$^{13}C_{12}$-4-MoCB[4,5]	3L	10:22	0.9889	0.9809-0.9968
$^{13}C_{12}$-4-MoCB[4,5]	3L	$^{13}C_{12}$-2,2',5,5'-TeCB[7]	52L	10:29	0.5561	0.5473-0.5650
4-MoCB	3	$^{13}C_{12}$-4-MoCB[4,5]	3L	10:29	1.0000	0.9968-1.0064
$^{13}C_{12}$-2,2'-DiCB[4]	4L	$^{13}C_{12}$-4,4'-DiCB[4,5]	15L	11:08	0.7591	0.7477-0.7705
2,2'-DiCB	4	$^{13}C_{12}$-2,2'-DiCB[4]	4L	11:08	1.0000	0.9925-1.0075
2,6-DiCB	10	$^{13}C_{12}$-4,4'-DiCB[4,5]	15L	11:10	0.7614	0.7500-0.7727
2,5-DiCB	9	$^{13}C_{12}$-4,4'-DiCB[4,5]	15L	12:08	0.8273	0.8216-0.8330
2,4-DiCB	7	$^{13}C_{12}$-4,4'-DiCB[4,5]	15L	12:09	0.8284	0.8227-0.8341
2,3'-DiCB	6	$^{13}C_{12}$-4,4'-DiCB[4,5]	15L	12:31	0.8534	0.8477-0.8591
2,4'-DiCB[6]	8	$^{13}C_{12}$-4,4'-DiCB[4,5]	15L	12:43	0.8670	0.8614-0.8727
2,3-DiCB	5	$^{13}C_{12}$-4,4'-DiCB[4,5]	15L	12:46	0.8705	0.8648-0.8761
$^{13}C_{12}$-2,2',6-TrCB[4]	19L	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	13:31	0.7990	0.7892-0.8089
2,2',6-TrCB	19	$^{13}C_{12}$-2,2',6-TrCB[4]	19L	13:31	1.0000	0.9975-1.0049
3,5-DiCB	14	$^{13}C_{12}$-4,4'-DiCB[4,5]	15L	13:36	0.9273	0.9216-0.9330
2,4,6-TrCB	30	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	14:06	0.8335	0.8286-0.8384
3,3'-DiCB	11	$^{13}C_{12}$-4,4'-DiCB[4,5]	15L	14:11	0.9670	0.9614-0.9727
3,4'-DiCB	13	$^{13}C_{12}$-4,4'-DiCB[4,5]	15L	14:26	0.9841	0.9784-0.9898
3,4-DiCB	12	$^{13}C_{12}$-4,4'-DiCB[4,5]	15L	14:27	0.9852	0.9795-0.9909
2,2',5-TrCB[6]	18	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	14:36	0.8631	0.8581-0.8680
$^{13}C_{12}$-4,4'-DiCB[4,5]	15L	$^{13}C_{12}$-2,2',5,5'-TeCB[7]	52L	14:40	0.7781	0.7692-0.7869
4,4'-DiCB	15	$^{13}C_{12}$-4,4'-DiCB[4,5]	15L	14:40	1.0000	0.9977-1.0043
2,2',4-TrCB	17	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	14:43	0.8700	0.8650-0.8749
2,3',6-TrCB	27	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	15:06	0.8926	0.8877-0.8975

Labeled or native CB[1]	IUPAC number[2]	Retention time and quantitation references	IUPAC number	RT	RRT	RRT QC limits[3]
2,3,6-TrCB	24	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	15:06	0.8926	0.8877-0.8975
2,2',3-TrCB	16	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	15:26	0.9123	0.9074-0.9172
2,4',6-TrCB	32	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	15:29	0.9153	0.9103-0.9202
$^{13}C_{12}$-2,2',6,6'-TeCB[4]	54L	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	16:02	0.6139	0.6075-0.6203
2,2',6,6'-TeCB	54	$^{13}C_{12}$-2,2',6,6'-TeCB[4]	54L	16:02	1.0000	0.9979-1.0042
2',3,5-TrCB	34	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	16:03	0.9488	0.9438-0.9537
2,3,5-TrCB	23	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	16:07	0.9527	0.9478-0.9576
2,4,5-TrCB	29	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	16:18	0.9635	0.9586-0.9685
2,3',5-TrCB	26	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	16:29	0.9744	0.9695-0.9793
2,3',4-TrCB	25	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	16:36	0.9813	0.9764-0.9862
2,4',5-TrCB	31	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	16:52	0.9970	0.9921-1.0020
$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	$^{13}C_{12}$-2,2',5,5'-TeCB[7]	52L	16:55	0.8974	0.8930-0.9019
2,4,4'-TrCB[5]	28	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	16:55	1.0000	0.9960-1.0039
2,2',4,6-TeCB	50	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	16:55	0.6477	0.6414-0.6541
2,3,4-TrCB	21	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	17:21	1.0256	1.0207-1.0305
2,2',5,6'-TeCB	53	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	17:26	0.6675	0.6611-0.6739
2,3,3'-TrCB	20	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	17:22	1.0266	1.0217-1.0315
2',3,4-TrCB	33	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	17:24	1.0286	1.0236-1.0335
2,2',4,6'-TeCB	51	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	17:42	0.6777	0.6713-0.6841
2,3,4'-TrCB	22	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	17:43	1.0473	1.0424-1.0522
2,2',3,6-TeCB	45	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	18:00	0.6892	0.6828-0.6956
3,3',5-TrCB	36	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	18:16	1.0798	1.0749-1.0847
2,2',3,6'-TeCB	46	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	18:24	0.7045	0.6981-0.7109
3,4',5-TrCB	39	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	18:37	1.1005	1.0956-1.1054
$^{13}C_{12}$-2,2',5,5'-TeCB[7]	52L	$^{13}C_{12}$-2,2',5,5'-TeCB[7]	52L	18:51	1.0000	0.9956-1.0044
2,2',5,5'-TeCB[6]	52	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	18:51	0.7218	0.7154-0.7281
2,3',4,6-TeCB	69	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	18:52	0.7224	0.7160-0.7288
2,3',5',6-TeCB	73	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	18:57	0.7256	0.7192-0.7320

Labeled or native CB[1]	IUPAC number[2]	Retention time and quantitation references	IUPAC number	RT	RRT	RRT QC limits[3]
2,2',4,5'-TeCB	49	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	19:00	0.7275	0.7211-0.7339
2,2',3,5-TeCB	43	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	19:04	0.7301	0.7237-0.7364
3,4,5-TrCB	38	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	19:12	1.1350	1.1300-1.1399
2,2',4,4'-TeCB	47	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	19:15	0.7371	0.7307-0.7435
2,4,4',6-TeCB	75	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	19:20	0.7403	0.7339-0.7466
2,2',4,5-TeCB	48	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	19:20	0.7403	0.7339-0.7466
2,3,5,6-TeCB	65	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	19:31	0.7473	0.7409-0.7537
2,3,4,6-TeCB	62	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	19:36	0.7505	0.7441-0.7569
3,3',4-TrCB	35	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	19:41	1.1635	1.1586-1.1685
$^{13}C_{12}$-2,2',4,6,6'-PeCB[4]	104L	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,6]	118L	19:45	0.7037	0.6977-0.7096
2,2',4,6,6'-PeCB	104	$^{13}C_{12}$-2,2',4,6,6'-PeCB[4]	104L	19:45	1.0000	0.9983-1.0034
2,2',3,5'-TeCB[3]	44	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	19:55	0.7626	0.7562-0.7690
$^{13}C_{12}$-3,4,4'-TrCB[4]	37L	$^{13}C_{12}$-2,4,4'-TrCB[5]	28L	20:03	1.1852	1.1803-1.1901
3,4,4'-TrCB	37	$^{13}C_{12}$-3,4,4'-TrCB[5]	37L	20:03	1.0000	0.9983-1.0033
2,3,3',6-TeCB	59	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	20:05	0.7690	0.7626-0.7754
2,2',3,4'-TeCB	42	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	20:07	0.7703	0.7639-0.7766
2,3',5,5'-TeCB	72	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	20:36	0.7888	0.7824-0.7951
2,3',4',6-TeCB	71	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	20:36	0.7888	0.7824-0.7951
2,3,4',6-TeCB	64	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	20:37	0.7894	0.7830-0.7958
2,2',3,4-TeCB	41	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	20:39	0.7907	0.7843-0.7971
2,2',3,6,6'-PeCB	96	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,6]	118L	20:48	0.7411	0.7352-0.7470
2,3',4,5'-TeCB	68	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	20:52	0.7990	0.7926-0.8054
2,2',3,3'-TeCB	40	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	20:58	0.8028	0.7996-0.8060
2,3,3',5-TeCB	57	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	21:21	0.8175	0.8143-0.8207
2,2',4,5,6-PeCB	103	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,6]	118L	21:22	0.7613	0.7553-0.7672
2,3',4,5-TeCB	67	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	21:38	0.8283	0.8251-0.8315
2,2',4,4',6-PeCB	100	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,6]	118L	21:41	0.7726	0.7666-0.7785
2,3,3',5'-TeCB	58	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	21:43	0.8315	0.8283-0.8347

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2,3,4',5-TeCB	63	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	21:51	0.8366	0.8334-0.8398
2,2',3,5,6'-PeCB	94	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	22:05	0.7868	0.7809-0.7928
2,4,4',5-TeCB	74	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	22:07	0.8468	0.8437-0.8500
2,3,4,5-TeCB	61	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	22:11	0.8494	0.8462-0.8526
2,3',4',5-TeCB	70	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	22:20	0.8551	0.8519-0.8583
2',3,4,5-TeCB	76	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	22:25	0.8583	0.8551-0.8615
2,2',3',4,6-PeCB	98	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	22:28	0.8005	0.7975-0.8034
2,3',4,4'-TeCB[6]	66	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	22:29	0.8609	0.8577-0.8641
2,2',4,5,6'-PeCB	102	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	22:32	0.8029	0.7999-0.8058
2,2',3,5',6-PeCB	95	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	22:34	0.8040	0.8011-0.8070
2,2',3,5,6-PeCB	93	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	22:36	0.8052	0.8023-0.8082
3,3',5,5'-TeCB	80	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	22:45	0.8711	0.8679-0.8743
2,2',3,4,6-PeCB	88	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	22:49	0.8129	0.8100-0.8159
2,2',3,4',6-PeCB	91	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	22:55	0.8165	0.8135-0.8195
2,3,3',4'-TeCB	55	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	22:57	0.8787	0.8756-0.8819
2,3',4,5,6-PeCB	121	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	23:04	0.8219	0.8189-0.8248
2,3,3',4'-TeCB	56	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	23:24	0.8960	0.8928-0.8992
2,3,4,4'-TeCB	60	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	23:24	0.8960	0.8928-0.8992
$^{13}C_{12}$-2,2',4,4',6,6'-HxCB[4]	155L	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	23:43	0.7104	0.7054-0.7154
2,2',4,4',6,6'-HxCB	155	$^{13}C_{12}$-2,2',4,4',6,6'-HxCB[4]	155L	23:43	1.0000	0.9986-1.0028
2,2',3,3',6-PeCB	84	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	23:44	0.8456	0.8426-0.8486
2,2',3,5,5'-PeCB	92	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	23:50	0.8492	0.8462-0.8521
2,2',3,4,6'-PeCB	89	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	23:53	0.8510	0.8480-0.8539
2,2',3,4',5-PeCB	90	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	24:07	0.8593	0.8563-0.8622
$^{13}C_{12}$-2,2',4,5,5'-PeCB[7]	101L	$^{13}C_{12}$-2,2',4,5,5'-PeCB[7]	101L	24:11	1.0000	0.9966-1.0034
2,2',4,5,5'-PeCB[6]	101	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	24:11	0.8616	0.8587-0.8646
2,3,3',5',6-PeCB	113	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	24:23	0.8688	0.8658-0.8717
3,3',4,5'-TeCB	79	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,6]	77L	24:27	0.9362	0.9330-0.9394

Labeled or native CB[1]	IUPAC number[2]	Retention time and quantitation references	IUPAC number	RT	RRT	RRT QC limits[3]
2,2',4,4',5-PeCB	99	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	24:28	0.8717	0.8688-0.8747
2,2',3,4',6,6'-HxCB	150	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	24:52	0.7449	0.7399-0.7499
2,3',4,4',6-PeCB	119	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	24:54	0.8872	0.8842-0.8901
2,3,3',5,6-PeCB	112	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	25:00	0.8907	0.8878-0.8937
2,3,3',4,5'-PeCB	108	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	25:09	0.8961	0.8931-0.8990
2,2',3,5,6,6'-HxCB	152	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	25:17	0.7574	0.7524-0.7624
2,2',3,3',5-PeCB	83	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	25:20	0.8919	0.8890-0.8949
2,2',3',4,5-PeCB	97	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	25:22	0.9038	0.9008-0.9068
2,2',3,4,5-PeCB	86	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	25:27	0.9068	0.9038-0.9097
$^{13}C_{12}$-3,4,4',5-TeCB[9]	81L	$^{13}C_{12}$-2,2',5,5'-TeCB[7]	52L	25:32	1.3546	1.3457-1.3634
3,4,4',5-TeCB[10]	81	$^{13}C_{12}$-3,4,4',5-TeCB[4,5,9]	77L	25:32	1.0000	0.9987-1.0026
2',3,4,5,6'-PeCB	125	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	25:36	0.9121	0.9091-0.9151
2,3,4',5,6-PeCB	117	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	25:37	0.9127	0.9097-0.9157
2,2',3,4,5'-PeCB	87	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	25:38	0.9133	0.9103-0.9163
3,3',4,5-TeCB	78	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	25:40	0.9598	0.9586-0.9630
2,2',3,4,6,6'-HxCB	145	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	25:42	0.7698	0.7649-0.7748
2,3,4,4',6-PeCB	115	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	25:44	0.9169	0.9139-0.9198
$^{13}C_{12}$-2,3,3',5,5'-PeCB[6]	111L	$^{13}C_{12}$-2,2',4,5,5'-PeCB[7]	101L	25:51	1.0689	1.0655-1.0724
2,3,3',5,5'-PeCB	111	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	25:51	0.9210	0.9181-0.9240
2,2',3,4,4'-PeCB	85	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	25:51	0.9210	0.9181-0.9240
2,3,4,5,6-PeCB	116	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	25:48	0.9192	0.9163-0.9222
$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	$^{13}C_{12}$-2,2',5,5'-TeCB[7]	52L	26:07	1.3855	1.3767-1.3943
3,3',4,4'-TeCB[8,10]	77	$^{13}C_{12}$-3,3',4,4'-TeCB[4,5,9]	77L	26:07	1.0000	0.9987-1.0026
2,2',3,3',6,6'-HxCB	136	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	26:10	0.7793	0.7743-0.7843
2,3',4,5,5'-PeCB	120	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	26:12	0.9335	0.9305-0.9365
2,2',3,4',5,6'-HxCB	148	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	26:14	0.7858	0.7808-0.7908
2,3,3',4',6-PeCB	110	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	26:16	0.9359	0.9329-0.9388
2,2',4,4',5,6'-HxCB	154	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	26:44	0.8008	0.7983-0.8033

Labeled or native CB[1]	IUPAC number[2]	Retention time and quantitation references	IUPAC number	RT	RRT	RRT QC limits[3]
2,2',3,3',4-PeCB	82	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	26:48	0.9549	0.9519-0.9578
2,2',3,5,5',6-HxCB	151	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	27:18	0.8178	0.8153-0.8203
2,2',3,3',5,6'-HxCB	135	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	27:31	0.8243	0.8218-0.8268
2',3,4,5,5'-PeCB	124	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	27:36	0.9834	0.9804-0.9863
2,2',3,4,5',6-HxCB	144	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	27:38	0.8278	0.8253-0.8303
2,3,3',4',5-PeCB	107	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,6]	118L	27:40	0.9857	0.9828-0.9887
2,2',3,4',5,6-HxCB	147	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,6]	167L	27:44	0.8308	0.8283-0.8333
2,3,3',4,6-PeCB	109	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,6]	118L	27:45	0.9887	0.9857-0.9917
2,2',3,4',5',6-HxCB	149	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	28:01	0.8392	0.8367-0.8417
2,2',3,3',5,6-HxCB	134	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	28:35	0.8562	0.8537-0.8587
2,2',3,4,5,6'-HxCB	143	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	28:34	0.8557	0.8532-0.8582
$^{13}C_{12}$-2',3,4,4',5-PeCB[9]	123L	$^{13}C_{12}$-2,2',4,5,5'-PeCB[7]	101L	27:53	1.1530	1.1496-1.1564
2',3,4,4',5-PeCB[10]	123	$^{13}C_{12}$-2',3,4,4',5-PeCB[9]	123L	27:53	1.0000	0.9988-1.0024
2,2',3,4,4',6-HxCB	139	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	28:01	0.8392	0.8367-0.8417
2,3,3',4,5-PeCB	106	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	28:04	1.0000	0.9970-1.0030
$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	$^{13}C_{12}$-2,2',4,5,5'-PeCB[7]	101L	28:04	1.1606	1.1571-1.1640
2,3',4,4',5-PeCB[6,10]	118	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	28:04	1.0000	0.9988-1.0024
2,2',3,4,4',6'-HxCB	140	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	28:12	0.8447	0.8422-0.8472
$^{13}C_{12}$-2,3,4,4',5-PeCB[6]	114L	$^{13}C_{12}$-2,2',4,5,5'-PeCB[7]	101L	28:38	1.1840	1.1806-1.1875
2,3,4,4',5-PeCB[10]	114	$^{13}C_{12}$-2,3,4,4',5-PeCB[9]	114L	28:38	1.0000	0.9988-1.0023
2',3,3',4,5-PeCB	122	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	28:48	1.0261	1.0232-1.0291
2,2',3,3',4,6-HxCB	131	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	28:52	0.8647	0.8622-0.8672
2,2',3,4,5,6-HxCB	142	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	28:59	0.8682	0.8657-0.8707
2,2',3,3',5,5'-HxCB	133	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	28:59	0.8682	0.8657-0.8707
2,2',3,3',4,6'-HxCB	132	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	29:32	0.8647	0.8622-0.8672
2,3,3',5,5',6-HxCB	165	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	29:21	0.8792	0.8767-0.8817
$^{13}C_{12}$-2,2',3,4',5,6,6'-HpCB[4]	188L	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[5,9]	189L	29:22	0.9511	0.7327-0.7411
2,2',3,4',5,6,6'-HpCB	188	$^{13}C_{12}$-2,2',3,4',5,6,6'-HpCB[4]	188L	29:22	1.0000	0.9989-1.0023

Labeled or native CB[1]	IUPAC number[2]	Retention time and quantitation references	IUPAC number	RT	RRT	RRT QC limits[3]
2,2',3,4',5,5'-HxCB	146	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[4,5]	167L	29:24	0.8807	0.8782-0.8832
$^{13}C_{12}$-2,3,3',4,4'-PeCB[6]	105L	$^{13}C_{12}$-2,2',4,5,5'-PeCB[7]	101L	29:30	1.2198	1.2130-1.2267
2,3,3',4,4'-PeCB[8,10]	105	$^{13}C_{12}$-2,3,3',4,4'-PeCB[6]	105L	29:30	1.0000	0.9989-1.0023
2,3,3',4,5',6-HxCB	161	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	29:32	0.8847	0.8822-0.8872
2,2',4,4',5,5'-HxCB[6]	153	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	29:48	0.8927	0.8902-0.8952
2,2',3,4,4',6,6'-HpCB	184	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	29:49	0.7482	0.7440-0.7524
3,3',4,5,5'-PeCB	127	$^{13}C_{12}$-2,3',4,4',5-PeCB[5,9]	118L	29:57	1.0671	1.0641-1.0701
2,3',4,4',5',6-HxCB	168	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	29:59	0.8982	0.8957-0.9006
2,2',3,4,5,5'-HxCB	141	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	30:31	0.9141	0.9116-0.9166
2,2',3,3',5,6,6'-HpCB	179	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	30:33	0.7666	0.7624-0.7708
2,2',3,4,4',5-HxCB	137	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	30:51	0.9241	0.9216-0.9266
2,2',3,3',4,5'-HxCB	130	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	30:57	0.9271	0.9246-0.9296
2,2',3,3',4,6,6'-HpCB	176	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	31:01	0.7783	0.7742-0.7825
$^{13}C_{12}$-2,2',3,4,4',5'-HxCB[7]	138L	$^{13}C_{12}$-2,2',3,4,4',5'-HxCB[7]	138L	31:20	1.0000	0.9973-1.0027
2,2',3,4,4',5'-HxCB[8]	138	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	31:20	0.9386	0.9361-0.9411
2,3,3',4',5',6-HxCB	164	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	31:22	0.9396	0.9371-0.9421
2,3,3',4',5,6-HxCB	163	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	31:28	0.9426	0.9401-0.9451
2,3,3',4,5,6-HxCB	160	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	31:33	0.9451	0.9426-0.9476
2,3,3',4,4',6-HxCB	158	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	31:35	0.9461	0.9436-0.9486
2,2',3,4,5,6,6'-HpCB	186	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	31:36	0.7930	0.7888-0.7972
2,2',3,3',4,5-HxCB	129	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	31:48	0.9526	0.9501-0.9551
$^{13}C_{12}$-3,3',4,4',5-PeCB[4,9]	126L	$^{13}C_{12}$-2,2',4,5,5'-PeCB[7]	101L	31:49	1.3156	1.3088-1.3225
3,3',4,4',5-PeCB[8,10]	126	$^{13}C_{12}$-3,3',4,4',5-PeCB[4,9]	126L	31:49	1.0000	0.9990-1.0021
2,3,4,4',5,6-HxCB	166	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	32:13	0.9651	0.9626-0.9675
$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB[7]	178L	$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB[7]	178L	32:14	1.0000	0.9974-1.0026
2,2',3,3',5,5',6-HpCB	178	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	32:14	0.8089	0.8068-0.8110
2,2',3,3',4,5',6-HpCB	175	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	32:33	0.8168	0.8147-0.8189
2,3,3',4,5,5'-HxCB	159	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,9]	167L	32:43	0.9800	0.9775-0.9825

Labeled or native CB[1]	IUPAC number[2]	Retention time and quantitation references	IUPAC number	RT	RRT	RRT QC limits[3]
2,2',3,4',5,5'6-HpCB[6]	187	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	32:46	0.8223	0.8202-0.8243
2,2',3,4,4',5,6'-HpCB	182	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	32:47	0.8227	0.8206-0.8248
2,2',3,3',4,4'-HxCB[6]	128	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,8]	167L	32:52	0.9845	0.9820-0.9870
2,3,3',4',5,5'-HxCB	162	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,8]	167L	33:00	0.9885	0.9860-0.9910
2,2',3,4,4',5',6-HpCB	183	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	33:06	0.8308	0.8285-0.8327
$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,8]	167L	$^{13}C_{12}$-2,2',3,4,4',5'-HxCB[7]	138L	33:23	1.0654	1.0628-1.0681
2,3',4,4',5,5'-HxCB[10]	167	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB[5,8]	167L	33:23	1.0000	0.9990-1.0020
2,2',3,4,5,5',6-HpCB	185	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	33:43	0.8461	0.8440-0.8482
2,2',3,3',4,5,6'-HpCB	174	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	34:07	0.8561	0.8540-0.8582
2,2',3,4,4',5,6-HpCB	181	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	34:11	0.8578	0.8557-0.8599
2,2',3,3',4',5,6-HpCB	177	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	34:22	0.8624	0.8603-0.8645
2,2'3,3',4,4',6-HpCB	171	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	34:40	0.8699	0.8678-0.8720
$^{13}C_{12}$-2,3,3',4,4',5 -HxCB[9]	156L	$^{13}C_{12}$-2,2',3,4,4',5'-HxCB[7]	138L	34:40	1.1064	1.1037-1.1090
2,3,3',4,4',5-HxCB[10]	156	$^{13}C_{12}$-2,3,3',4,4',5 -HxCB[9]	156L	34:40	1.0000	0.9990-1.0019
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-OcCB[4]	202L	$^{13}C_{12}$-Cl8-PCB-194[5]	194L	34:56	0.8265	0.8245-0.8285
2,2',3,3',5,5',6,6'-OcCB	202	$^{13}C_{12}$-2,2',3,3',5,5',6,6'-OcCB[4]	202L	34:56	1.0000	0.9990-1.0019
$^{13}C_{12}$-2,3,3',4,4',5'-HxCB[5]	157L	$^{13}C_{12}$-2,2',3,4,4',5'-HxCB[7]	138L	34:57	1.1154	1.1128-1.1181
2,3,3',4,4',5'-HxCB[10]	157	$^{13}C_{12}$-2,3,3',4,4',5'-HxCB[9]	157L	34:57	1.0000	0.9990-1.0019
2,2',3,3',4,5,6-HpCB	173	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	35:04	0.8800	0.8779-0.8821
2,2',3,3',4,5',6,6'-OcCB	201	$^{13}C_{12}$-Cl8-PCB-194[5]	194L	35:25	0.8379	0.8360-0.8399
2,2',3,4,4',5,6,6'-OcCB	204	$^{13}C_{12}$-Cl8-PCB-194[5]	194L	35:36	0.8423	0.8403-0.8442
2,2',3,3',4,5,5'-HpCB	172	$^{13}C_{12}$-2',3,3',4,4',5,5-HpCB[4,5,9]	189L	35:41	0.8954	0.8934-0.8975
2,3,3',4,5,5',6-HpCB	192	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	35:51	0.8996	0.8975-0.9017
2,2',3,3',4,4',6,6'-OcCB	197	$^{13}C_{12}$-Cl8-PCB-194[5]	194L	35:55	0.8498	0.8478-0.8517
2,2',3,4,4',5,5'-HpCB[3]	180	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	36:07	0.9063	0.9042-0.9084
2,3,3',4',5,5',6-HpCB	193	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	36:20	0.9118	0.9097-0.9138
2,3,3',4,4',5',6-HpCB	191	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	36:34	0.9176	0.9155-0.9197
2,2',3,3',4,5,6,6'-OcCB	200	$^{13}C_{12}$-Cl8-PCB-194[5]	194L	36:49	0.8711	0.8691-0.8730

Labeled or native CB[1]	IUPAC number[2]	Retention time and quantitation references	IUPAC number	RT	RRT	RRT QC limits[3]
$^{13}C_{12}$-3,3',4,4',5,5'-HxCB[4,8]	169L	$^{13}C_{12}$-2,2',3,4,4',5'-HxCB[7]	138L	37:19	1.1910	1.1883-1.1936
3,3',4,4',5,5'-HxCB[5,10]	169	$^{13}C_{12}$-3,3',4,4',5,5'-HxCB[4,9]	169L	37:19	1.0000	0.9991-1.0018
2,2',3,3',4,4',5-HpCB[6]	170	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	37:44	0.9469	0.9448-0.9490
2,3,3',4,4',5,6-HpCB	190	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	37:56	0.9519	0.9498-0.9540
2,2',3,3',4,5,5',6-OcCB	198	$^{13}C_{12}$-Cl8-PCB-194[5]	194L	38:34	0.9125	0.9105-0.9144
2,2',3,3',4,5,5',6'-OcCB	199	$^{13}C_{12}$-Cl8-PCB-194[5]	194L	38:43	0.9160	0.9140-0.9180
2,2',3,3',4,4',5,6'-OcCB	196	$^{13}C_{12}$-Cl8-PCB-194[5]	194L	39:05	0.9247	0.9227-0.9267
2,2',3,4,4',5,5',6-OcCB	203	$^{13}C_{12}$-Cl8-PCB-194[5]	194L	39:05	0.9247	0.9227-0.9267
$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB[7]	178L	39:51	1.2363	1.2311-1.2415
2,3,3',4,4',5,5'-HpCB[10]	189	$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB[4,5,9]	189L	39:51	1.0000	0.9992-1.0017
2,2',3,3',4,4',5,6-OcCB[3]	195	$^{13}C_{12}$-Cl8-PCB-194[5]	194L	40:45	0.9641	0.9621-0.9661
$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-NoCB[4]	208L	$^{13}C_{12}$-Cl9-PCB-206[4,5]	206L	41:03	0.9149	0.9131-0.9168
2,2',3,3',4,5,5',6,6'-NoCB	208	$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-NoCB[4]	208L	41:03	1.0000	0.9992-1.0016
2,2',3,3',4,4',5,6,6'-NoCB	207	$^{13}C_{12}$-Cl9-PCB-206[4,5]	206L	41:32	0.9257	0.9238-0.9276
$^{13}C_{12}$-2,2',3,3',4,4',5,5'-OcCB[5]	194L	$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB[7]	178L	42:16	1.3113	1.3061-1.3164
2,2',3,3',4,4',5,5'-OcCB	194	$^{13}C_{12}$-Cl8-PCB-194[5]	194L	42:16	1.0000	0.9992-1.0016
$^{13}C_{12}$-2,3,3',4,4',5,5',6-OcCB[4]	205L	$^{13}C_{12}$-Cl8-PCB-194[5]	194L	42:44	1.0110	1.0091-1.0130
2,3,3',4,4',5,5',6-OcCB	205	$^{13}C_{12}$-2,3,3',4,4',5,5',6-OcCB[4]	205L	42:44	1.0000	0.9992-1.0016
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-NoCB[4,5]	206L	$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB[7]	178L	44:52	1.3919	1.3868-1.3971
2,2',3,3',4,4',5,5',6-NoCB[6]	206	$^{13}C_{12}$-Cl9-PCB-206[4,5]	206L	44:52	1.0000	0.9993-1.0015
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6,6'-DeCB[4,5]	209L	$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB[7]	178L	46:55	1.4555	1.4504-1.4607
2,2',3,3',4,4',5,5',6,6'-DeCB[6]	209	$^{13}C_{12}$-Cl10-PCB-209[4,5]	209L	46:55	1.0000	0.9993-1.0014

1. Abbreviations for chlorination levels
   - MoCB = monochlorobiphenyl
   - DiCB = dichlorobiphenyl
   - TrCB = trichlorobiphenyl
   - TeCB = tetrachlorbiphenyl
   - PeCB = pentachlorobiphenyl
   - HxCB = hexachlorobiphenyl

HpCB = heptachlorobiphenyl
OcCB = octachlorobiphenyl
NoCB = nonachlorobiphenyl
DeCB = decachlorobiphenyl

2 Suffix "L" indicates labeled compound.

3 For native CBs determined by isotope dilution quantitation, RRT QC limits were constructed using -2 to +4 seconds around the the retention time for the labeled analog. For native CBs determined by internal standard quantitation, RRT QC limits were constructed using a ±2 percent window around the retention time for retention times in the range of 0.8-1.2 and a ±4 percent window around the retention time for retention times <0.8 and >1.2. These windows may not be adequate for analyte identification (See the note in Section 16.4)

4. Labeled level of chlorination (LOC) window-defining congener

5. Labeled level of chlorination (LOC) quantitation congener

6. National Oceanic and Atmospheric Administration (NOAA) congener of interest

7. Instrument internal standard

8. Clean-up standard

9. Labeled internal standard for World Health Organization (WHO) toxic congener

10 WHO toxic congener

Table A-2 Scan descriptors, levels of chlorination, m/z information, and substances monitored by HRGC/HRMS

Function and chlorine level	m/z	m/z type	m/z formula	Substance
Fn-1	188.0393	M	$^{12}C_{12}H_9{}^{35}Cl$	Cl-1 PCB
Cl-1	190.0363	M+2	$^{12}C_{12}H_9{}^{37}Cl$	Cl-1P CB
	200.0795	M	$^{13}C_{12}H_9{}^{35}Cl$	$^{13}C_{12}$ Cl-1 PCB
	202.0766	M+2	$^{13}C_{12}H_9{}^{37}Cl$	$^{13}C_{12}$ Cl-1 PCB
	218.9856	lock	C_4F_9	PFK
Fn-2	222.0003	M	$^{12}C_{12}H_8{}^{35}Cl_2$	Cl-2 PCB
Cl-2,3	223.9974	M+2	$^{12}C_{12}H_8{}^{35}Cl\,{}^{37}Cl$	Cl-2 PCB
	225.9944	M+4	$^{12}C_{12}H_8{}^{37}Cl_2$	Cl-2 PCB
	234.0406	M	$^{13}C_{12}H_8{}^{35}Cl_2$	$^{13}C_{12}$ Cl-2 PCB
	236.0376	M+2	$^{13}C_{12}H_8{}^{35}Cl\,{}^{37}Cl$	$^{13}C_{12}$ Cl-2 PCB
	242.9856	lock	C_5F_9	PFK
	255.9613	M	$^{12}C_{12}H_7{}^{35}Cl_3$	Cl-3 PCB
	257.9584	M+2	$^{12}C_{12}H_7{}^{35}Cl_2{}^{37}Cl$	Cl-3 PCB
Fn-3	255.9613	M	$^{12}C_{12}H_7{}^{35}Cl_3$	Cl-3 PCB
Cl-3,4,5	257.9584	M+2	$^{12}C_{12}H_7{}^{35}Cl_2{}^{37}Cl$	Cl-3 PCB
	259.9554	M+4	$^{12}C_{12}H_7{}^{35}Cl\,{}^{37}Cl_2$	Cl-3 PCB
	268.0016	M	$^{13}C_{12}H_7{}^{35}Cl_3$	$^{13}C_{12}$ Cl-3 PCB
	269.9986	M+2	$^{13}C_{12}H_7{}^{35}Cl_2{}^{37}Cl$	$^{13}C_{12}$ Cl-3 PCB
	280.9825	lock	C_6F_{11}	PFK
	289.9224	M	$^{12}C_{12}H_6{}^{35}Cl_4$	Cl-4 PCB
	291.9194	M+2	$^{12}C_{12}H_6{}^{35}Cl_3{}^{37}Cl$	Cl-4 PCB
	293.9165	M+4	$^{12}C_{12}H_6{}^{35}Cl_2{}^{37}Cl_2$	Cl-4 PCB
	301.9626	M	$^{13}C_{12}H_6{}^{35}Cl_4$	$^{13}C_{12}$ Cl-4 PCB
	303.9597	M+2	$^{13}C_{12}H_6{}^{35}Cl_3{}^{37}Cl$	$^{13}C_{12}$ Cl-4 PCB
	323.8834	M	$^{12}C_{12}H_5{}^{35}Cl_5$	Cl-5 PCB

Function and chlorine level	m/z	m/z type	m/z formula	Substance
	325.8804	M+2	$^{12}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	Cl-5 PCB
	327.8775	M+4	$^{12}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	Cl-5 PCB
	337.9207	M+2	$^{13}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	$^{13}C_{12}$ Cl-5 PCB
	339.9178	M+4	$^{13}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	$^{13}C_{12}$ Cl-5 PCB
Fn-4	289.9224	M	$^{12}C_{12}H_6{}^{35}Cl_4$	Cl-4 PCB
Cl-4,5,6	291.9194	M+2	$^{12}C_{12}H_6{}^{35}Cl_3{}^{37}Cl$	Cl-4 PCB
	293.9165	M+4	$^{12}C_{12}H_6{}^{35}Cl_2{}^{37}Cl_2$	Cl-4 PCB
	301.9626	M+2	$^{13}C_{12}H_6{}^{35}Cl_3{}^{37}Cl$	$^{13}C_{12}$ Cl-4 PCB
	303.9597	M+4	$^{13}C_{12}H_6{}^{35}Cl_2{}^{37}Cl_2$	$^{13}C_{12}$ Cl-4 PCB
	323.8834	M	$^{12}C_{12}H_5{}^{35}Cl_5$	Cl-5 PCB
	325.8804	M+2	$^{12}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	Cl-5 PCB
	327.8775	M+4	$^{12}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	Cl-5 PCB
	330.9792	lock	C_7F_{15}	PFK
	337.9207	M+2	$^{13}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	$^{13}C_{12}$ Cl-5 PCB
	339.9178	M+4	$^{13}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	$^{13}C_{12}$ Cl-5 PCB
	359.8415	M+2	$^{13}C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	Cl-6 PCB
	361.8385	M+4	$^{13}C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	Cl-6 PCB
	363.8356	M+6	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}Cl_3$	Cl-6 PCB
	371.8817	M+2	$^{13}C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	$^{13}C_{12}$ Cl-6 PCB
	373.8788	M+4	$^{13}C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	$^{13}C_{12}$ Cl-6 PCB
Fn-5	323.8834	M	$^{12}C_{12}H_5{}^{35}Cl_5$	Cl-5 PCB
Cl-5,6,7,8	325.8804	M+2	$^{12}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	Cl-5 PCB
	327.8775	M+4	$^{12}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	Cl-5 PCB
	337.9207	M+2	$^{13}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	$^{13}C_{12}$ Cl-5 PCB
	339.9178	M+4	$^{13}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	$^{13}C_{12}$ Cl-5 PCB
	354.9792	lock	C_9F_{13}	PFK
	359.8415	M+2	$^{12}C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	Cl-6 PCB
	361.8385	M+4	$^{12}C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	Cl-6 PCB

Function and chlorine level	m/z	m/z type	m/z formula	Substance
	363.8356	M+6	$^{12}C_{12}H_4{}^{35}Cl_3{}^{37}Cl_3$	Cl-6 PCB
	371.8817	M+2	$^{13}C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	$^{13}C_{12}$ Cl-6 PCB
	373.8788	M+4	$^{13}C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	$^{13}C_{12}$ Cl-6 PCB
	393.8025	M+2	$^{12}C_{12}H_3{}^{35}Cl_6{}^{37}Cl$	Cl-7 PCB
	395.7995	M+4	$^{12}C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$	Cl-7 PCB
	397.7966	M+6	$^{12}C_{12}H_3{}^{35}Cl_4{}^{37}Cl_3$	Cl-7 PCB
	405.8428	M+2	$^{13}C_{12}H_3{}^{35}Cl_6{}^{37}Cl$	$^{13}C_{12}$ Cl-7 PCB
	407.8398	M+4	$^{13}C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$	$^{13}C_{12}$ Cl-7 PCB
	427.7635	M+2	$^{12}C_{12}H_2{}^{35}Cl_7{}^{37}Cl$	Cl-8 PCB
	429.7606	M+4	$^{12}C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$	Cl-8 PCB
	431.7576	M+6	$^{12}C_{12}H_2{}^{35}Cl_5{}^{37}Cl_3$	Cl-8 PCB
	439.8038	M+2	$^{13}C_{12}H_2{}^{35}Cl_7{}^{37}Cl$	$^{13}C_{12}$ Cl-8 PCB
	441.8008	M+4	$^{13}C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$	$^{13}C_{12}$ Cl-8 PCB
	454.9728	QC	$C_{11}F_{17}$	PFK
Fn-6	427.7635	M+2	$^{12}C_{12}H_2{}^{35}Cl_7{}^{37}Cl$	Cl-8 PCB
Cl-8,9,10	429.7606	M+4	$^{12}C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$	Cl-8 PCB
	431.7576	M+6	$^{12}C_{12}H_2{}^{35}Cl_5{}^{37}Cl_3$	Cl-8 PCB
	439.8038	M+2	$^{13}C_{12}H_2{}^{35}Cl_7{}^{37}Cl$	$^{13}C_{12}$ Cl-8 PCB
	441.8008	M+4	$^{13}C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$	$^{13}C_{12}$ Cl-8 PCB
	442.9728	QC	$C_{10}F_{19}$	PFK
	454.9728	lock	$C_{11}F_{13}$	PFK
	461.7246	M+2	$^{12}C_{12}H_1{}^{35}Cl_8{}^{37}Cl$	Cl-9 PCB
	463.7216	M+4	$^{12}C_{12}H_1{}^{35}Cl_7{}^{37}Cl_2$	Cl-9 PCB
	465.7187	M+6	$^{12}C_{12}H_1{}^{35}Cl_6{}^{37}Cl_3$	Cl-9 PCB
	473.7648	M+2	$^{13}C_{12}H_1{}^{35}Cl_8{}^{37}Cl$	$^{13}C_{12}$ Cl-9 PCB
	475.7619	M+4	$^{13}C_{12}H_1{}^{35}Cl_7{}^{37}Cl_2$	$^{13}C_{12}$ Cl-9 PCB
	495.6856	M+2	$^{13}C_{12}H_4{}^{35}Cl_9{}^{37}Cl$	Cl-10 PCB
	499.6797	M+4	$^{12}C_{12}{}^{35}Cl_7{}^{37}Cl_3$	Cl-10 PCB

Function and chlorine level	m/z	m/z type	m/z formula	Substance
	501.6767	M+6	$^{12}C_{12}{}^{35}Cl_6{}^{37}Cl_4$	Cl-10 PCB
	507.7258	M+2	$^{13}C_{12}H_4{}^{35}Cl_9{}^{37}Cl$	$^{13}C_{12}$ Cl-10 PCB
	509.7229	M+4	$^{13}C_{12}H_4{}^{35}Cl_8{}^{37}Cl_2$	$^{13}C_{12}$ Cl-10 PCB
	511.7199	M+6	$^{13}C_{12}H_4{}^{35}Cl_7{}^{37}Cl_4$	$^{13}C_{12}$ Cl-10 PCB

1 Isotopic masses used for accurate mass calculation

^{1}H	1.0078
^{12}C	12.0000
^{13}C	13.0034
^{35}Cl	34.9689
^{37}Cl	36.9659
^{19}F	18.9984

Analytical Methods

Pesticides

8081a

METHOD 8081A

ORGANOCHLORINE PESTICIDES BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8081 is used to determine the concentrations of various organochlorine pesticides in extracts from solid and liquid matrices, using fused-silica, open-tubular, capillary columns with electron capture detectors (ECD). When compared to the packed columns, these columns offer improved resolution, better selectivity, increased sensitivity, and faster analysis. The compounds listed below may be determined by either a single- or dual-column analysis system.

Compound	CAS Registry No.
Aldrin	309-00-2
α-BHC	319-84-6
β-BHC	319-85-7
γ-BHC (Lindane)	58-89-9
δ-BHC	319-86-8
Chlorobenzilate	510-15-6
α-Chlordane	5103-71-9
γ-Chlordane	5103-74-2
Chlordane - not otherwise specified	57-74-9
DBCP	96-12-8
4,4'-DDD	72-54-8
4,4'-DDE	72-55-9
4,4'-DDT	50-29-3
Diallate	2303-16-4
Dieldrin	60-57-1
Endosulfan I	959-98-8
Endosulfan II	33213-65-9
Endosulfan sulfate	1031-07-8
Endrin	72-20-8
Endrin aldehyde	7421-93-4
Endrin ketone	53494-70-5
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
Hexachlorobenzene	118-74-1
Hexachlorocyclopentadiene	77-47-4
Isodrin	465-73-6
Methoxychlor	72-43-5
Toxaphene	8001-35-2

1.2 This revision of Method 8081 no longer includes the PCBs as Aroclors in the list of target analytes. The analysis of PCBs should be undertaken using Method 8082, which includes specific cleanup and quantitation procedures designed for PCB analysis. This change was made to obtain PCB data of better quality and to eliminate the complications inherent in a combined organochlorine pesticide and PCB method. Therefore, if the presence of PCBs is expected, use Method 8082 for

PCB analyses, and this method (8081) for the organochlorine pesticides. If there is no information of the likely presence of PCBs, either employ a PCB-specific screening procedure such as an immunoassay (e.g., Method 4020), or split the sample extract *prior to* any cleanup steps, and process part of the extract for organochlorine pesticide analysis and the other portion for PCB analysis using Method 8082.

1.3 The analyst must select columns, detectors and calibration procedures most appropriate for the specific analytes of interest in a study. Matrix-specific performance data must be established and the stability of the analytical system and instrument calibration must be established for each analytical matrix (e.g., hexane solutions from sample extractions, diluted oil samples, etc.).

1.4 Although performance data are presented for many of the target analytes, it is unlikely that all of them could be determined in a single analysis. The chemical and chromatographic behaviors of many of these chemicals can result in co-elution of some target analytes. Several cleanup/fractionation schemes are provided in this method and in Method 3600.

1.5 Several multi-component mixtures (i.e., Chlordane and Toxaphene) are listed as target analytes. When samples contain more than one multi-component analyte, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. The same is true of multi-component analytes that have been subjected to environmental degradation or degradation by treatment technologies. These result in "weathered" multi-component mixtures that may have significant differences in peak patterns than those of standards.

1.6 Compound identification based on single-column analysis should be confirmed on a second column, or should be supported by at least one other qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm the measurements made with the primary column. GC/MS Method 8270 is also recommended as a confirmation technique, if sensitivity permits (Sec. 8.0).

1.7 This method includes a dual-column option. The option allows a hardware configuration of two analytical columns joined to a single injection port. The option allows one injection to be used for dual-column analysis. Analysts are cautioned that the dual-column option may not be appropriate when the instrument is subject to mechanical stress, many samples are to be run in a short period, or when contaminated samples are analyzed.

1.8 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatographs (GC) and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.9 Extracts suitable for analysis by this method may also be analyzed for organophosphorus pesticides (Method 8141). Some extracts may also be suitable for triazine herbicide analysis, if low recoveries (normally samples taken for triazine analysis must be preserved) are not a problem.

1.10 The following compounds may also be determined using this method:

Compound	CAS Registry No.
Alachlor	15972-60-8
Captafol	2425-06-1
Chloroneb	2675-77-6

Compound	CAS Registry No.
Chloropropylate	99516-95-7
Chlorothalonil	1897-45-6
DCPA	1861-32-1
Dichlone	117-80-6
Dicofol	115-32-2
Etridiazole	2593-15-9
Halowax-1000	58718-66-4
Halowax-1001	58718-67-5
Halowax-1013	12616-35-2
Halowax-1014	12616-36-3
Halowax-1051	2234-13-1
Halowax-1099	39450-05-0
Mirex	2385-85-5
Nitrofen	1836-75-5
PCNB	82-68-8
Permethrin	51877-74-8
Perthane	72-56-0
Propachlor	1918-16-7
Strobane	8001-50-1
trans-Nonachlor	39765-80-5
Trifluralin	1582-09-8

1.11 Kepone extracted from samples or standards exposed to water or methanol may produce peaks with broad tails that elute later than the standard by up to 1 minute. This shift is presumably the result of the formation of a hemi-acetal from the ketone functionality. As a result, Method 8081 is not recommended for determining Kepone. Method 8270 may be more appropriate for the analysis of Kepone.

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample (approximately 1 L for liquids, 2 g to 30 g for solids) is extracted using the appropriate matrix-specific sample extraction technique.

2.2 Liquid samples are extracted at neutral pH with methylene chloride using either Method 3510 (separatory funnel), Method 3520 (continuous liquid-liquid extractor), or other appropriate technique.

2.3 Solid samples are extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using Method 3540 (Soxhlet), Method 3541 (automated Soxhlet), Method 3545 (pressurized fluid extraction), Method 3550 (ultrasonic extraction), or other appropriate technique.

2.4 A variety of cleanup steps may be applied to the extract, depending on the nature of the matrix interferences and the target analytes. Suggested cleanups include alumina (Method 3610), Florisil (Method 3620), silica gel (Method 3630), gel permeation chromatography (Method 3640), and sulfur (Method 3660).

2.5 After cleanup, the extract is analyzed by injecting a 1-µL sample into a gas chromatograph with a narrow- or wide-bore fused silica capillary column and electron capture detector (GC/ECD) or an electrolytic conductivity detector (GC/ELCD).

3.0 INTERFERENCES

3.1 Refer to Methods 3500 (Sec. 3.0, in particular), 3600, and 8000, for a discussion of interferences.

3.2 Sources of interference in this method can be grouped into three broad categories.

3.2.1 Contaminated solvents, reagents, or sample processing hardware.

3.2.2 Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.

3.2.3 Compounds extracted from the sample matrix to which the detector will respond.

3.2.4 Interferences co-extracted from the samples will vary considerably from waste to waste. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation.

3.3 Interferences by phthalate esters introduced during sample preparation can pose a major problem in pesticide determinations.

3.3.1 These materials may be removed prior to analysis using Method 3640 (Gel Permeation Cleanup) or Method 3630 (Silica Gel Cleanup).

3.3.2 Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations.

3.3.3 Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled.

3.3.4 Interferences from phthalate esters can best be minimized by avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination. Exhaustive cleanup of solvents, reagents and glassware may be required to eliminate background phthalate ester contamination.

3.4 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water, and rinses with tap water and organic-free reagent water. Drain the glassware and dry it in an oven at 130°C for several hours, or rinse with methanol and drain. Store dry glassware in a clean environment.

3.5 The presence of elemental sulfur will result in broad peaks that interfere with the detection of early-eluting organochlorine pesticides. Sulfur contamination should be expected with sediment samples. Method 3660 is suggested for removal of sulfur. Since the recovery of Endrin aldehyde (using the TBA procedure) is drastically reduced, this compound must be determined prior to sulfur cleanup.

3.6 Waxes, lipids, and other high molecular weight materials can be removed by Method 3640 (gel-permeation cleanup).

3.7 Other halogenated pesticides or industrial chemicals may interfere with the analysis of pesticides. Certain co-eluting organophosphorus pesticides are eliminated by Method 3640 (gel permeation cleanup - pesticide option). Co-eluting chlorophenols may be eliminated by using Method 3630 (silica gel). Method 3620 (florisil), or Method 3610 (alumina). Polychlorinated biphenyls (PCBs) also may interfere with the analysis of the organochlorine pesticides. The problem may be most severe for the analysis of multicomponent analytes such as Chlordane, Toxaphene, and Strobane. If PCBs are known or expected to occur in samples, the analyst should consult Methods 3620 and 3630 for techniques that may be used to separate the pesticides from the PCBs.

3.8 Co-elution among the many target analytes in this method can cause interference problems. The following target analytes may coelute on the GC columns listed, when using the single-column analysis scheme:

DB 608	Trifluralin/Diallate isomers
	PCNP/Dichlone/Isodrin
DB 1701	Captafol/Mirex
	Methoxychlor/Endosulfan sulfate

3.9 The following compounds may coelute using the dual-column analysis scheme. In general, the DB-5 column resolves fewer compounds that the DB-1701.

DB-5	Permethrin/Heptachlor epoxide
	Endosulfan I/α-Chlordane
	Perthane/Endrin
	Endosulfan II/Chloropropylate/Chlorobenzilate
	4,4'-DDT/Endosulfan sulfate
	Methoxychlor/Dicofol
DB-1701	Chlorothalonil/β-BHC
	δ-BHC/DCPA/Permethrin
	α-Chlordane/*trans*-Nonachlor

Nitrofen, Dichlone, Carbophenothion, Dichloran exhibit extensive peak tailing on both columns. Simazine and Atrazine give poor responses on the ECD detector. Triazine compounds should be analyzed using Method 8141 (NPD option).

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph: an analytical system complete with gas chromatograph suitable for on-column and split-splitless injection and all required accessories including syringes, analytical columns, gases, electron capture detectors (ECD), and recorder/integrator or data system.

4.2 GC columns

This method describes procedures for both single-column and dual-column analyses. The single-column approach involves one analysis to determine that a compound is present, followed by a second analysis to confirm the identity of the compound (Sec. 8.4 describes how GC/MS

confirmation techniques may be employed). The single-column approach may employ either narrow-bore (≤0.32 mm ID) columns or wide-bore (0.53 mm ID) columns. The dual-column approach involves a single injection that is split between two columns that are mounted in a single gas chromatograph. The dual-column approach employs only wide-bore (0.53 mm ID) columns.

The columns listed in this section were the columns used to develop the method performance data. The mention of these columns in this method is not intended to exclude the use of other columns that may be developed. Laboratories may use other capillary columns provided that they document method performance data (e.g., chromatographic resolution, analyte breakdown, and MDLs) that equals or exceeds the performance described in this method, or as appropriate for the intended application.

4.2.1 Narrow-bore columns for single-column analysis (use both columns to confirm compound identifications unless another confirmation technique such as GC/MS is employed).

4.2.1.1 30 m x 0.25 or 0.32 mm ID fused silica capillary column chemically bonded with SE-54 (DB-5 or equivalent), 1 µm film thickness.

4.2.1.2 30 m x 0.25 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, or equivalent), 2.5 µm coating thickness, 1 µm film thickness.

4.2.1.3 Narrow bore columns should be installed in split/splitless (Grob-type) injectors.

4.2.2 Wide-bore columns for single-column analysis (use two of the three columns listed to confirm compound identifications unless another confirmation technique such as GC/MS is employed).

4.2.2.1 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, RTx-35, or equivalent), 0.5 µm or 0.83 µm film thickness.

4.2.2.2 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 50 percent phenyl methylpolysiloxane (DB-1701, or equivalent), 1.0 µm film thickness.

4.2.2.3 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 95 percent dimethyl - 5 percent diphenyl polysiloxane (DB-5, SPB-5, RTx-5, or equivalent), 1.5 µm film thickness.

4.2.2.4 Wide-bore columns should be installed in 1/4 inch injectors, with deactivated liners designed specifically for use with these columns.

4.2.3 Wide-bore columns for dual-column analysis (choose one of the two pairs of columns listed below).

4.2.3.1 Column pair 1

30 m x 0.53 mm ID fused silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 1.5 µm film thickness.

30 m x 0.53 mm ID fused silica capillary column chemically bonded with 50 percent phenyl methylpolysiloxane (DB-1701, or equivalent), 1.0 µm film thickness.

Column pair 1 is mounted in a press-fit Y-shaped glass 3-way union splitter (J&W Scientific, Catalog No. 705-0733) or a Y-shaped fused-silica connector (Restek, Catalog No. 20405), or equivalent.

4.2.3.2 Column pair 2

30 m x 0.53 mm ID fused silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 0.83 µm film thickness.

30 m x 0.53 mm ID fused silica capillary column chemically bonded with 50 percent phenyl methylpolysiloxane (DB-1701, or equivalent), 1.0 µm film thickness.

Column pair 2 is mounted in an 8 in. deactivated glass injection tee (Supelco, Catalog No. 2-3665M), or equivalent.

4.3 Column rinsing kit: Bonded-phase column rinse kit (J&W Scientific, Catalog No. 430-3000), or equivalent.

4.4 Volumetric flasks, 10-mL and 25-mL, for preparation of standards.

5.0 REAGENTS

5.1 Reagent grade or pesticide grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

NOTE: Store the standard solutions (stock, composite, calibration, internal, and surrogate) at 4°C in polytetrafluoroethylene (PTFE)-sealed containers in the dark. When a lot of standards is prepared, it is recommended that aliquots of that lot be stored in individual small vials. All stock standard solutions must be replaced after one year or sooner if routine QC tests (Sec. 8.0) indicate a problem. All other standard solutions must be replaced after six months or sooner if routine QC (Sec. 8.0) indicates a problem.

5.2 Solvents used in the extraction and cleanup procedures (appropriate 3500 and 3600 series methods) include n-hexane, diethyl ether, methylene chloride, acetone, ethyl acetate, and isooctane (2,2,4-trimethylpentane) and must be exchanged to n-hexane or isooctane prior to analysis.

Therefore, n-hexane and isooctane will be required in this procedure. Acetone or toluene may be required for the preparation of some standard solutions (see Sec. 5.4.2). All solvents should be pesticide quality or equivalent, and each lot of solvent should be determined to be phthalate free.

5.3 Organic-free reagent water - All references to water in this method refer to organic-free reagent water as defined in Chapter One.

5.4 Stock standard solutions (1000 mg/L) - May be prepared from pure standard materials or can be purchased as certified solutions.

5.4.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure compound. Dissolve the compound in isooctane or hexane and dilute to volume in a 10-mL volumetric flask. If compound purity is 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard solution. Commercially prepared stock standard solutions can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.4.2 β-BHC, Dieldrin, and some other standards may not be adequately soluble in isooctane. A small amount of acetone or toluene should be used to dissolve these compounds during the preparation of the stock standard solutions.

5.5 Composite stock standard - May be prepared from individual stock solutions.

5.5.1 For composite stock standards containing less than 25 components, take exactly 1 mL of each individual stock solution at a concentration of 1000 mg/L, add solvent, and mix the solutions in a 25-mL volumetric flask. For example, for a composite containing 20 individual standards, the resulting concentration of each component in the mixture, after the volume is adjusted to 25 mL, will be 1 mg/25 mL. This composite solution can be further diluted to obtain the desired concentrations.

5.5.2 For composite stock standards containing more than 25 components, use volumetric flasks of the appropriate volume (e.g., 50 mL, 100 mL), and follow the procedure described above.

5.6 Calibration standards should be prepared at a minimum of five different concentrations by dilution of the composite stock standard with isooctane or hexane. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector.

5.6.1 Although all single component analytes can be resolved on a new 35 percent phenyl methyl silicone column (e.g., DB-608), two calibration mixtures should be prepared for the single component analytes of this method. This procedure is established to minimize potential resolution and quantitation problems on confirmation columns or on older 35 percent phenyl methyl silicone (e.g. DB-608) columns and to allow determination of Endrin and DDT breakdown for method QC (Sec. 8.0).

5.6.2 Separate calibration standards are required for each multi-component target analyte (e.g., Toxaphene and Chlordane). Analysts should evaluate the specific Toxaphene standard carefully. Some Toxaphene components, particularly the more heavily chlorinated components, are subject to dechlorination reactions. As a result, standards from different vendors may exhibit marked differences which could lead to possible false negative results or to large differences in quantitative results.

5.7 Internal standard (optional)

5.7.1 Pentachloronitrobenzene is suggested as an internal standard for the single-column analysis, when it is not considered to be a target analyte. 1-bromo-2-nitrobenzene may also be used. Prepare a solution of 5000 mg/L (5000 ng/µL) of pentachloronitrobenzene or 1-bromo-2-nitrobenzene. Spike 10 µL of this solution into each 1 mL sample extract.

5.7.2 1-bromo-2-nitrobenzene is suggested as an internal standard for the dual-column analysis. Prepare a solution of 5000 mg/L (5000 ng/µL) of 1-bromo-2-nitrobenzene. Spike 10 µL of this solution into each 1 mL of sample extract.

5.8 Surrogate standards

The performance of the method should be monitored using surrogate compounds. Surrogate standards are added to all samples, method blanks, matrix spikes, and calibration standards. The following compounds are recommended as possible surrogates.

5.8.1 Decachlorobiphenyl and tetrachloro-m-xylene have been found to be a useful pair of surrogates for both the single-column and dual-column configurations. Method 3500, Sec. 5.0, describes the procedures for preparing these surrogates.

5.8.2 4-Chloro-3-nitrobenzotrifluoride may also be useful as a surrogate if the chromatographic conditions of the dual-column configuration cannot be adjusted to preclude co-elution of a target analyte with either of the surrogates in Sec. 5.8.1. However, this compound elutes early in the chromatographic run and may be subject to other interference problems. A recommended concentration for this surrogate is 500 ng/µL. Use a spiking volume of 100 µL for a 1-L aqueous sample.

5.8.3 Store surrogate spiking solutions at 4°C in PTFE-sealed containers in the dark.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Four, Organic Analytes, Sec. 4.0, for sample collection and preservation instructions.

6.2 Extracts must be stored under refrigeration in the dark and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Sample extraction

Refer to Chapter Two and Method 3500 for guidance in choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral pH with methylene chloride using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520), or other appropriate technique. Solid samples are extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using one of the Soxhlet extraction (Method 3540 or 3541), pressurized fluid extraction (Method 3545), ultrasonic extraction (Method 3550), or other appropriate technique.

NOTE: Hexane-acetone (1:1) may be more effective as an extraction solvent for organochlorine pesticides in some environmental and waste matrices than is methylene chloride-acetone (1:1). Relative to the methylene chloride-acetone mixture, use of hexane-acetone generally reduces the amount of interferences that are extracted and improves signal-to-noise.

Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. Each sample type must be spiked with the compounds of interest to determine the percent recovery and the limit of detection for that sample (see Chapter One). See Method 8000 for guidance on demonstration of initial method proficiency as well as guidance on matrix spikes for routine sample analysis.

7.2 Extract cleanup

Cleanup procedures may not be necessary for a relatively clean sample matrix, but most extracts from environmental and waste samples will require additional preparation before analysis. The specific cleanup procedure used will depend on the nature of the sample to be analyzed and the data quality objectives for the measurements. General guidance for sample extract cleanup is provided in this section and in Method 3600.

7.2.1 If a sample is of biological origin, or contains high molecular weight materials, the use of Method 3640 (GPC cleanup - pesticide option) is recommended. Frequently, one of the adsorption chromatographic cleanups (alumina, silica gel, or florisil) may also be required following the GPC cleanup.

7.2.2 Method 3610 (alumina) may be used to remove phthalate esters.

7.2.3 Method 3620 (florisil) may be used to separate organochlorine pesticides from aliphatic compounds, aromatics, and nitrogen-containing compounds.

7.2.4 Method 3630 (silica gel) may be used to separate single component organochlorine pesticides from some interferants.

7.2.5 Elemental sulfur, which may be present in certain sediments and industrial wastes, interferes with the electron capture gas chromatography of certain pesticides. Sulfur should be removed by the technique described in Method 3660.

7.3 GC conditions

This method allows the analyst to choose between a single-column or a dual-column configuration in the injector port. Either wide- or narrow-bore columns may be used. Identifications based on retention times from a single-column must be confirmed on a second column or with an alternative qualitative technique.

7.3.1 Single-column analysis

This capillary GC/ECD method allows the analyst the option of using 0.25-0.32 mm ID capillary columns (narrow-bore) or 0.53 mm ID capillary columns (wide-bore). Performance data are provided for both options. Figures 1-6 provide example chromatograms.

7.3.1.1 The use of narrow-bore ($\leq$0.32 mm ID) columns is recommended when the analyst requires greater chromatographic resolution. Use of narrow-bore columns is suitable for relatively clean samples or for extracts that have been prepared with one or more of the clean-up options referenced in the method. Wide-bore columns (0.53 mm ID) are suitable for more complex environmental and waste matrices.

7.3.1.2 Table 1 lists average retention times and method detection limits (MDLs) for the target analytes in water and soil matrices, using wide-bore capillary

columns. Table 2 lists average retention times and method detection limits (MDLs) for the target analytes in water and soil matrices, using narrow-bore capillary columns. The MDLs for the components of a specific sample are dependent upon the nature of interferences in the sample matrix and may differ from those listed in Tables 1 and 2. Table 3 lists the Estimated Quantitation Limits (EQLs) for other matrices.

7.3.1.3 Table 4 lists the GC operating conditions for the single-column method of analysis.

7.3.2 Dual-column analysis

The dual-column/dual-detector approach involves the use of two 30 m x 0.53 mm ID fused-silica open-tubular columns of different polarities, thus, different selectivities towards the target analytes. The columns are connected to an injection tee and separate electron capture detectors.

7.3.2.1 Retention times for the organochlorine analytes on dual-columns are in Table 6. The GC operating conditions for the compounds in Table 6 are given in Table 7.

7.3.2.2 Multi-component mixtures of Toxaphene and Strobane were analyzed separately (Figures 5 and 6) using the GC operating conditions found in Table 7.

7.3.2.3 Figure 6 is a sample chromatogram for a mixture of organochlorine pesticides. The retention times of the individual components detected in these mixtures are given in Tables 6 and 7.

7.3.2.4 Operating conditions for a more heavily loaded DB-5/DB-1701 pair are given in Table 8. This column pair was used for the detection of multi-component organochlorine compounds.

7.3.2.5 Operating conditions for a DB-5/DB-1701 column pair with thinner films, a different type of splitter, and a slower temperature programming rate are provided in Table 7. These conditions gave better peak shapes for Nitrofen and Dicofol. Table 6 lists the retention times for the compounds detected on this column pair.

7.4 Calibration

7.4.1 Prepare calibration standards using the procedures in Sec. 5.0. Refer to Method 8000 (Sec. 7.0) for proper calibration techniques for both initial calibration and calibration verification. The procedure for either internal or external calibration may be used. In most cases, external standard calibration is used with Method 8081 because of the sensitivity of the electron capture detector and the probability of the internal standard being affected by interferences. Because several of the pesticides may co-elute on any single-column, analysts should use two calibration mixtures (see Sec. 3.8). The specific mixture should be selected to minimize the problem of peak overlap.

NOTE: Because of the sensitivity of the electron capture detector, the injection port and column should always be cleaned prior to performing the initial calibration.

7.4.1.1 Unless otherwise necessary for a specific project, the analysis of the multi-component analytes employs a single-point calibration. A single calibration standard near the mid-point of the expected calibration range of each multi-component analyte is included with the initial calibration of the single component analytes for pattern recognition, so that the analyst is familiar with the patterns and retention times on each column.

7.4.1.2 For calibration verification (each 12-hour shift) all target analytes required in the project plan must be injected.

7.4.2 Establish the GC operating conditions appropriate for the configuration (single-column or dual column, Sec. 7.3) using Tables 4, 5, 7, or 8 as guidance. Optimize the instrumental conditions for resolution of the target analytes and sensitivity. An initial oven temperature ≤140 -150°C is required to resolve the four BHC isomers. A final temperature of 240 - 270°C is required to elute decachlorobiphenyl. Use of injector pressure programming will improve the chromatography of late eluting peaks.

NOTE: Once established, the same operating conditions must be used for both calibrations and sample analyses.

7.4.3 A 2 µL injection volume of each calibration standard is recommended. Other injection volumes may be employed, provided that the analyst can demonstrate adequate sensitivity for the compounds of interest.

7.4.4 Because of the low concentration of pesticide standards injected on a GC/ECD, column adsorption may be a problem when the GC has not been used for a day or more. Therefore, the GC column should be primed (or deactivated) by injecting a pesticide standard mixture approximately 20 times more concentrated than the mid-concentration standard. Inject this standard mixture prior to beginning the initial calibration or calibration verification.

CAUTION: Several analytes, including Aldrin, may be observed in the injection just following this system priming. Always run an acceptable blank prior to running any standards or samples.

7.4.5 Calibration factors

When external standard calibration is employed, calculate the calibration factor for each analyte at each concentration, the mean calibration factor, and the relative standard deviation (RSD) of the calibration factors, using the formulae below. If internal standard calibration is employed, refer to Method 8000 for the calculation of response factors.

7.4.5.1 Calculate the calibration factor for each analyte at each concentration as:

$$CF = \frac{\text{Peak Area (or Height) of the Compound in the Standard}}{\text{Mass of the Compound Injected (in nanograms)}}$$

7.4.5.2 Calculate the mean calibration factor for each analyte as:

$$\text{mean CF} = \overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

where n is the number of standards analyzed.

7.4.5.3 Calculate the standard deviation (SD) and the RSD of the calibration factors for each analyte as:

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (CF_i - \overline{CF})^2}{n-1}} \qquad RSD = \frac{SD}{\overline{CF}} \times 100$$

If the RSD for each analyte is ≤ 20%, then the response of the instrument is considered linear and the mean calibration factor can be used to quantitate sample results. If the RSD is greater than 20%, then linearity through the origin cannot be assumed. The analyst must use a calibration curve or a non-linear calibration model (e.g., a polynomial equation) for quantitation. See Method 8000 for information on non-linear calibrations.

7.4.6 Retention time windows

Absolute retention times are used for compound identification. Retention time windows are crucial to the identification of target compounds, and should be established by one of the approaches described in Method 8000.

7.4.6.1 Before establishing the retention time windows, make sure the gas chromatographic system is operating within optimum conditions.

7.4.6.2 The widths of the retention time windows are defined as described in Method 8000. However, the experience of the analyst should weigh heavily in the interpretation of the chromatograms.

7.5 Gas chromatographic analysis of sample extracts

7.5.1 The same GC operating conditions used for the initial calibration must be employed for samples analyses.

7.5.2 Verify calibration each 12-hour shift by injecting calibration verification standards prior to conducting any sample analyses. Analysts should alternate the use of high and low concentration mixtures of single-component analytes and multi-component analytes for calibration verification. A calibration standard must also be injected at intervals of not less than once every twenty samples (after every 10 samples is *recommended* to minimize the number of samples requiring re-injection when QC limits are exceeded) and at the end of the analysis sequence. See Sec. 8.4.4 for additional guidance on the frequency of the standard injections.

7.5.2.1 The calibration factor for each analyte should not exceed a ± 15 percent difference from the mean calibration factor calculated for the initial calibration. If a non-

linear calibration model or a linear model not through the origin has been employed for the initial calibration, consult Sec. 7 of Method 8000 for the specifics of calibration verification.

$$\% \text{ Difference} = \frac{CF - \overline{CF_v}}{\overline{CF}} \times 100$$

7.5.2.2 If this criterion is exceeded for any analyte, use the approach described in Sec. 7 of Method 8000 to calculate the average percent difference across all analytes. If the average of the responses for all analytes is within ±15%, then the calibration has been verified. However, the conditions in Sec. 7 of Method 8000 also apply, e.g., the average must include all analytes in the calibration, regardless of whether they are target analytes for a specific project, and the data user must be provided with the calibration verification data or a list of those analytes that exceeded the ±15% limit.

7.5.2.3 If the calibration does not meet the ±15% limit (either on the basis of each compound or the average across all compounds), check the instrument operating conditions, and if necessary, restore them to the original settings, and inject another aliquot of the calibration verification standard. If the response for the analyte is still not within ±15%, then a new initial calibration must be prepared. The effects of a failing calibration verification standard on sample results are discussed in Sec. 7.5.7.

7.5.3 Compare the retention time of each analyte in the calibration standard with the absolute retention time windows established in Sec. 7.4.6. As described in Method 8000, the center of the absolute retention time window for each analyte is its retention time in the mid-concentration standard analyzed during the initial calibration. Each analyte in each standard must fall within its respective retention time window. If not, the gas chromatographic system must either be adjusted so that a second analysis of the standard does result in all analytes falling within their retention time windows, or a new initial calibration must be performed and new retention time windows established.

7.5.4 Inject a 2-µL aliquot of the concentrated sample extract. Record the volume injected to the nearest 0.05 µL and the resulting peak size in area units.

7.5.5 Tentative identification of an analyte occurs when a peak from a sample extract falls within the absolute retention time window. Each tentative identification must be confirmed using either a second GC column of dissimilar stationary phase or using another technique such as GC/MS (see Sec. 7.7).

When results are confirmed using a second GC column of dissimilar stationary phase, the analyst should check the agreement between the quantitative results on both columns once the identification has been confirmed. See Sec. 7 of Method 8000 for a discussion of such a comparison. Unless otherwise specified in an approved project plan, the higher result should be reported, as this is a conservative approach relative to protection of the environment. If the relative percent difference of the results exceeds 40%, consult Method 8000 for steps that may be taken to address the discrepancy.

7.5.6 When using the external calibration procedure (Method 8000), determine the quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes, as follows. Proper quantitation requires the appropriate selection of a baseline from which the peak area or height can be determined.

7.5.6.1 For aqueous samples

$$\text{Concentration } (\mu g/L) = \frac{(A_x)(V_t)(D)}{(\overline{CF})(V_i)(V_s)}$$

where:

A_x = Area (or height) of the peak for the analyte in the sample.

V_t = Total volume of the concentrated extract (µL).

D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1. The dilution factor is always dimensionless.

$\overline{CF}$ = Mean calibration factor from the initial calibration (area/ng).

V_i = Volume of the extract injected (µL). The injection volume for samples and calibration standards must be the same. For purge-and-trap analysis, V_i is not applicable and therefore is set at 1.

V_s = Volume of the aqueous sample extracted in mL. If units of liters are used for this term, multiply the results by 1000.

Using the units specified here for these terms will result in a concentration in units of ng/mL, which is equivalent to µg/L.

7.5.6.2 For non-aqueous samples

$$\text{Concentration } (\mu g/kg) = \frac{(A_x)(V_t)(D)}{(\overline{CF})(V_i)(W_s)}$$

where A_x, V_t, D, $\overline{CF}$, and V_i are the same as for aqueous samples, and

W_s = Weight of sample extracted (g). The wet weight or dry weight may be used, depending upon the specific application of the data. If units of kilograms are used for this term, multiply the results by 1000.

Using the units specified here for these terms will result in a concentration in units of ng/g, which is equivalent to µg/kg.

7.5.6.3 See Method 8000 for the equation used for internal standard quantitation.

7.5.6.4 If the responses exceed the calibration range of the system, dilute the extract and reanalyze. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

7.5.6.5 If partially overlapping or coeluting peaks are found, change GC columns or try GC/MS quantitation (see Sec. 8.0 and Method 8270).

7.5.7 Each sample analysis must be bracketed with an acceptable initial calibration, calibration verification standard(s) (each 12-hour analytical shift), or calibration standards interspersed within the samples.

Although analysis of a single mid-concentration standard (standard mixture or multi-component analyte) will satisfy the minimum requirements, analysts are urged to use different calibration verification standards during organochlorine pesticide analyses. Also, multi-level standards (mixtures or multi-component analytes) are highly recommended to ensure that the detector response remains stable for all the analytes over the calibration range.

The results from these bracketing standards must meet the calibration verification criteria in Sec. 7.5.2. When a calibration verification standard fails to meet the QC criteria, all samples that were injected after the last standard that last met the QC criteria must be evaluated to prevent mis-quantitations and possible false negative results, and re-injection of the sample extracts may be required. More frequent analyses of standards will minimize the number of sample extracts that would have to be reinjected if the QC limits are violated for the standard analysis.

However, if the standard analyzed after a group of samples exhibits a response for an analyte that is above the acceptance limit, i.e., >15%, and the analyte was not detected in the specific samples analyzed during the analytical shift, then the extracts for those samples do not need to be reanalyzed, as the verification standard has demonstrated that the analyte would have been detected were it present. In contrast, if an analyte above the QC limits was detected in a sample extract, then re-injection is necessary to ensure accurate quantitation. If an analyte was not detected in the sample and the standard response is more than 15% below the initial calibration response, then re-injection is necessary to ensure that the detector response has not deteriorated to the point that the analyte would not have been detected even though it was present (i.e., a false negative result).

7.5.8 Sample injections may continue for as long as the calibration verification standards and standards interspersed with the samples meet instrument QC requirements. It is *recommended* that standards be analyzed after every 10 samples (*required* after every 20 samples and at the end of a set) to minimize the number of samples that must be re-injected when the standards fail the QC limits. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

7.5.9 If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The analyst should consult with the source of the sample to determine whether further concentration of the sample is warranted.

7.5.10 Validation of GC system qualitative performance

7.5.10.1 Use the calibration standards analyzed during the sequence to evaluate retention time stability. The retention time windows are established using the absolute retention time of each analyte as described in Method 8000.

7.5.10.2 Each subsequent injection of a standard during the 12-hour analytical shift (i.e., those standards injected every 20 samples, or more frequently) must be checked against the retention time windows. If any of these subsequent standards fall outside their absolute retention time windows, the GC system is out of control. Determine the cause of the problem and correct it. If the problem cannot be corrected, a new initial calibration must be performed.

7.5.11 Identification of mixtures (i.e. Chlordane and Toxaphene) is based on the characteristic "fingerprint" retention time and shape of the indicator peak(s), and quantitation is based on the area under the characteristic peaks as compared to the area under the corresponding calibration peak(s) of the same retention time and shape generated using either internal or external calibration procedures.

7.5.12 If compound identification or quantitation is precluded due to interference (e.g., broad, rounded peaks or ill-defined baselines are present) cleanup of the extract or replacement of the capillary column or detector is warranted. Rerun the sample on another instrument to determine if the problem results from analytical hardware or the sample matrix. Refer to Method 3600 for the procedures to be followed in sample cleanup.

7.6 Quantitation of multi-component analytes - Multi-component analytes present problems in measurement. Suggestions are offered in the following sections for handing Toxaphene, Strobane, Chlordane, BHC, and DDT.

7.6.1 Toxaphene and Strobane - Toxaphene is manufactured by the chlorination of camphenes, whereas Strobane results from the chlorination of a mixture of camphenes and pinenes. Quantitation of Toxaphene or Strobane is difficult, but reasonable accuracy can be obtained. To calculate Toxaphene from GC/ECD results:

7.6.1.1. Adjust the sample size so that the major Toxaphene peaks are 10-70% of full-scale deflection (FSD).

7.6.1.2 Inject a Toxaphene standard that is estimated to be within ± 10 ng of the sample amount.

7.6.1.3 Quantitate Toxaphene using the total area of the Toxaphene pattern or using 4 to 6 major peaks.

7.6.1.3.1 While Toxaphene contains a large number of compounds that will produce well resolved peaks in a GC/ECD chromatogram, it also contains many other components that are not chromatographically resolved. This unresolved complex mixture results in the "hump" in the chromatogram that is characteristic of this mixture. Although the resolved peaks are important for the identification of the mixture, the area of the unresolved complex mixture contributes a significant portion of the area of the total response.

7.6.1.3.2 To measure total area, construct the baseline of Toxaphene in the sample chromatogram between the retention times of the first and last eluting Toxaphene components in the standard. In order to use the total area approach, the pattern in the sample chromatogram must be compared to that of the standard to ensure that all of the major components in the standard are present in the sample. Otherwise, the sample concentration may be significantly underestimated.

7.6.1.3.3 Toxaphene may also be quantitated on the basis of 4 to 6 major peaks. A collaborative study of a series of Toxaphene residues evaluated several approaches to quantitation of this compound, including the use of the total area of the peaks in the Toxaphene chromatogram and the use of a subset of 4 to 6 peaks. That study indicated that the use of 4 to 6 peaks provides

results that agree well with the total peak area approach and may avoid difficulties when interferences with Toxaphene peaks are present in the early portion of the chromatogram from compounds such as DDT. Whichever approach is employed should be documented and available to the data user, if necessary.

7.6.1.3.4 When Toxaphene is determined using the 4 to 6 peaks approach, the analyst must take care to evaluate the relative areas of the peaks chosen in the sample and standard chromatograms. It is highly unlikely that the peaks will match exactly, but the analyst should not employ peaks from the sample chromatogram whose relative sizes or areas appear to be disproportionally larger or smaller in the sample compared to the standard.

7.6.1.3.5 The heights or areas of the 4 to 6 peaks should be summed together and used to determine the Toxaphene concentration. Alternatively, use each peak in the standard to calculate a calibration factor for that peak, using the total mass of Toxaphene in the standard. These calibration factors are then used to calculate the concentration of each corresponding peak in the sample chromatogram and the 4 to 6 resulting concentrations are averaged to provide the final result for the sample.

7.6.2 Chlordane - Technical Chlordane is a mixture of at least 11 major components and 30 or more minor components that is used to prepare specific pesticide formulations. The CAS Registry number for Technical Chlordane is properly given as 12789-03-6. *Trans*-Chlordane (or α-Chlordane, CAS RN 5103-71-9) and *cis*-Chlordane (γ-Chlordane, CAS RN 5103-74-2), are the two most prevalent major components of Technical Chlordane. However, the exact percentage of each in the technical material is not completely defined, and is not consistent from batch to batch. Moreover, changes may occur when the technical material is used to prepare specific pesticide formulations. The approach used for evaluating and reporting Chlordane results will often depend on the end use of the results and the analyst's skill in interpreting this multi-component pesticide residue. The following sections discuss three specific options: reporting Technical Chlordane (12789-03-6), reporting Chlordane (not otherwise specified, 57-74-9), and reporting the individual Chlordane components that can be identified under their individual CAS numbers.

7.6.2.1 When the GC pattern of the residue resembles that of Technical Chlordane, the analyst may quantitate Chlordane residues by comparing the total area of the Chlordane chromatogram using three to five major peaks or the total area. If the Heptachlor epoxide peak is relatively small, include it as part of the total Chlordane area for calculation of the residue. If Heptachlor and/or Heptachlor epoxide are much out of proportion, calculate these separately and subtract their areas from the total area to give a corrected Chlordane area.

NOTE: Octachloro epoxide, a metabolite of Chlordane, can easily be mistaken for Heptachlor epoxide on a nonpolar GC column.

To measure the total area of the Chlordane chromatogram, inject an amount of a Technical Chlordane standard which will produce a chromatogram in which the major peaks are approximately the same size as those in the sample chromatograms. Construct the baseline of Technical Chlordane in the standard chromatogram between the retention times of the first and last eluting toxaphene components. Use this area and the mass of Technical Chlordane in the standard to calculate a calibration factor.

Construct a similar baseline in the sample chromatogram, measure the area, and use the calibration factor to calculate the concentration in the sample.

7.6.2.2 The GC pattern of a Chlordane residue in a sample may differ considerably from that of the Technical Chlordane standard. In such instances, it may not be practical to relate a sample chromatogram back to the pesticide active ingredient Technical Chlordane. Therefore, depending on the objectives of the analysis, the analyst may choose to report the sum of all the identifiable Chlordane components as "Chlordane (n.o.s.)" under the CAS number 57-74-9.

7.6.2.3 The third option is to quantitate the peaks of α-Chlordane, γ-Chlordane, and Heptachlor separately against the appropriate reference materials, and report these individual components under their respective CAS numbers.

7.6.2.4 To measure the total area of the Chlordane chromatogram, inject an amount of a Technical Chlordane standard which will produce a chromatogram in which the major peaks are approximately the same size as those in the sample chromatograms.

7.6.3 Hexachlorocyclohexane - Hexachlorocyclohexane is also known as BHC, from the former name, benzene hexachloride. Technical grade BHC is a cream-colored amorphous solid with a very characteristic musty odor. It consists of a mixture of six chemically distinct isomers and one or more heptachlorocyclohexanes and octachlorocyclohexanes. Commercial BHC preparations may show a wide variance in the percentage of individual isomers present. Quantitate each isomer (α, β, γ, and δ) separately against a standard of the respective pure isomer.

7.6.4 DDT - Technical DDT consists primarily of a mixture of 4,4'-DDT (approximately 75%) and 2,4'-DDT (approximately 25%). As DDT weathers, 4,4'-DDE, 2,4'-DDE, 4,4'-DDD, and 2,4'-DDD are formed. Since the 4,4'-isomers of DDT, DDE, and DDD predominate in the environment, these are the isomers normally regulated by EPA. Therefore, sample extracts should be quantitated against standards of the respective pure isomers of 4,4'-DDT, 4,4'-DDE, and 4,4'-DDD.

7.7 GC/MS confirmation may be used in conjunction with either single-column or dual-column analysis if the concentration is sufficient for detection by GC/MS.

7.7.1 Full-scan GC/MS will normally require a concentration of approximately 10 ng/µL in the final extract for each single-component compound. Ion trap or selected ion monitoring will normally require a concentration of approximately 1 ng/µL.

7.7.2 The GC/MS must be calibrated for the specific target pesticides when it is used for quantitative analysis.

7.7.3 GC/MS may not be used for confirmation when concentrations are below 1 ng/µL in the extract.

7.7.4 GC/MS confirmation should be accomplished by analyzing the same extract that is used for GC/ECD analysis and the extract of the associated method blank.

7.7.5 The base/neutral/acid extract and the associated blank may be used for GC/MS confirmation if the surrogates and internal standards do not interfere and if it is demonstrated

that the analyte is stable during acid/base partitioning. However, if the compounds are *not* detected in the base/neutral/acid extract, then GC/MS analysis of the pesticide extract should be performed.

7.7.6 A QC reference sample containing the compound must also be analyzed by GC/MS. The concentration of the QC reference sample must demonstrate that those pesticides identified by GC/ECD can be confirmed by GC/MS.

7.8 Suggested chromatographic system maintenance - When system performance does not meet the established QC requirements, corrective action is required, and may include one or more of the following.

7.8.1 Splitter connections - For dual-columns which are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector, clean and deactivate the splitter port insert or replace with a cleaned and deactivated splitter. Break off the first few centimeters (up to 30 cm) of the injection port side of the column. Remove the columns and solvent backflush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the columns.

7.8.2 GC injector ports can be of critical concern, especially in the analysis of DDT and Endrin. Injectors that are contaminated, chemically active, or too hot can cause the degradation ("breakdown") of the analytes. Endrin and DDT breakdown to Endrin aldehyde, Endrin ketone, DDD, or DDE. When such breakdown is observed, clean and deactivate the injector port, break off at least 30 cm of the column and remount it. Check the injector temperature and lower it to 205°C, if required. Endrin and DDT breakdown are less of a problem when ambient on-column injectors are used.

7.8.3 Metal injector body - Turn off the oven and remove the analytical columns when the oven has cooled. Remove the glass injection port insert (instruments with on-column injection). Lower the injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

7.8.3.1 Place a beaker beneath the injector port inside the oven. Using a wash bottle, serially rinse the entire inside of the injector port with acetone and then toluene, catching the rinsate in the beaker.

7.8.3.2 Prepare a solution of a deactivating agent (Sylon-CT or equivalent) following manufacturer's directions. After all metal surfaces inside the injector body have been thoroughly coated with the deactivation solution, rinse the injector body with toluene, methanol, acetone, then hexane. Reassemble the injector and replace the columns.

7.8.4 Column rinsing - The column should be rinsed with several column volumes of an appropriate solvent. Both polar and nonpolar solvents are recommended. Depending on the nature of the sample residues expected, the first rinse might be water, followed by methanol and acetone. Methylene chloride is a good final rinse and in some cases may be the only solvent required. The column should then be filled with methylene chloride and allowed to stand flooded overnight to allow materials within the stationary phase to migrate into the solvent. The column is then flushed with fresh methylene chloride, drained, and dried at room temperature with a stream of ultrapure nitrogen.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation techniques can be found in Method 3500. If an extract cleanup procedure was performed, refer to Method 3600 for the appropriate quality control procedures. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000, Sec. 7.0 and include evaluation of retention time windows, calibration verification, and chromatographic analysis of samples.

8.3 Initial Demonstration of Proficiency

8.3.1 Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made.

8.3.2 It is suggested that the quality control (QC) reference sample concentrate (as discussed in Section 8.0 of Methods 8000 and 3500) contain each analyte of interest at 10 mg/L. If this method is to be used for analysis of Chlordane or Toxaphene only, the QC reference sample concentrate should contain the most representative multi-component mixture at a suggested concentration of 50 mg/L in acetone. See Method 8000, Sec. 8.0 for additional information on how to accomplish this demonstration.

8.3.3 Calculate the average recovery and the standard deviation of the recoveries of the analytes in each of the four QC reference samples. Refer to Sec. 8.0 of Method 8000 for procedures for evaluating method performance.

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, a matrix spike, a duplicate, a laboratory control sample (LCS), and the addition of surrogates to each field sample and QC sample.

8.4.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, the laboratories should use a matrix spike and matrix spike duplicate pair.

8.4.2 In-house method performance criteria should be developed using the guidance found in Sec. 8.0 of Method 8000 for procedures for evaluating method performance.

8.4.3 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same

concentrations as the matrix spike. When the results of the matrix spike analysis indicates a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.4.4 Include a calibration standard after each group of 20 samples (it is *recommended* that a calibration standard be included after every 10 samples to minimize the number of repeat injections) in the analysis sequence as a calibration check. Thus, injections of method blank extracts, matrix spike samples, and other non-standards are counted in the total. Solvent blanks, injected as a check on cross-contamination, need not be counted in the total. The response factors for the calibration should be within ±15% of the initial calibration (see Sec. 7.5.2). When this calibration verifiction standard falls out of this acceptance window, the laboratory should stop analyses and take corrective action.

8.4.5 Whenever quantitation is accomplished using an internal standard, internal standards must be evaluated for acceptance. The measured area of the internal standard must be no more than 50 percent different from the average area calculated during calibration. When the internal standard peak area is outside the limit, all samples that fall outside the QC criteria must be reanalyzed.

8.4.6 DDT and Endrin are easily degraded in the injection port. Breakdown occurs when the injection port liner is contaminated high boiling residue from sample injection or when the injector contains metal fittings. Check for degradation problems by injecting a standard containing only 4,4'-DDT and Endrin. Presence of 4,4'-DDE, 4,4'-DDD, Endrin ketone or Endrin indicates breakdown. If degradation of either DDT or Endrin exceeds 15%, take corrective action before proceeding with calibration.

8.4.6.1 Calculate percent breakdown as follows:

$$\% \text{ breakdown of DDT} = \frac{\text{sum of degradation peak areas (DDD + DDE)}}{\text{sum of all peak areas (DDT + DDE + DDD)}} \times 100$$

$$\% \text{ breakdown of Endrin} = \frac{\text{sum of degradation peak areas (aldehyde + ketone)}}{\text{sum of all peak areas (Endrin + aldehyde + ketone)}} \times 100$$

8.4.6.2 The breakdown of DDT and Endrin should be measured before samples are analyzed and at the beginning of each 12-hour shift. Injector maintenance and recalibration should be completed if the breakdown is greater than 15% for either compound (Sec. 7.8.2).

8.4.7 Whenever silica gel (Method 3630) or Florisil (Method 3620) cleanups are used, the analyst must demonstrate that the fractionation scheme is reproducible. Batch to batch variation in the composition of the silica gel or Florisil or overloading the column may cause a change in the distribution patterns of the organochlorine pesticides. When compounds are found in two fractions, add the concentrations found in the fractions, and correct for any additional dilution.

8.4.8 See Method 8000, Sec. 8.0 for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries: The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method

8000, Sec. 8.0 for information on evaluating surrogate data and developing and updating surrogate limits.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined in Chapter One. A laboratory should develop its own matrix-specific MDLs using the guidance found in Chapter One.

9.2 The chromatographic separations in this method have been tested in a single laboratory by using clean hexane and liquid and solid waste extracts that were spiked with the test compounds at three concentrations. Single-operator precision, overall precision, and method accuracy were found to be related to the concentration of the compound and the type of matrix.

9.3 This method has been applied in a variety of commercial laboratories for environmental and waste matrices. Performance data were obtained for a limited number of target analytes spiked into sewage sludge and dichloroethene stillbottoms at high concentrations. These data are provided in Tables 9 and 10.

9.4 The accuracy and precision obtainable with this method depend on the sample matrix, sample preparation technique, optional cleanup techniques, and calibration procedures used.

9.5 Tables 9 and 10 contain precision and recovery data generated for sewage sludge and dichloroethane stillbottoms. Table 11 contains recovery data for a clay soil, taken from Reference 10. The spiking concentration was for the clay soil was 500 µg/kg. The spiking solution was mixed into the soil and then immediately transferred to the extraction device and immersed in the extraction solvent. The spiked sample was then extracted by Method 3541 (Automated Soxhlet). The data represent a single determination. Analysis was by capillary column gas chromatography/electron capture detector following Method 8081 for the organochlorine pesticides.

10.0 REFERENCES

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TABLE 1

GAS CHROMATOGRAPHIC RETENTION TIMES
FOR THE ORGANOCHLORINE PESTICIDES
USING WIDE-BORE CAPILLARY COLUMNS
SINGLE-COLUMN METHOD OF ANALYSIS

Compound	Retention Time (min) DB 608[a]	DB 1701[a]
Aldrin	11.84	12.50
α-BHC	8.14	9.46
β-BHC	9.86	13.58
δ-BHC	11.20	14.39
γ-BHC (Lindane)	9.52	10.84
α-Chlordane	15.24	16.48
γ-Chlordane	14.63	16.20
4,4'-DDD	18.43	19.56
4,4'-DDE	16.34	16.76
4,4'-DDT	19.48	20.10
Dieldrin	16.41	17.32
Endosulfan I	15.25	15.96
Endosulfan II	18.45	19.72
Endosulfan Sulfate	20.21	22.36
Endrin	17.80	18.06
Endrin aldehyde	19.72	21.18
Heptachlor	10.66	11.56
Heptachlor epoxide	13.97	15.03
Methoxychlor	22.80	22.34
Toxaphene	MR	MR

NA = Data not available.

MR = Multiple response compound.

[a] See Table 4 for GC operating conditions.

TABLE 2

GAS CHROMATOGRAPHIC RETENTION TIMES
FOR THE ORGANOCHLORINE PESTICIDES
USING NARROW-BORE CAPILLARY COLUMNS
SINGLE-COLUMN METHOD OF ANALYSIS

Compound	Retention Time (min) DB 608*	DB 5*
Aldrin	14.51	14.70
α-BHC	11.43	10.94
β-BHC	12.59	11.51
δ-BHC	13.69	12.20
γ-BHC (Lindane)	12.46	11.71
α-Chlordane	NA	NA
γ-Chlordane	17.34	17.02
4,4'-DDD	21.67	20.11
4,4'-DDE	19.09	18.30
4,4'-DDT	23.13	21.84
Dieldrin	19.67	18.74
Endosulfan I	18.27	17.62
Endosulfan II	22.17	20.11
Endosulfan sulfate	24.45	21.84
Endrin	21.37	19.73
Endrin aldehyde	23.78	20.85
Heptachlor	13.41	13.59
Heptachlor epoxide	16.62	16.05
Methoxychlor	28.65	24.43
Toxaphene	MR	MR

NA = Data not available.

MR = Multiple response compound.

* See Table 4 for GC operating conditions.

TABLE 3

FACTORS FOR DETERMINATION OF ESTIMATED QUANTITATION LIMITS[a] (EQLs) FOR VARIOUS MATRICES

Matrix	Factor
Ground water	10
Low-concentration soil by sonication with GPC cleanup	670
High-concentration soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a] Laboratories may estimate the quantitation limits of the target analytes in environmental and waste media by generating MDLs in organic-free reagent water and using the following equation (see Sec. 5.0 of Chapter One for information on generating MDL data):

EQL = [MDL in water] times [factor in this table]

For nonaqueous samples, the factor is on a wet-weight basis. Sample EQLs are highly matrix-dependent. EQLs determined using these factors are provided as guidance and may not always be achievable.

TABLE 4

GC OPERATING CONDITIONS FOR ORGANOCHLORINE COMPOUNDS
SINGLE-COLUMN ANALYSIS USING NARROW-BORE COLUMNS

Column 1 - 30 m x 0.25 or 0.32 mm ID fused silica capillary column chemically bonded with SE-54 (DB-5 or equivalent), 1 µm film thickness.

Carrier gas	Helium
Carrier gas pressure	16 psi
Injector temperature	225°C
Detector temperature	300°C
Initial temperature	100°C, hold 2 minutes
Temperature program	100°C to 160°C at 15°C/min, followed by 160°C to 270°C at 5°C/min
Final temperature	270°C

Column 2 - 30 m x 0.25 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, or equivalent), 25 µm coating thickness, 1 µm film thickness.

Carrier gas	Nitrogen
Carrier gas pressure	20 psi
Injector temperature	225°C
Detector temperature	300°C
Initial temperature	160°C, hold 2 minutes
Temperature program	160°C to 290°C at 5°C/min
Final temperature	290°C, hold 1 min

TABLE 5

GC OPERATING CONDITIONS FOR ORGANOCHLORINE COMPOUNDS
SINGLE-COLUMN ANALYSIS USING WIDE-BORE COLUMNS

Column 1 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, RTx-35, or equivalent), 0.5 µm or 0.83 µm film thickness.

Column 2 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 50 percent phenyl methylpolysiloxane (DB-1701, or equivalent), 1.0 µm film thickness.

Both Column 1 and Column 2 use the same GC operating conditions.

Carrier gas	Helium
Carrier gas flow rate	5-7 mL/minute
Makeup gas	argon/methane (P-5 or P-10) or nitrogen
Makeup gas flow rate	30 mL/min
Injector temperature	250°C
Detector temperature	290°C
Initial temperature	150°C, hold 0.5 minute
Temperature program	150°C to 270°C at 5°C/min
Final temperature	270°C, hold 10 min

Column 3 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 1.5 µm film thickness.

Carrier gas	Helium
Carrier gas flow rate	6 mL/minute
Makeup gas	argon/methane (P-5 or P-10) or nitrogen
Makeup gas flow rate	30 mL/min
Injector temperature	205°C
Detector temperature	290°C
Initial temperature	140°C, hold 2 min
Temperature program	140°C to 240°C at 10°C/min, hold 5 minutes at 240°C, 240°C to 265°C at 5°C/min
Final temperature	265°C, hold 18 min

TABLE 6

RETENTION TIMES OF THE ORGANOCHLORINE PESTICIDES[a]
DUAL-COLUMN METHOD OF ANALYSIS

Compound	DB-5 RT (min)	DB-1701 RT (min)
DBCP	2.14	2.84
Hexachlorocyclopentadiene	4.49	4.88
Etridiazole	6.38	8.42
Chloroneb	7.46	10.60
Hexachlorobenzene	12.79	14.58
Diallate	12.35	15.07
Propachlor	9.96	15.43
Trifluralin	11.87	16.26
α-BHC	12.35	17.42
PCNB	14.47	18.20
γ-BHC	14.14	20.00
Heptachlor	18.34	21.16
Aldrin	20.37	22.78
Alachlor	18.58	24.18
Chlorothalonil	15.81	24.42
Alachlor	18.58	24.18
β-BHC	13.80	25.04
Isodrin	22.08	25.29
DCPA	21.38	26.11
δ-BHC	15.49	26.37
Heptachlor epoxide	22.83	27.31
Endosulfan-I	25.00	28.88
γ-Chlordane	24.29	29.32
α-Chlordane	25.25	29.82
trans-Nonachlor	25.58	30.01
4,4'-DDE	26.80	30.40
Dieldrin	26.60	31.20
Perthane	28.45	32.18
Endrin	27.86	32.44
Chloropropylate	28.92	34.14
Chlorobenzilate	28.92	34.42
Nitrofen	27.86	34.42
4,4'-DDD	29.32	35.32
Endosulfan II	28.45	35.51
4,4'-DDT	31.62	36.30
Endrin aldehyde	29.63	38.08
Mirex	37.15	38.79
Endosulfan sulfate	31.62	40.05
Methoxychlor	35.33	40.31
Captafol	32.65	41.42

(continued)

TABLE 6 (continued)

RETENTION TIMES OF THE ORGANOCHLORINE PESTICIDES[a]
DUAL-COLUMN METHOD OF ANALYSIS

Compound	DB-5 RT (min)	DB-1701 RT (min)
Endrin ketone	33.79	42.26
Permethrin	41.50	45.81
Kepone	31.10	[b]
Dicofol	35.33	[b]
Dichlone	15.17	[b]
α,α'-Dibromo-m-xylene	9.17	11.51
2-Bromobiphenyl	8.54	12.49

[a] See Table 7 for GC operating conditions.

[b] Not detected at 2 ng per injection.

TABLE 7

GC OPERATING CONDITIONS FOR ORGANOCHLORINE PESTICIDES
FOR DUAL-COLUMN METHOD OF ANALYSIS
LOW TEMPERATURE, THIN FILM

Column 1:	DB-1701 or equivalent 30 m x 0.53 mm ID 1.0 µm film thickness
Column 2:	DB-5 or equivalent 30 m x 0.53 mm ID 0.83 µm film thickness
Carrier gas	Helium
Carrier gas flow rate	6 mL/minute
Makeup gas	Nitrogen
Makeup gas flow rate	20 mL/min
Injector temperature	250°C
Detector temperature	320°C
Initial temperature	140°C, hold 2 minutes
Temperature program	140°C to 270°C at 2.8°C/min
Final temperature	270°C, hold 1 minute

TABLE 8

GC OPERATING CONDITIONS FOR ORGANOCHLORINE PESTICIDES
FOR THE DUAL COLUMN METHOD OF ANALYSIS
HIGH TEMPERATURE, THICK FILM

Column 1:	DB-1701 (J&W) or equivalent 30 m x 0.53 mm ID 1.0 µm
Column 2:	DB-5 (J&W) or equivalent 30 m x 0.53 mm ID 1.5 µm
Carrier gas:	Helium
Carrier gas flowrate:	6 mL/minute
Makeup gas:	Nitrogen
Makeup gas flowrate:	20 (mL/min)
Injector temperature:	250°C
Detector temperature:	320°C
Initial temperature:	150°C, hold 0.5 min
Temperature program:	150°C to 190°C at 12°C/min, hold 2 min 190°C to 275°C at 4°C/min
Final temperature	275°C, hold 10 min

TABLE 9

ANALYTE RECOVERY FROM SEWAGE SLUDGE

Compound	Ultrasonic Extraction %Recovery	%RSD	Soxhlet %Recovery	%RSD
Hexachloroethane	80	7	79	1
2-Chloronapthalene	50	56	67	8
4-Bromodiphenyl ether	118	4	nd	nd
α-BHC	88	25	265	18
γ-BHC	55	9	155	29
Heptachlor	60	13	469	294
Aldrin	92	33	875	734
β-BHC	351	71	150	260
δ-BHC	51	11	57	2
Heptachlor epoxide	54	11	70	3
Endosulfan I	52	11	70	4
γ-Chlordane	50	9	65	1
α-Chlordane	49	8	66	0
DDE	52	11	74	1
Dieldrin	89	19	327	7
Endrin	56	10	92	15
Endosulfan II	52	10	88	11
DDT	57	10	95	17
Endrin aldehyde	45	6	42	10
DDD	57	11	99	8
Tetrachloro-m-xylene	71	19	82	1
Decachlorobiphenyl	26	23	28	48

Concentration spiked in the sample: 500-1000 ng/g, three replicates analyses.

Soxhlet extraction by Method 3540 with methylene chloride.

Ultrasonic extraction by Method 3550 with methylene chloride/acetone (1:1).

Cleanup by Method 3640.

GC column: DB-608, 30 m x 0.53 mm ID.

TABLE 10

ANALYTE RECOVERY FROM DICHLOROETHANE STILLBOTTOMS

Compound	Ultrasonic Extraction %Recovery	%RSD	Soxhlet %Recovery	%RSD
Hexachloroethane	70	2	50	30
2-Chloronapthalene	59	3	35	35
4-Bromodiphenyl ether	159	14	128	137
α-BHC	55	7	47	25
β-BHC	43	6	30	30
Heptachlor	48	6	55	18
Aldrin	48	5	200	258
β-BHC	51	7	75	42
δ-BHC	43	4	119	129
Heptachlor epoxide	47	6	66	34
Endosulfan I	47	4	41	18
γ-Chlordane	48	5	47	13
α-Chlordane	45	5	37	21
DDE	45	4	70	40
Dieldrin	45	5	58	24
Endrin	50	6	41	23
Endosulfan II	49	5	46	17
DDT	49	4	40	29
Endrin aldehyde	40	4	29	20
DDD	48	5	35	21
Tetrachloro-m-xylene	49	2	176	211
Decachlorobiphenyl	17	29	104	93

Concentration spiked in the sample: 500-1000 ng/g, three replicates analyses.

Soxhlet extraction by Method 3540 with methylene chloride.

Ultrasonic extraction by Method 3550 with methylene chloride/acetone (1:1).

Cleanup by Method 3640.

GC column: DB-608, 30 m x 0.53 mm ID.

TABLE 11

SINGLE LABORATORY ACCURACY DATA FOR THE EXTRACTION OF ORGANOCHLORINE PESTICIDES FROM SPIKED CLAY SOIL BY METHOD 3541 (AUTOMATED SOXHLET)[a]

Compound Name	% Recovery DB-5	DB-1701
α-BHC	89	94
β-BHC	86	ND
Heptachlor	94	95
Aldrin	ND	92
Heptachlor epoxide	97	97
trans-Chlordane	94	95
Endosulfan I	92	92
Dieldrin	ND	113
Endrin	111	104
Endosulfan II	104	104
4,4'-DDT	ND	ND
Mirex	108	102

[a] The operating conditions for the automated Soxhlet were:

Immersion time 45 min; extraction time 45 min; 10 g sample size; extraction solvent, 1:1 acetone/hexane. No equilibration time following spiking.

ND = Not able to determine because of interference.

All compounds were spiked at 500 µg/kg.

Data taken from Reference 10.

TABLE 12

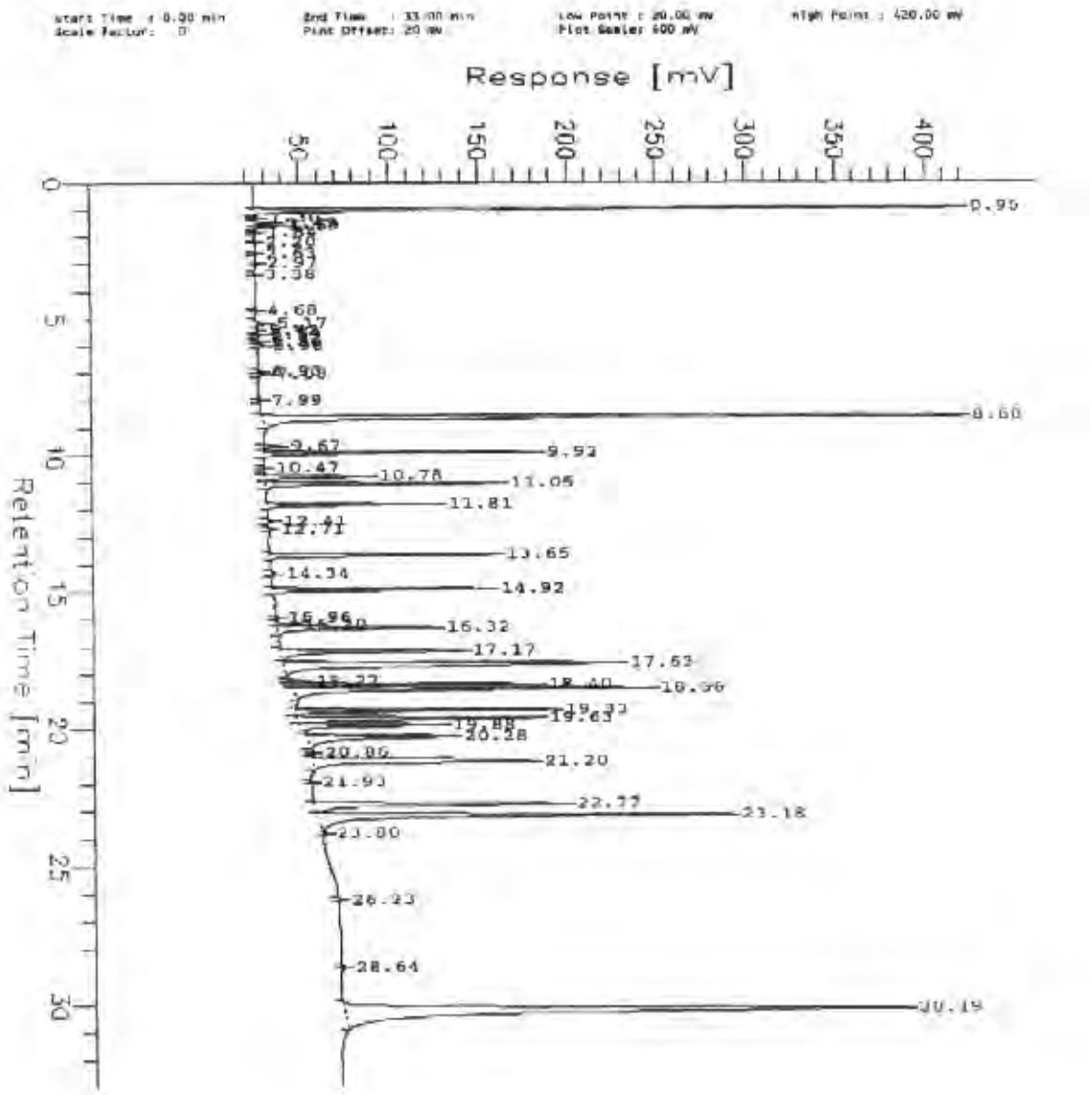
SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR SOLID PHASE EXTRACTION BY METHOD 3535[1]

Compound	Bias (%)				Precision (%)				MDL (µg/L)	
	Ground water (low)	Ground water (high)	Waste water (low)	Waste water (high)	Ground water (low)	Ground water (high)	Waste water (low)	Waste water (high)	Ground water	Waste water
Aldrin	37.3	93.5	79.3	94.0	23.7	5.5	6.7	3.4	1.4	0.83
β-BHC	89.2	107.8	79.7	82.3	6.5	2.5	1.6	4.2	0.91	0.20
δ-BHC	106.2	86.0	88.9	83.4	5.6	2.4	2.5	4.2	0.93	0.35
α-Chlordane	75.4	112.3	78.9	89.5	12.8	2.7	4.7	2.4	1.5	0.58
γ-Chlordane	70.7	98.9	79.9	93.9	15.8	2.7	4.6	2.9	1.8	0.58
Dieldrin	83.4	96.1	81.2	93.3	7.1	2.3	3.8	3.6	0.9	0.49
Endosulfan I	79.6	99.1	79.6	87.9	10.6	2.3	4.1	3.8	1.3	0.51
Endosulfan II	94.5	101.6	82.7	93.5	5.8	2.8	4.2	4.1	0.9	0.54
Endrin	88.3	98.4	85.1	89.6	6.2	2.3	3.1	2.9	1.7	0.82
Endrin Aldehyde	87.5	99.9	69.0	80.2	6.0	4.0	3.3	5.9	0.8	0.36
Heptachlor	43.1	95.4	71.8	78.6	19.2	3.9	5.0	2.8	1.3	0.56
Heptachlor Epoxide	76.4	97.6	75.3	83.4	12.1	2.4	2.9	3.3	1.5	0.34
Lindane	81.3	115.2	82.1	85.3	11.1	3.2	2.4	3.1	1.4	0.32
p,p'-DDE	80.3	96.0	85.1	97.9	8.3	2.5	4.4	2.4	1.0	0.59
p,p'-DDT	86.6	105.4	105	111	4.4	2.7	4.3	4.7	0.6	0.71
p,p'-TDE (DDD)	90.5	101.1	74.9	79.6	4.8	2.4	4.6	2.9	1.4	0.85

[1]All results determined from seven replicates of each sample type. Two spiking levels were used. "Low" samples were spiked at 5-10 µg/L for each analyte, while "high" samples were spiked at 250 - 500 µg/L. MDL values were determined from the "low" samples without further consideration of the spiking level.

FIGURE 1

GAS CHROMATOGRAM OF THE MIXED ORGANOCHLORINE PESTICIDE STANDARD

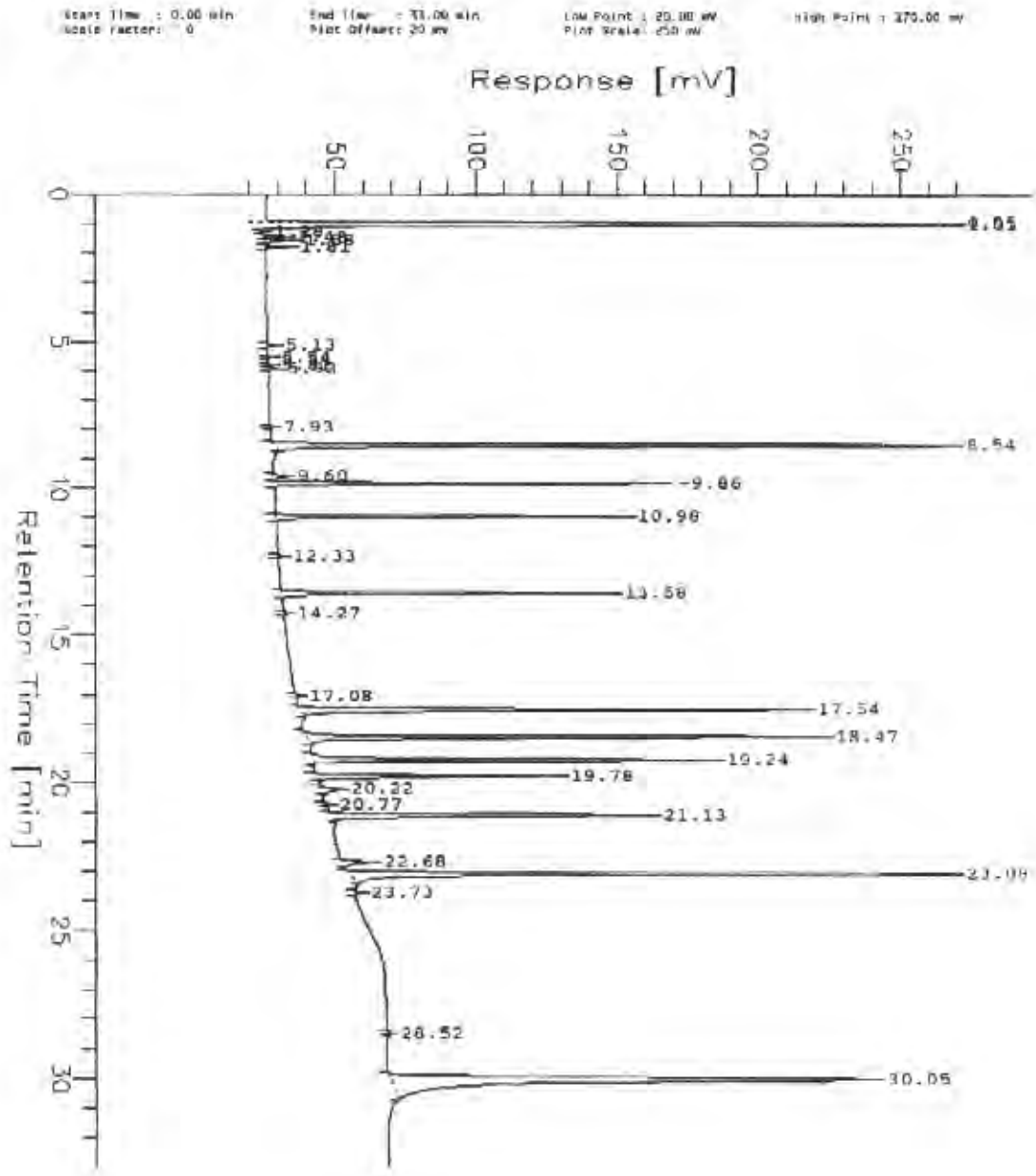


Column: 30 m x 0.25 mm ID, DB-5

Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C carrier He at 18 psi.

FIGURE 2

GAS CHROMATOGRAM OF INDIVIDUAL ORGANOCHLORINE PESTICIDE STANDARD MIX A

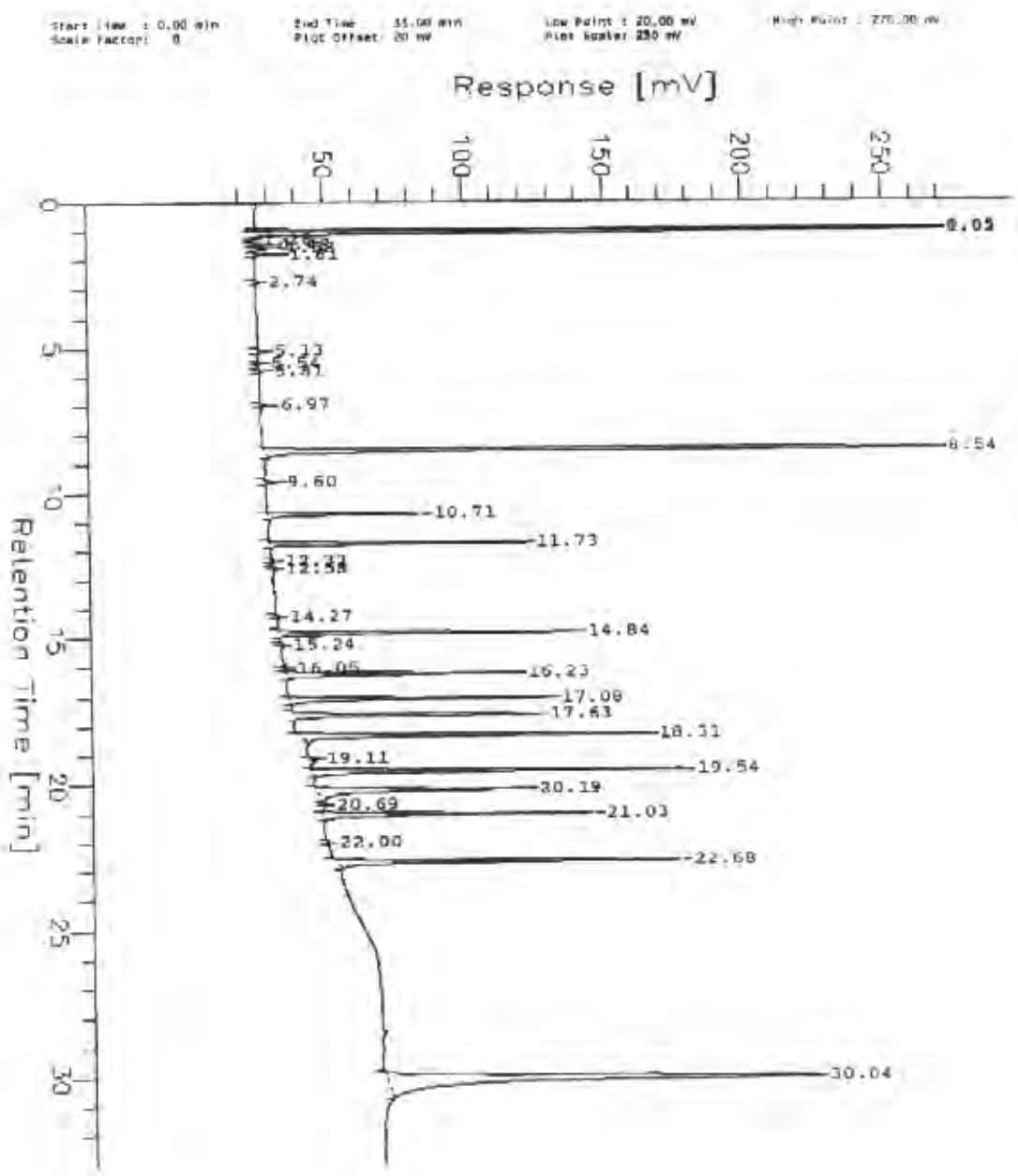


Column: 30 m x 0.25 mm ID, DB-5

Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

FIGURE 3

GAS CHROMATOGRAM OF INDIVIDUAL ORGANOCHLORINE PESTICIDE STANDARD MIX B

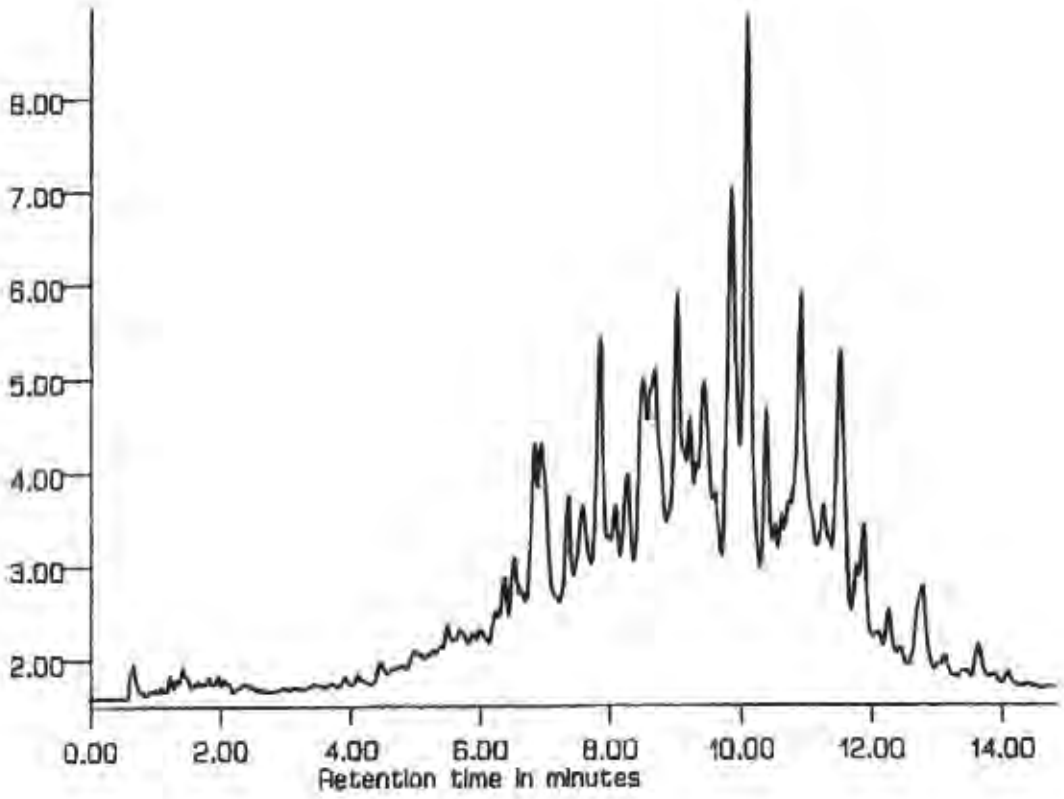


Column: 30 m x 0.25 mm ID, DB-5

Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

FIGURE 4

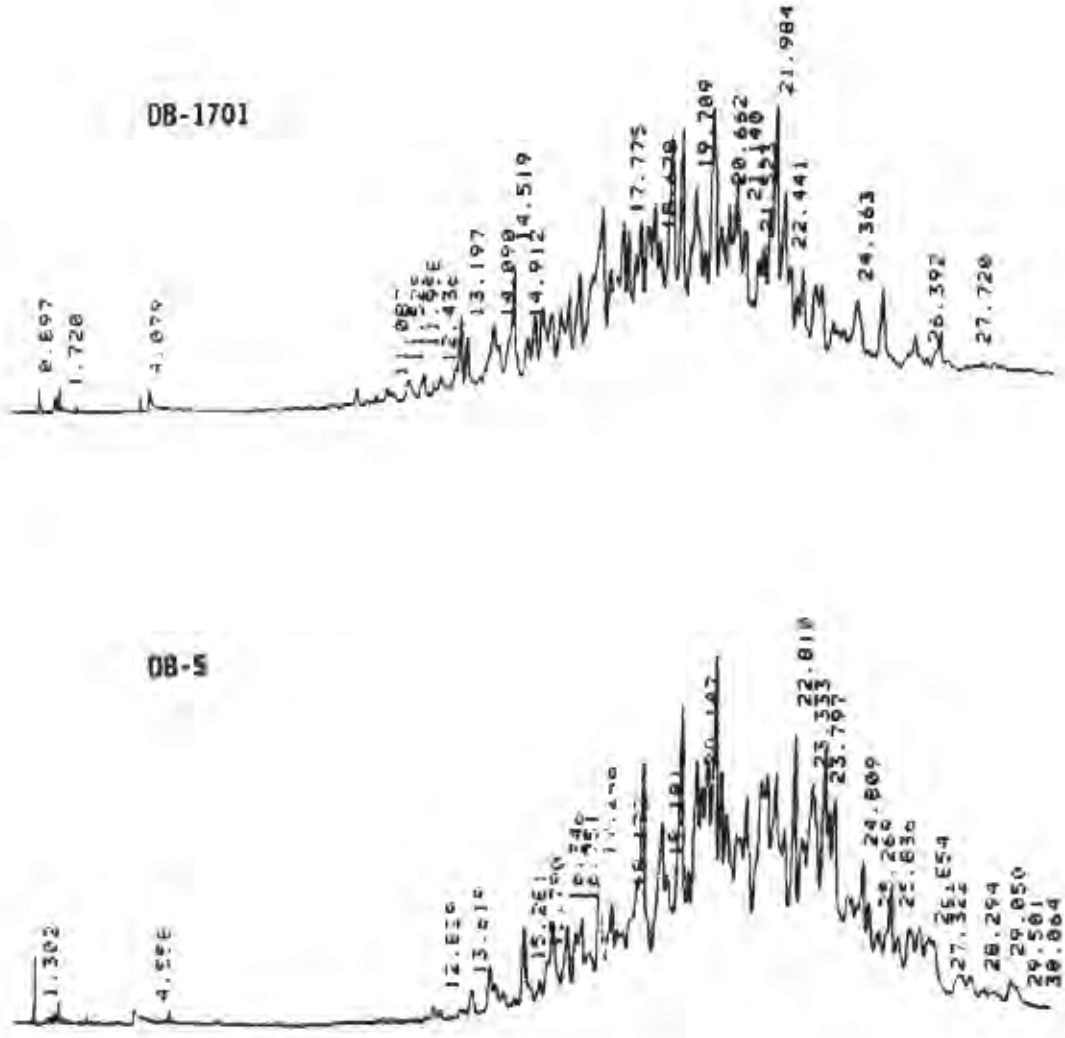
GAS CHROMATOGRAM OF TOXAPHENE



Toxaphene analyzed on an SPB-608 fused-silica open-tubular column. The GC operating conditions were as follows: 30 m x 0.53 mm ID SPB-608. Temperature program: 200°C (2 min hold) to 290°C at 6°C/min.

FIGURE 5

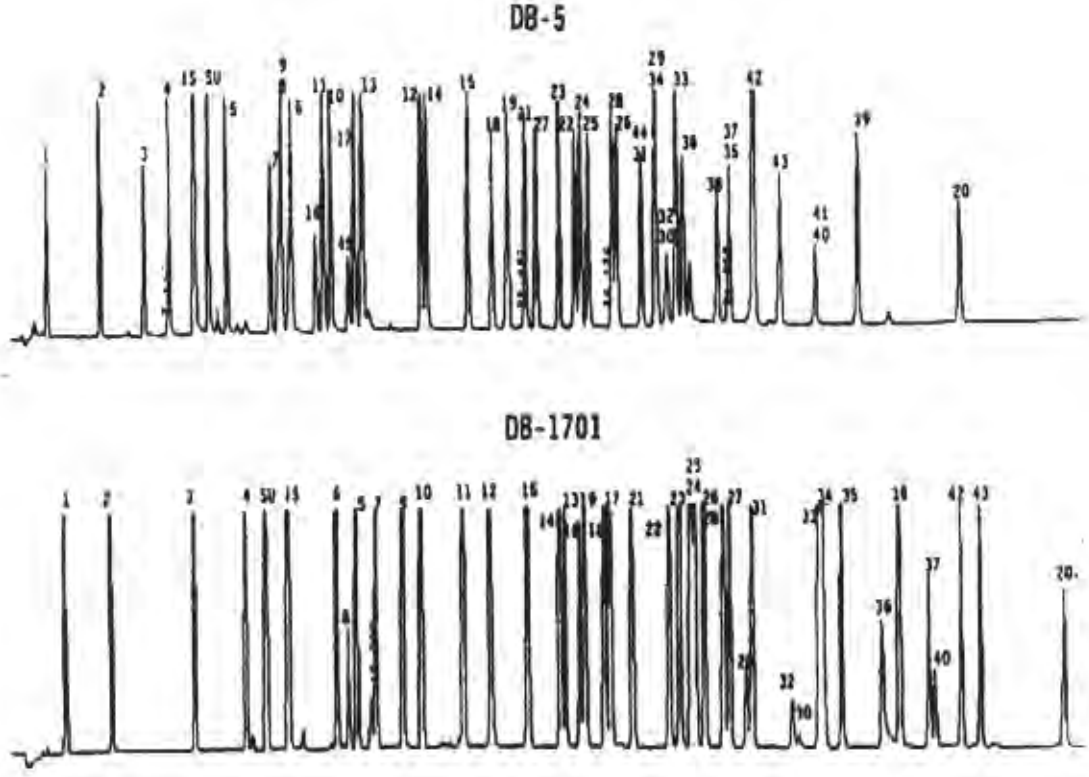
GAS CHROMATOGRAM OF STROBANE



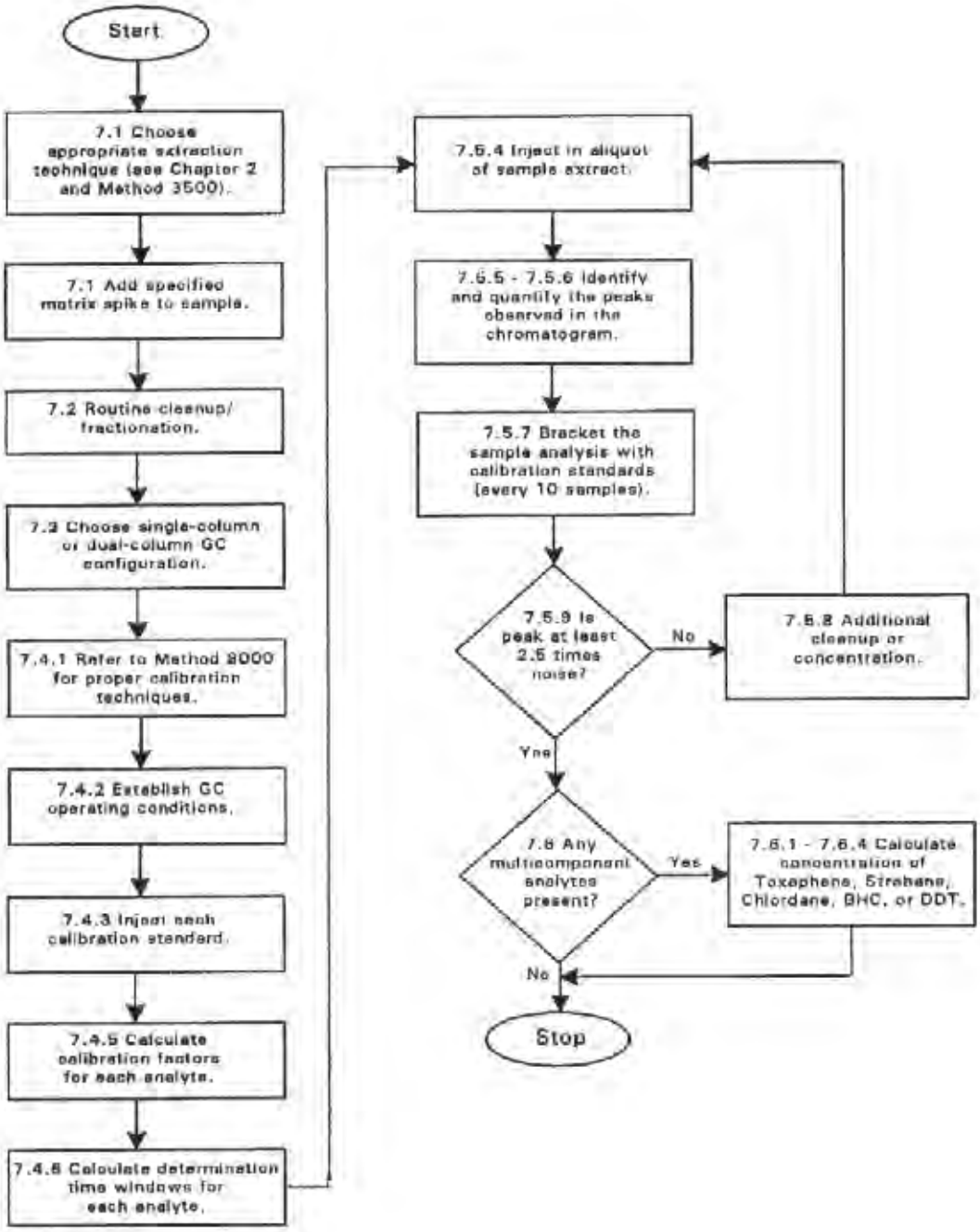
Strobane analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

FIGURE 6

GAS CHROMATOGRAM OF ORGANOCHLORINE PESTICIDES



Organochlorine pesticides analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (0.83-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to an 8 in. injection tee (Supelco Inc.). Temperature program: 140°C (2 min hold) to 270°C (1 min hold) at 2.8°C/min.


Start
7.1 Choose appropriate extraction technique (see Chapter 2 and Method 3500).
7.1 Add specified matrix spike to sample.
7.2 Routine cleanup/ fractionation.
7.3 Choose single-column or dual-column GC configuration.
7.4.1 Refer to Method 8000 for proper calibration techniques.
7.4.2 Establish GC operating conditions.
7.4.3 Inject each calibration standard.
7.4.5 Calculate calibration factors for each analyte.
7.4.6 Calculate determination time windows for each analyte.
7.5.4 Inject in aliquot of sample extract.
7.5.5 - 7.5.6 Identify and quantify the peaks observed in the chromatogram.
7.5.7 Bracket the sample analysis with calibration standards (every 10 samples).
7.5.9 Is peak at least 2.5 times noise?
No
7.5.8 Additional cleanup or concentration.
Yes
7.6 Any multicomponent analytes present?
Yes
7.6.1 - 7.6.4 Calculate concentration of Toxaphene, Strobane, Chlordane, BHC, or DDT.
No
Stop

Analytical Methods

Radiochemistry

Paragon Analytics SOPs:

SOP 713 REV 8
SOP 739 REV 8
SOP 704 REV 7
SOP 726 REV 4

PARAGON ANALYTICS, INC.
STANDARD OPERATING PROCEDURE 713 REVISION 8

TITLE: ANALYSIS OF GAMMA EMITTING RADIONUCLIDES BY GAMMA SPECTROSCOPY – METHOD EPA 901.1

FORMS None

APPROVAL:
Technical Manager _____ Date 4/6/03
Quality Assurance Manager _____ Date 04.04.03
Laboratory Manager _____ Date 4-6-03

HISTORY: Rev 0, 06/01/92; Rev 1, 07/27/93; Rev 2, 10/15/93; Rev 3, 04/26/96, Rev 4, 05/16/96, Rev 5, 03/20/00; Rev 6, 06/15/01; Rev 7, 08/24/02; Rev 8, 04/07/03. *dbh*

1. SUMMARY, SCOPE AND APPLICATION

1.1 SUMMARY

Gamma emissions from radionuclides are detected by a semiconductor germanium crystal, which provides a small electronic pulse for each gamma interaction, where the pulse height is proportional to the gamma incident energy. This electronic data is converted to digital data by an analog to digital converter (ADC) and stored in a multichannel analyzer (MCA). The data collected by the MCA is subsequently interpreted by a complex software program, generating results in units of radioactivity per unit sample volume. The analysis software used by PAI is Seeker®, Gamma Spectroscopy Software, Version 2.2., a product of Vertechs Software Solution, Inc.. This procedure is a more detailed variant of EPA Procedure 901.1 and DOE/EML Procedure 4.5.2.3, and incorporates all of the intentions of EPA 901.1 and DOE 4.5.2.3.

1.2 SCOPE AND APPLICATION

This procedure describes the steps necessary to perform gamma emissions analysis of samples of various media using high-resolution intrinsic germanium gamma spectrometry. This procedure is applicable to all gamma spectrometry analyses performed at Paragon.

2. DISCUSSION/COMMENTS

The physical shape of the source and its proximity to the detector is critical to the efficiency calibration and these factors define the "counting geometry". The calibration geometry and the sample geometry must match within +/- 0.5cm of the line on the sample container.

3. REAGENTS AND APPARATUS

3.1. REAGENTS

No reagents are used by this procedure. The operator should be aware, however, that

water samples are preserved to pH <2 with HNO_3.

3.2. APPARATUS

This procedure is conducted with the use of installed gamma detection and analysis equipment consisting of ten intrinsic germanium gamma spectrometers mounted in lead shields for the reduction of ambient background radiation, a personal computer analysis system with multichannel analyzer interfaces, three NIM-bin based multichannel analyzers, gamma analysis software, and associated nuclear electronics and cabling.

4. PROCEDURE

4.1. OPERATING CONDITIONS

The gamma spectrometry systems shall be operating with detector bias as specified by the detector manufacturer and amplifier and MCA settings as required to obtain a nominal 0.5 keV/channel energy calibration across a range of 47.5 to 2000 keV. The operating conditions shall be verified daily by performance of the daily quality control checks (see Section 5.1).

4.2. PROCEDURE

4.2.1. Spectrum Acquisition

The detector must be calibrated for the geometry that is being loaded. Efficiency calibration procedures are defined in Section 5.2. A list of current geometries, calibration date and the dates the calibrations expire, and standards used for calibration is attached to the top of each detector. Samples shall be placed directly on the detector, inside the lead shield, and should be level and centered over the detector.

After samples have been loaded in the detectors, select the desired detector in the spectral display control menu. After the detector has been selected, select the 'TOOLS' icon. The next prompt will ask for the ID and the desired live time or count time. Enter the sample ID as it appears on the benchsheet followed by a space and then the batch ID (i.e. 0011222-3 GS09999). After the ID has been entered, select the 'ID SET' icon to save the sample ID. Enter the desired count time in seconds in the box labeled 'LIVE TIME' and then select the 'PRE SET' icon to save the count time. Sample count times depend on the sample volume, geometry, and the client's required MDC. An outline of the geometries and their respective matrix and/or volume can be found in Appendix C. The LCS samples are typically counted for 1800 seconds (30 minutes) and blank samples will be counted for as long as the longest sample count time. After the sample ID and count time have been entered and saved, clear the previous spectrum by selecting the erase icon. Begin spectrum acquisition by selecting the 'GO' icon and exit the 'TOOLS' window by selecting 'DONE'.

Enter all samples that are analyzed in the Gamma Spectroscopy Logbook, on the

current page with the date that the sample is being counted. Ensure that the detectors being used have passed the Daily QC checks. Necessary information includes: the PAI sample ID , the detector number, the geometry, the duration of the count, the count start time, and the operators initials. Additionally, for counting geometries 7 and 8 a puck must be used. A run log notation should be entered denoting that the puck was used for these geometries.

4.2.2. Spectrum Analysis

Upon completion of the sample count the data must be transferred to the workspace and analyzed . First select the appropriate analysis/application type in the application select on the menu bar. Then select <Read MCA> on the menu bar. By "reading the MCA", the data acquired during the analysis count is transferred to the workspace and default settings and files from the application are applied. (i.e., efficiency, library, units, etc.) When "Read MCA" is selected the spectrum parameters screen is prompted. At this time the file name is generated and should be recorded in the gamma spec. run log. The analyst will need to enter some parameters and also has the opportunity to change existing parameters for a particular analysis.

Sample ID: This should be automatically transferred, but corrections can be made here.

Spec. Code: This is entered the same as the file ID, except ends in a given letter instead of .SPC. For example if the file ID is 001111.SPC, the Spec. Code would be 001111A. This code is used to store the spectral data in the database file and later transfer the data to Radchem for reporting. The letter is used to designate multiple analyses of the same spectra (ie. 001111A for the first analysis and 001111D for the fourth analysis).

Sample Size: Enter the volume, weight, or number of filters as appropriate.

Units: This will be transferred automatically as a default, but can be changed as needed.

Sampling Start and Stop: Enter the collection date of the sample in both boxes. This is normally the same date and time for both the start and stop. The time of day is generally 12:00:00 for all samples.

Efficiency File: This line should be generated automatically by the computer and is in the form (Dxx)(ShGG).EFF where xx is the detector number, and GG is the geometry of the sample. If changing the efficiency file, make sure the detector of the efficiency file is for the detector the sample was counted on and that the efficiency file has not expired.

After all the parameters and values are satisfactory, select 'OK' to exit the 'Read MCA' window. By selecting 'OK', all of the parameters and values are saved under the file ID and can be retrieved later to further analyze. By selecting

'CANCEL', all of the parameters are lost and the file ID is not saved.

Next, the spectrum must be analyzed to identify peaks at the various energies. To do this, select 'PEAK SEARCH' on the menu bar and the software will apply the resolution calibration to the acquired spectrum to define peaks and peak height. This will prompt the next window, which allows the analyst to see all of the peaks identified, and the counts acquired for each peak. The analyst shall review the peak search results to identify peak shifts, multiplets, etc. After the peak search results are considered to be satisfactory, select 'DONE' to exit the peak search results window.

To calculate activity concentrations, select the 'Calculate' icon under 'Activity' on the menu tool bar. This will prompt an activity report parameters window. Select the desired library to be used in the column labeled 'Library File'. Next select the background file to be used according to the detector and the count date. Background files are named so that the first two numbers correlate to the detector, the next two correlate to the month the background counted, and the next two correlate to the day of the month. Background files can be used for one week after counting. The LSF File should remain as 'NONE'. The 'Results File' and the 'Printout File' should be the same as the .SPC file, except ending in .RSF and .TXT, respectively.

Select 'OK' after the correct library and background have been selected and the library search results window will be shown. This allows the analyst to review peaks that have been matched to specific peaks in the library.

To finish the calculations, select 'OK' to prompt the raw data printout. This window allows the analyst to review all of the parameters used in the analysis. To save the data select 'Database' to prompt the results export parameters window. Here the Spec. Code is used to transfer the raw data to a database later used for reporting. Select 'GAMMA.SDF: Example' in the Export Defs File column and then select 'OK' to transfer the data. Then print the raw data by selecting the printer icon.

5. QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

5.1. QC MONITORING

Quality Assurance and Quality Control practices will be performed in accordance with the procedures set forth in PAI's Environmental Radiochemistry Quality Assurance Plan. Standards for Daily QC Checks shall be traceable to the National Institute for Standards and Technology (NIST). All Daily QC monitoring should be recorded in the gamma spectroscopy run log.

5.1.1. Daily QC Energy Calibration Checks

A daily QC check involves performing an energy calibration (as well as monitoring the resolution and efficiency calibrations). Each detector has a labeled calibration

standard. Center the appropriate calibration standard on the corresponding detector. Count each Daily Check standard as described above for 20 minutes using the sample ID "DAILY CHECK". When the count is complete select 'Daily Performance Check' under the Application Select menu and then select 'Read MCA' and the edit parameters screen is then prompted. Select 'OK', as the parameters should be the default.. On the menu bar select <PEAk Search> as described above and then select <Q.C.> on the menu bar and then <Detector> . The calibration parameters screen is then prompted and the energy bullet should be selected. Select <OK>. Choose <Merge PSR> , then select <Curve Fit> and then select <Save>. This will save the energy calibration for that day The program then compares the results of the energy recalibration to the Q.C. parameters (found in the Q.C. editor) established for the specified detector.

5.1.2. Corrective Action for Daily QC failures

If a detector is not within established control limits for any of the bounds tests corrective action must be taken. The first course of action is to re-run the QC check. If the observed parameter is still outside normal acceptance criteria after the second analysis, the procedure is as follows:

5.1.2.1. Daily Energy Calibrations

If one of the centroids exceeds the bounds test (i.e. 662 keV), the peak location should be adjusted. This is done by placing a calibration source on the detector (preferably a Laboratory Control Sample--LCS) and starting the detector Clear the current spectrum by typing <F4> (Clear). The acquisition can then be started by typing <F2> . Move the cursor to the appropriate centroid (i.e. 662 keV) and check the actual location. The peak can be moved by adjusting the fine gain, located on the amplifier. Note that it only requires a minute adjustment (one click) to move the peak three to five keV.

After the peak has been moved to the correct location, re-run the energy calibration.

If the failure includes one of the other parameters (i.e. FWHM or efficiency), the Daily QC can be re-run (if the QC fails for a second time the detector is taken off-line and the lab supervisor should be contacted). Note: A gain adjustment or/and a pole-zero adjustment can be conducted in the case of a FWHM failure. 1. Attach a co-axial cable from the "1 Meg" port associated with the vertical input on the oscilloscope to the "uni" output on the amplifier. 2. The scope settings should be as follows:

Volts/Div(Vertical)= 0.1
Polarity= DC
Trigger Selector= EXT(-)
Mode= DC
Triggering Level=0
Stability= Preset
Time/Div= 20μs

Variable= Calibrated
3.Place a source on the detector and adjust the signal so that it is as close to the baseline as possible by using the "PZ ADJ" dial found on the amplifier.
The energy calibration can now be run again. If any parameter still fails, tag the detector out of service and notify the lab supervisor.

NOTE: Record all calibration operations in the run log, including fine gain adjustments, bounds re-calculations with start and end dates, and calibration re-runs.

5.2. EFFICIENCY CALIBRATION PROCEDURES

Standards for calibration shall be traceable to the National Institute for Standards and Technology (NIST). Standards will normally be of the mixed-gamma, multiple-energy type available from several commercial suppliers. The analysis systems shall be calibrated for each physical form of sample to be analyzed (e.g., water, soil, filter, etc.) at least annually. A FWHM calibration should also be performed at least annually. Note that there is only one FWHM calibration per detector, and it is not geometry specific. Before starting an efficiency calibration, consult with a Senior Instrument Technician. All efficiency calibrations should be recorded in the gamma spectroscopy run log.

5.2.1. Spectrum Acquisition

Place the calibration source for the appropriate geometry on the detector to be calibrated. The efficiency calibration will be initiated like that of a sample count. First, an internal workorder number must be obtained from the current non-client workorder notebook (located in the radium/strontium lab). Use this workorder number and follow the same procedure used to count a sample. Be sure to enter the appropriate dates and time for the calibration standard. (2 hours and/or a duration long enough to acquire 10,000 cts/per energy line that will be used in the calibration.

5.2.2. Spectrum Analysis

5.2.2.1. After the acquisition is complete the MCA of the sample spectrum should be read. In the edit parameters screen enter the standard calibration origin date, and the appropriate volume/sample size. Select <Pk Search> and then select <Calibrate>. The types of calibrations given are: Energy, FWHM, and Efficiency, select <Efficiency>. The calibration parameters screen is prompted, at which time the operator must choose the appropriate calibration standard, aliquot size and the appropriate fit formula for the efficiency curve (exponential fit is used in most cases). Select <OK>, at which time the calibration workspace is prompted. Transfer the peak search results by selecting <Merge PSR> , then select <Curve fit>. View the results of the calibration. The % difference for the measured efficiency should be less than +/- 5 for all nuclides, but may be up to 10% with specific written approval

from the instrument lab supervisor . If the measured difference exceeds this criteria5 the calibration will have to be redone. If efficiency limits are met select <OK> , <Save>, and then print the calibration printout. This calibration should be done annually or when extensive maintenance has been conducted on the detector.

5.2.2.2. If the observed efficiencies need to be adjusted to optimize the fit of the calibration curve this may be done with the approval of the lab supervisor. DO NOT ADJUST THE CS-137 EFFICIENCY. If the other efficiencies need to be adjusted, manually calculate the new efficiency, by either increasing or decreasing by a known percentage (usually 5 to 10%). After adjusting a peak re-start the calibration process (choose the print to screen option until the efficiencies have been accurately adjusted). Manual adjustments are conducted in the calibration work space.
NOTE: DO NOT MANUALLY ADJUST EFFICIENCIES WITHOUT FIRST CONFERRING WITH A SENIOR INSTRUMENT TECHNICIAN.
In all cases, manual adjustments of peak efficiencies will be noted on the calibration output page.

5.2.2.3. After the calibration has been stored, analyze an LCS with the appropriate geometry for 1800 sec to verify the calibration. This analysis must pass normal LCS acceptance criteria.

5.3. Weekly Background Calibration

5.3.1 A background calibration is performed weekly. If this is the first weekly calibration of the month check out an internal work order number from the logbook located in the preparation laboratory. If you are running the second set of calibrations since the beginning of the month, add 10, etc. to the sample number. Assume that one set of calibrations has been run since the beginning of the month, and the second calibration is about to be started. The counts would be named, for example, 9813001-11 for detector 1, 9813001-12 for detector 2, and so on.

5.3.2 Make sure there is no sample in the detector shield. Consult the Gamma Spec Maintenance Logbook to see if the detectors have been cleaned within the past month, if not the detectors need to be cleaned as described in Section 5.3.5.

5.3.3 Start the counts for 1000 minutes (60000 seconds) for each detector in service. Geometry and aliquot are irrelevant.

5.3.4 Record detectors that have been started in the logbook. After the count is complete, read the MCA and do a peak search as described above. In the peak search results save the background calibration by selecting 'Save As BkgSub'. Save each background file as DET##MMDD.BKG, where '##' is the detector number and

'MM' and 'DD' is the month and day the background was started. Then select 'Background' under 'QC' on the menu bar. Select 'OK' to analyze the background and see if the count is within control limits. Record any failures in the run log , clean the detector, and restart the background calibrations.

5.3.5 Weekly Calibration Failures

The inside of the detector must be thoroughly cleaned with a paper towel dampened with Radiacwash®, or an equivalent EDTA solution. Then wipe the detector with a paper towel dampened with DI water. Record the cleaning date in the Gamma Spec Maintenance Logbook.

After this has been done, the background calibration can be run again. If the detector fails after cleaning, the lab supervisor must be notified and the detector must be tagged out of service until the problem is resolved.

5.4 QC Samples

One LCS and blank, per geometry, should be analyzed with every 20 samples. A set of shared QC samples can be used for multiple work orders.

6. INTERPRETATION OF DATA

6.1. RESULTS INTERPRETATION

The spectrum analysis capabilities of the analytical software are only as good as the software set up. It is essential that appropriate analysis geometries, efficiency files, and library file be used to ensure accurate analyses. Results data must be reviewed as soon as it becomes available to ensure that the efficiency file used was appropriate to the sample volume and container design, to ensure that all peaks in the spectrum were matched to a radionuclide, and that, where applicable, the presence of a given radionuclide is supported by the presence of other significant gamma emissions from that radionuclide. All unknown peaks greater than 5 times the listed critical level must be qualitatively identified in the case narrative. In some cases, at the supervisor's or client's request, these radionuclide concentrations may need to be quantified..

The spectrum must also be reviewed to ensure that characteristic peaks, such as K-40 at 1460 keV, and the annihilation peak at 511 keV, do not show evidence of a gain shift. A gain shift would show up as a secondary peak slightly offset from all the normal characteristic peaks in the spectrum. A spectrum that shows evidence of a gain shift must be rejected and the sample re-counted. The detector showing the gain shift must have the fine gain on the amplifier adjusted as described above.

7. PERIODIC MAINTENANCE

7.1. LIQUID NITROGEN

Each detector has a Dewar filled with liquid nitrogen to keep the germanium detector cold. Twice per week, the detector Dewar must be filled with liquid nitrogen. Allow 15 minutes after filling before resuming data acquisition.

If a Dewar runs out of liquid nitrogen between fillings, the red bias display, located on

the "BIAS SUPPLY" control board, will be shutdown. If this occurs, tag the detector out of service, and do not operate the detector until the Dewar can be re-filled. The detector may need to be cycled through ambient room temperature before being re-cooled. The lab supervisor must be notified before proceeding.

7.1.1 Filling the Dewar

After the nitrogen lines have been attached to the "LIQUID" output of the new tank, flip the "SOLENOID CONTROL" switches to the "ON" position. This switch is located on the "AUTO FILL EXPANSION CONTROL" board. Then depress the red "Manual" fill button on the "AUTO FILL CONTROLLER". Once the Dewars have been filled, the red LED read-out on the "AUTO FILL CONTROLLER" should read "168.0", which indicates the number of hours until the next fill should be done.

If a tank has not been completely filled, an alarm will sound. To silence the alarm, depress the "ALARM RESET" button on the "AUTO FILL CONTROLLER". Once the alarm is shut off, check the "AUTO FILL EXPANSION CONTROL" board to see which detector LED lights are on (note that the "SOLENOID CONTROL" switch will still be in the "ON" position if a Dewar has not been completely filled).

To re-fill a partially filled Dewar, the nitrogen lines must be allowed to defrost for about 4 hours. After the lines have defrosted, depress the two red "ERROR RESET" buttons on the "AUTO FILL EXPANSION CONTROL" board and then depress the "MANUAL" fill button.

Each detector is equipped with an overflow line. If this line appears to be bleeding an excessive amount of liquid nitrogen, the "SOLENOID CONTROL" switch should be turned to the "OFF" position.

Record all liquid nitrogen fills and re-fills in the "Gamma LN2 Fill" logbook.

8. DEVIATIONS FROM THE METHOD

Where EPA drinking water methodologies are required by the client, the LCS and Matrix Spike recovery acceptance criteria shall be ± 20%, irrespective of the lab's internally derived acceptance criteria.

9. SAFETY, HAZARDS, AND WASTE DISPOSAL

9.1. SAFETY

Normal laboratory safety procedures (gloves, safety glasses, and lab coats, where necessary) must be complied with during the conduct of this procedure. No special safety requirements are mandated by this procedure.

9.2. HAZARDS

9.2.1 Bias applied to detectors is typically in the range of 1000 to 4000 volts DC. This can result in electric shock if bias cables are disconnected while bias is applied.

To minimize the possibility of electric shock, bias will be turned off to any detector before any cabling is disconnected.

9.2.2 The liquid nitrogen used to fill the Dewars is at -196°C. Exposure to the skin can cause severe frostbite. Use insulated gloves when handling frozen lines, valves, etc.

9.2.3 Large spills can displace room oxygen and cause asphyxiation. In case of a large spill, open the lab doors and allow the liquid nitrogen to dissipate before re-entering the lab.

9.3. WASTE DISPOSAL

The gamma spec instrument technician is responsible for returning the samples to the sample custodian or to the sample storage area after analysis, completing the internal chain of custody paperwork.

Some samples will be returned to the client after analysis. Samples or sample wastes containing radioactive materials, which are not being returned to the client, must be disposed of according to PAI's procedures for disposal of radioactive materials. Contact the site WDC for more information.

10. REFERENCES

10.1. Lloyd A. Currie, "Limits for Qualitative Detection and Quantitative Determination," Anal. Chem. 40, 586-93, March 1968.

10.2 ANSI N42.14, American National Standards Institute, Calibration and Usage of Germanium Detectors for Measurement of Gamma Ray Emission of Radionuclides, April 1978, Reaffirmed April 1985.

10.3 EPA-600/4-80-032, Prescribed Procedures for Measurement of Radioactivity in Drinking Water, Method 901.1, Gamma Emitting Radionuclides, August 1980.

APPENDIX A
MINIMUM DETECTABLE ACTIVITY CALCULATION

The equation below is taken from "The Minimum Detectable Activity Concept"[1], and implemented by Paragon's gamma analysis software.

$$MDA = K * (2.71 + 3.29 * S_b),$$

where $K = 1/(VATCE\ e^{(-\lambda t)})$;

A = the fractional abundance of the radiation emission;

V = the sample volume;

T = the counting time for the background count;

C = the conversion from count rate to activity units;

E = the fractional counting efficiency;

$e^{(-\lambda t)}$ = the decay correction from sampling to counting;

S_b = the standard deviation of the background counts.

APPENDIX B
COMMON GAMMA ENERGIES AND CHANNEL LOCATIONS

This section is provided to assist in determining proper channel locations during calibrations and QC checks.

NUCLIDE	ENERGY (keV)	TARGET CHANNEL
Am-241	59	120
Cd-109	88.04	176
Co-57	122.06	244
Cs-137	661.65	1324
Y-88	898.04	1796
Co-60	1173.22	2346
Co-60	1332.49	2664
Y-88	1836.06	3672

NOTE: Paragon uses a 2.0 keV matching tolerance for nuclide/energy matching; this will allow up to a 4 channel deviation from target channels. In addition, the QC checks perform energy versus channel calibrations each time they are run (normally daily), correcting for small changes in peak channel locations.

APPENDIX C
GEOMETRY/EFFICIENCY LIST

Geometry number	Geometry Description	Default count time (min.)	Efficiency file number	Standard file number
01	1 liter H_2O in 2 liter Marinelli	300	01	01
02	3.5 liter H_2O in 4 liter Marinelli	300	02	02
07	47 mm Filter	60	07	07
13	500 g Solid	30	13	13
11	100 g Solid	30	11	11
17	215 g Solid	30	17	17
26	215 g Solid (Ra-226)	30	26	26

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APPENDIX D. SUMMARY OF INTERNAL QUALITY CONTROL (QC) PROCEDURES AND CORRECTIVE ACTION

QC Check	Frequency	Acceptance Criteria	Corrective Action
Efficiency Check	Daily	Within derived control limits.	Recount, re-evaluate, service instrument, if necessary or document why condition is acceptable.
Peak Resolution Check	Daily	Within derived control limits.	Recount, re-evaluate, perform pole-zero adjustment, if necessary, and repeat daily performance checks.
Energy Calibration	Daily	Within derived control limits.	Recount, re-evaluate, perform fine gain adjustment, if necessary, and repeat daily performance checks.
Peak Background Calibration	Weekly	Within derived control limits	Clean detector, recount, re-evaluate, or document why condition is acceptable.
Efficiency Calibration	Yearly, for each counting geometry.	Each fitted value is within 5% of the observed value. Subsequent LCSs pass within normal acceptance criteria.	Tag geometry off-line. Determine and correct problem; verify source activity; recount and/or recalibrate. With supervisors written approval, fitted values may be within 10% of observed value.
Peak Resolution (FWHM) Calibration	Yearly	Each fitted value is within 10% of the observed value. Subsequent LCSs pass within normal acceptance criteria.	Perform pole-zero adjustment, if necessary, and repeat.
Gain shift	Each sample	Review each spectrum to ensure that characteristic peaks @ 511, 1460 KeV are present, not shifted during the count, and properly ID'd by software.	Recount sample after daily performance checks are successfully performed.

Note: This SOP and SOP 715 contain acceptance criteria and corrective action for method blank, laboratory control samples, duplicate samples and matrix spike/matrix spike duplicates.

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 739 REVISION 8

TITLE: **PREPARATION OF SAMPLES FOR ANALYSIS BY GAMMA SPECTROSCOPY**

FORMS: **302**

APPROVED BY:
TECHNICAL MANAGER _____ DATE 1/31/05
QUALITY ASSURANCE MANAGER _____ DATE 1/31/05
LABORATORY MANAGER _____ DATE 1/31/05

HISTORY: Rev0, 9/20/93; Rev1, PCN #104, 1/24/94; Rev2, PCN #412, 3/21/95; Rev4, 10/12/00; Rev5, 3/11/02; Rev6, 4/07/03; Rev7, 8/27/03; Rev8, 10/3/03 and 1/31/05 (no revisions).

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the steps used to prepare soil, water and sludge samples for gamma spectroscopy analysis. Vegetation, air filter and bioassay samples are not addressed in this SOP, and must be handled on a case-by-case basis.

2. SUMMARY

Soils and sludges are prepared (i.e., dried and sieved) per SOP 721, prior to beginning the procedure outlined in this SOP. Some soils and sludges may omit such preparations if approval is given by the Radiochemistry Manager or Project Manager. Waters are either filtered or left unfiltered prior to preparation as per work order or Radiochemistry Manager instructions. Waters are measured volumetrically into an appropriately sized Marinelli beaker. Soils are measured gravimetrically into a Lermer jar or an aluminum can, as appropriate for the sample size and the analyte. The gamma spec containers are sealed with their lids, and wiped with a damp paper towel to remove potential contamination.

3. RESPONSIBILITIES

3.1 It is the responsibility of the technician to perform these procedures according to this SOP and to complete all documentation required for review.

3.2 These procedures are to be performed only by personnel who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.3 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events. Any discrepancies must

be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Gamma spec samples must be produced only in the specific geometry for which the Instrumentation Group has calibrated their spectrometers.

4.2 New containers ordered for gamma spec must be equivalent to those currently in use. The Instrumentation Laboratory Supervisor must approve the use of alternate containers or supplies in advance.

4.3 Gamma spec containers are not reusable due to the possibility of carry-over in the next analysis. Once the analysis is complete, the container is returned to the sample storage area.

4.4 The prep and instrumentation technicians maintain the internal Chain of Custody (COC). When the original client sample container is taken by a prep technician from the sample storage area, he/she logs the sample out as normal. Because gamma spec is a non-destructive test, samples that are designated for other tests may be used. Check with Group Supervisors if there are questions concerning sample availability or if samples are turn-around-time sensitive.

The prep technician is responsible for creating a gamma fraction on the chain of custody. The prep analyst logs out the gamma container on behalf of the counting room analyst and relinquishes the sample along with the benchsheet. After counting, the gamma spec analyst will return the samples to the sample storage area and check them in on the COC. If the aliquot taken for gamma spec is needed for other analyses, log in/log out activities are recorded on the chain of custody.

4.5 The standard filter geometry is a 47mm diameter filter mounted in a 2" stainless steel planchet. For Ra-226 analysis of a solid/soil sample, the packing must be done in a can as a GEO 17. Usually the can packing will be done on an "As Received" basis, and the % moisture data will be provided to report on a dry weight basis. If the sample volume is limited, regular Gamma can be packed as a GEO 11 and the "Ra-can" could be packed with the available sample. If the can is not filled to the top, the technician should mark a line on the outside of the container indicating the height of the actual sample and write a Quality Assurance Summary Sheet (QASS), Form 302. This documentation will help the counting analyst write a narrative about the unusual situation.

4.6 Filter samples can be digested using SOP 773 or SOP 767, then the digestate is diluted to 1000mL with DI water and packed for Gamma as GEO 1. Samples like vegetation, debris, gloves, wipes, iron bar, lead blocks, ashes, fruits, fish, cloth, wood chips etc., will be treated with different methods based on the nature of the

samples and conditions. The samples may be leached using different acids or digested and packed with different GEO. However, all geometry preparations will be documented on a QASS and a copy will be attached to the benchsheet.

5. REAGENTS AND APPARATUS

5.1 Deionized (DI) water, obtained from the laboratory's DI water system

5.2 Balance, top loading, 0.01g sensitivity

5.3 Scoops, spatulas, and tongue depressors

5.4 Graduated cylinders, 1L, type TD (to deliver)

5.5 Marinelli beakers, 2L Ga-ma # 138G, with lids, or equivalent*

5.6 Lerner Jars, 16oz., plastic, with 89mm screw lid *

5.7 Large glass/plastic funnel

5.8 Vinyl tape

5.9 Parafilm

5.10 Qualitative filter, VWR brand 313 fluted filter paper or equivalent

5.11 Cans for Geo 17, House of Cans #3104 or equivalent*

* ***Equivalent containers require approval by the Instrumentation Laboratory Supervisor.***

6. PROCEDURE

6.1 PROCEDURE FOR WATER SAMPLES

6.1.1 Samples must be properly preserved before aliquotting. Verify that the pH is less than 2, per SOP 733. If the sample contains visible sediment or other conditions exist that make preservation impractical, notify the Project Manager (PM) of the lab's intent to proceed with the unpreserved sample and document the situation on a Quality Assurance Summary Sheet.

6.1.2 Do not prepare water samples in the same workspace where soil samples are being prepared. This avoids cross contamination by dust.

6.1.3 If the sample contains sediment or suspended solids, check the work order for specific instructions as to whether or not the sample should be filtered. If it is not specified, filter per SOP 721. If the project instructions specify "Dissolved" or "Filtered", filter the sample through a fluted filter into a clean 1L graduated cylinder. Pre-filtering may be required for especially turbid samples. If the project instructions specify "Total" or "As Received," shake the sample

container to mix thoroughly and aliquot as received.

6.1.4 Liquid samples are prepared in 2L Marinelli beakers. Measure the appropriate volume of water sample in a clean 1L type TD graduated cylinder to the nearest 0.01L (i.e., 10mL). Empty the sample into a clean, labeled Marinelli beaker.

6.1.5 The gravimetric method is adapted for liquid samples other than water. Place an empty Marinelli beaker on the top loading balance and tare the balance to zero. Add the sample slowly into the Marinelli beaker until the final weight is 1000 ± 0.01g.

NOTE: If the sample volume provided falls short of the desired geometry, dilute to the appropriate geometry with DI water (e.g., dilute 600mL to 1L). *Make sure to record the original volume on the container and on the benchsheet.*

6.1.6 A method blank is made by adding a representative volume of DI water to an empty, labeled Marinelli beaker. The aliquot size used for the blank is the average volume of the sample volumes involved in the batch. The collection date for the blank is the date the samples are packed.

6.1.7 A Laboratory Control Sample (LCS) needs to be created on the benchsheet for every batch of twenty samples. The prep technician does not physically prepare the LCS, instead, the gamma spec analyst uses a pre-made LCS obtained from an outside vendor. The information to be filled in on the benchsheet for the LCS varies depending on the GEO size. For waters, indicate the following:

GEO NUMBER	LCS ALIQ.SIZE
1	1.0L

6.1.8 Attach the lid of the Marinelli beaker and seal the lid using vinyl tape. Wipe the exterior of the container with a damp paper towel to remove potential contamination. Make sure the container is labeled with the sample ID, aliquot size, date of prep and initials.

6.1.9 Submit the prepared samples to the counting room. The counting room will analyze the samples in the manner described in SOP 713. Upon completion of gamma counting, the sample fraction will be returned to the sample storage area and the gamma spec analyst will check the sample back in to the storage area and fill out the internal COC.

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6.2 PROCEDURE FOR SOIL AND SLUDGE SAMPLES

6.2.1 Unless approval to the contrary is given, all soil samples must be dried and sieved through a number 4 sieve prior to preparation for gamma spec analysis. Consult SOP 721 for drying and sieving procedures.

Containers for gamma spec soils are usually prepared when the soil is being prepared for other analyses under SOP 721. The gamma spec prep worksheet for soils should be filled out manually by the prep technician at the time of packing gamma, and the electronic benchsheet will be created later on. The prep worksheet will be attached to the benchsheet when the sample is relinquished to the counting room.

The benchsheet provides information about the prep date, technician, balance number, report basis, etc., as well as all the information about how the sample was packed. Any unusual situation will be documented on a QASS (Form 302).

6.2.2 When using Lermer jars, fill the container to the appropriate level according to the desired geometry. If enough sample is provided, use Geometry 13 (500g). If not, reduce the sample volume to Geometry 11 (100g).

6.2.2.1 Sample volumes should be maintained to within ½ cm of the correct geometry height in the container.

6.2.2.2 Zero out the container weight on the balance prior to weighing out a sample.

6.2.2.3 Soil samples should be well settled into their containers by gentle shaking with the lid on. Do not pack or compress soils into the containers.

6.2.2.4 Consult the Radiochemistry Manager or Group Supervisor if the sample volume provided is less than a Geometry 11. The analysis will usually still be conducted, but the Project Manager will need to be informed because of the effects on the efficiency calibration and detection limits.

6.2.3 For Ra-226 analysis by gamma spec, the samples will be packed as a GEO 17. Generally, the samples will be packed on a "Dry" basis, however, due to rush turn around times, the sample can be packed "As Received". To accomplish this, transfer the sample to an aluminum can (appropriate for GEO 17), until it is filled to the top. Tap the can to remove air pockets and to settle the sample. Do not press or "pack" the

sample into the can. Add more sample to fill the can to the top. To ensure a tight seal, place a piece of Parafilm over the top of the can then cap the can with the metal lid and seal with the can sealer. Remove any excess Parafilm from the outside of the can.

6.2.4 A Laboratory Control Sample (LCS) needs to be created on the benchsheet for every batch of twenty samples. The prep technician does not physically prepare the LCS, instead, the gamma spec analyst uses a pre-made LCS obtained from an outside vendor. The information to be filled in on the benchsheet for the LCS varies depending on the GEO size as follows:

GEO NUMBER	LCS ALIQ.SIZE
11	100g
13	500g
17	215g
26	215g
7	1s
8	1s

6.2.5 After the preparation worksheet and the benchsheet are completed, fill out the tracking sheet and attach a copy of the work order(s) to the benchsheet. Submit the packet for a peer review.

6.2.6 Submit the samples prepared as above to the counting room. The counting room will analyze the samples in the manner described in SOP 713. Upon completion of gamma counting, the sample fraction will be returned to the sample storage area and the instrument analyst will check the sample back in to the storage area and fill out the internal COC.

6.2.7 Update the status sheet with a "c" indicating that the prep is complete.

6.3 CALCULATIONS

TPU FACTORS. As defined in SOP 743, the following preparation uncertainty factors should be applied during the final reporting stage of the analysis as a component of the Total Propagated Uncertainty (TPU).

6.3.1 Water samples require a preparation uncertainty factor of 0.0504 at the one-sigma level. This is based on one gross aliquoting (sample homogeneity) and one volumetric measurement. See the following equation:

$$0.0504 = \sqrt{0.05^2 + 0.006^2}$$

6.3.2 Solid samples require a preparation uncertainty factor of 0.0501 at the one-sigma level. This is based on one gross aliquoting (sample homogeneity) and one mass measurement. See the following equation:

$$0.0501 = \sqrt{0.05^2 + 0.003^2}$$

6.3.3 In practice, these two TPU factors are substantially equivalent. To simplify the data reporting procedure, the greater of the two (0.0504) may be used for both matrices.

7. QUALITY ASSURANCE

7.1 Method blanks will be run at a frequency of five-percent (i.e., one per 20 field samples) with a minimum of one per batch. Method blanks for water consist of deionized (DI) water. Method blanks for solid samples consist of an empty container, appropriate for the geometry (i.e., 13, 11, 17).

7.2 Laboratory Control Samples (LCS) will be run at a frequency of five-percent with a minimum of one per batch. The LCS consists of a pre-made source from an outside vendor.

7.3 Duplicate samples will be run at a frequency of ten-percent with a minimum of one per batch. If insufficient volume is available for a duplicate, a count duplicate may be used.

8. SAFETY, HAZARDS AND WASTE DISPOSAL

8.1 SAFETY AND HAZARDS

8.1.1 Read the MSDSs prior to preparing standards or using any solvents or reagents for the first time.

8.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or when handling materials or equipment potentially contaminated with chemicals.

8.1.3 Soil samples should be handled in a hood as much as possible to avoid inhalation and cross contamination with dust. Workspaces should be wiped down with damp paper towels whenever dust is evident and always at the end of the shift.

8.1.4 Any non-original containers that are used to hold reagents (e.g., wash bottles or automatic dispenser bottles), shall be labeled at minimum with: 1) the compound name, 2) NFPA Health, Flammability, and

Reactivity ratings, and 3) date.

8.2 WASTE DISPOSAL

8.2.1 All waste materials (e.g., filter papers, paper towels, etc.) shall be surveyed for radioactivity and disposed of accordingly.

8.2.2 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced prior to disposal.

9. REFERENCES

SOP 743, "Estimating Total Propagated Uncertainties for Radiometric Analyses."

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PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 704 REVISION 7

TITLE: **ANALYSIS OF TRITIUM AND OTHER BETA-EMITTING NUCLIDES BY LIQUID SCINTILLATION COUNTING -- METHOD EPA 906.0**

FORMS: **NONE**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 12/14/04
QUALITY ASSURANCE MANAGER _____ DATE 12/14/04
LABORATORY MANAGER _____ DATE 12-15-04

HISTORY: Rev0, 9/18/92; Rev1, 3/8/93; Rev2, 5/10/93; Rev3, 7/27/93; Rev4, PCN #148, 3/2/94; Rev5, 10/8/99; Reviewed and distributed without revision, 3/14/02; Rev6, 4/7/03; Rev7, 12/13/04.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the steps necessary to perform analysis of samples of various media using Paragon's two Beckman (LS6000 and LS6500) liquid scintillation counters (LSCs). These counters are each capable of sequentially and automatically acquiring data from more than 300 samples. Samples will normally be liquids in a 20mL scintillation vial, which may represent the sample directly (water samples) or indirectly (extracts from soil samples).

This procedure provides the analysis portions of EPA Method 906.0. This procedure is applicable to the determination of tritium, as well as ^{14}C, ^{63}Ni, ^{99}Tc, ^{241}Pu, ^{210}Pb, ^{147}Pm, ^{55}Fe and other beta-emitting nuclides.

Paragon also utilizes one Wallec LSC. Operation of the Wallec instrument is found in Paragon SOP 784.

2. SUMMARY

Beta emissions are detected by a fluor (i.e., a fluorescing molecule) mixed with the sample in a 20mL liquid scintillation vial, which in turn emits light in direct proportion to the beta emission energy and intensity. This light pulse is converted to an electronic pulse and recorded as a beta emission event on the instrument's multi-channel analyzer (MCA). The data collected by the MCA are subsequently interpreted by a software program, generating results in units of radioactivity per unit sample volume.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or

the successful completion of an unknown proficiency test sample.

3.3 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the workorder file indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.4 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. APPARATUS AND MATERIALS

This procedure is conducted with the use of installed beta detection and analysis equipment, consisting of a liquid scintillation counter (LSC), analysis software, and associated nuclear electronics and cabling. In the case of the LS6000, the data may be transferred directly to a floppy disk using a PC with the appropriate interface hardware and software. The LS6500 has these features built-in and can write to a floppy disk with an internal disk drive.

5. REAGENTS

None.

6. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

Chemical preparation steps performed for this analysis are detailed in Paragon SOPs 700, 754, 737, 799, 755, 748, 758, 726 and 772. Samples to be analyzed by this procedure will have been prepared by radiochemical procedures that include distillation of liquids, or azeotropic distillation of soils/solids.

7. PROCEDURE

7.1 OPERATING CONDITIONS

The liquid scintillation counter shall be operated according to the instructions provided by the manufacturer. All instrument settings shall be as determined during instrument installation and/or calibration. The operating conditions shall be verified daily by performance of the daily quality control checks (discussed subsequently in this SOP).

7.2 SAMPLE LOADING

Be sure the samples have been allowed to dark-adapt for a period of at least 3 hours. Normally, the samples will be placed in the rack in the order they are listed on the benchsheet. Place the rack(s) in the counter with the front (side with rack number and/or user number) facing away from the operator. The first rack to be counted must have a user number (see below for a description of user number) installed in the left (looking at the front of the rack) card slot. Subsequent racks will not have a user number card unless a different analysis is required for that rack. Ensure that the counting position of each sample is correctly recorded on

the liquid scintillation benchsheet and that the user number has the correct settings.

7.3 USER NUMBERS

User numbers provide the count and data output parameters. User number programs can be set by pressing the "Main Menu" button, then using the cursor arrows to highlight "Review and Edit User Programs". Using the cursor arrows, highlight the user number to be edited, then highlight the parameter to be set, and follow any prompts given at the bottom of the screen. For more details on setting the user number parameters, see the instrument's operating manual.

Default settings for all of the user numbers are:

- Count Blank: NO
- Two Phase: NO
- Scintillator: LIQUID
- Low Level: YES
- H#: YES
- IC#: NO
- LUMEX: YES (This option is available only on the LS6000. The LS6500 doesn't correct for luminescence.)
- Half Life Correction Date: NONE
- Sample Repeats: 1
- Cycle Repeats: 1
- Cycle Repeats: 1
- Low Sample Reject: 0
- Printer: STD
- RS232: STD

Other parameters may vary for each user number. These are:

- Manual Window Settings: In order to determine the manual window settings, a source and blank are counted on the instrument. The user number is set with Window 1 at WIDE, and the raw data output is set for Spectral Data, to give a channel by channel output. Once the data are collected, a figure of merit (FOM) is calculated to optimize the windows in order to minimize the MDC (minimum detectable concentration). Windows are set for each analysis type (i.e., ^{3}H, ^{14}C, etc.), and for each geometry type (i.e., 10mL or 5mL).
- Count Time: This depends on the required MDC and sample volume.

- Counting Precision: The instrument can be set to stop counting once a required numbers of counts have been accumulated.

7.4 DATA COLLECTION

7.4.1 **The following procedure is for the LS6000 only.** To use this option, the user number used to count the samples must have the STD RS232 Format selected.

- From the Main Menu of the support computer for the LS6000, choose "Tritium Data Capture" and press <Enter>. When the Data Capture software starts, choose "1. LS6000" <Enter>, then "1. RECEIVE data from instrument" <Enter>.

  The program will provide a table with the header "Drive and Subdirectory"; press <Enter>. Send the data to the b:\ drive (be sure that a disk is inserted into the b drive). The upper left corner of the display will read "Awaiting Response".

- Press the "Main Menu" key on the front panel of the counter. Use the cursor arrows to highlight "Automatic Counting", then press "Start" to begin counting.

  The counter will analyze each sample and generate results in CPM for each vial counted. The Data Capture software will have a message in the upper left corner which reads: "Status: Receiving Record XXXX", where XXXX is the number of the data record which will increase as samples are analyzed. The Data Capture software will now also display the filename in which the data is stored in the center of the screen. This file is named "\TRITIUM\UNXX-YYY.BSF", where XX is the user number, YYY is the next sequential number for files created with that user number, and .BSF is the default extension for Beckman Standard Format files. *Note this file name in the filename section of the benchsheet.*

- When the count is complete (i.e., LS6000 Main Menu has returned to the display), complete the liquid scintillation run log.

  To process the data, press <Esc> on the LS6000 support computer. The Status message in the upper left corner of the display, will read "Capture Completed". Press <Esc> twice to return to the Data Capture software main menu. Remove the disk from the b:\ drive and take the disk to the tritium reporting PC.

  Copy the correct file to the c:\ drive of the reporting PC. Open the "dc" program on the c:\ drive by typing "dc" then <Enter>. Use the cursor arrows to move the highlight bar to "DATA CAPTURE SUPPORT", press <Enter> to choose

this option, then choose "3. Convert BSF to dBASE File", then press <Enter>. Press 1 (Convert); the software will then prompt for "Input Filename (.BSF)" and "Output Filename (.DBF)". Type the name of the file recorded on the benchsheet, without an extension (for example, "UN01-001"), and press <Enter> for each prompt. The software will then present a default format titled "Tritium"; press <Enter> to accept this format.

A message at the bottom of the screen will read "Use actual dBase file structure (Y/N) [Y]"; press <Enter> to accept the default "Y". Then data will then be converted and displayed on the screen, with the message "Conversion Completed !".

Press <Esc> 4 times to return to the PC's Main Menu. Copy the new file to the r:\tritium directory. The data may now be accessed from any PC that is a part of the Paragon network.

7.4.2 **The following procedure is for the LS6500 only.**

- To start the sample count, press the "Main Menu" key on the front panel of the counter. Use the cursor arrows to highlight "Automatic Counting", then press "Start" to begin counting. The counter will analyze each sample and generate results in CPM for each vial counted.

- When the count is complete (LS6500 Main Menu has returned to the display), complete the liquid scintillation run log.

- To create a disk to transfer run information from the LSC to the tritium reporting PC, select "Data Management" from the main menu on the LS6500. Next select "Access Data Buffer/Disk", then select "Move Files to Disk". Enter the user number for the files that you want to move.

7.5 SAMPLE ANALYSIS (FROM EITHER THE LS6000 OR LS6500)

- Move the desired .ASC file into "I:\Operations\LSC\LIMS Data." When the file is moved, add the letter "Y" in front of the file name to denote that the file is from instrument LS6500 or add the letter "X" in front of the file name to denote that the file is from instrument LS6000. The file can be opened in Excel and reviewed to ensure that the correct file has been chosen. *CAUTION - when exiting Excel, be sure that the file is not saved in the incorrect format.*

- The tritium data is analyzed using the LIMS (Laboratory Information Management System). Open the LIMS program and create an analytical run by selecting "Laboratory" and "Analytical Run Entry"

from the main menu. Analytical runs are typically named by adding a letter to the prep batch ID. For example, the analytical run created from prep batch 3H051204-2 would be 3H051204-2a.

For the analytical run, the instrument ID is 'LIQSCINT', the analytical department is 'LS,' and the analysis method is 'PAI 704'. *Note there are several PAI 704s listed (i.e., PAI 704_Tc99).*

- Enter the "RackNum" and "PosNum." These are the rack and position numbers. Go to the "Radiochemistry Data Import Menu" page. Enter the file name (i.e., YU0573102) and the analysis method, and click 'Import Data Files'.

  After the data is imported, select 'Review Import Results'. This is the location where the background values are entered (in the BkgCPM column) and efficiency values (in the EffBase column).

- The efficiency will be entered as a decimal (i.e., enter 0.347 for an efficiency of 34.7%). Next select "Move Data Files to Holding Area", followed by "Merge Analytical Run".

- Return to the "Analytical Run Information" page. Select "Validate Run". After the run is validated, return to the "Radiochemistry Data Import Menu".

- Select "Process Preliminary Results", followed by "Merge Analytical Data". Return to the main menu and select "Reporting" and "Results – Reporting". Enter the Analytical Run ID, the Prep Batch ID, the QC Batch ID, and the QC Order Number.

  Select "Manage Data Packages" and "Create/Add" to create the data package. You may print out a Raw Data Results Summary page by selecting "Radchem/Summary Review" and "Generate Reports". This print out should be checked for accuracy. *If the data was manually entered, every data point needs to be checked.*

7.6 CALIBRATION PROCEDURES

7.6.1 Efficiency Calibration Standards for calibration shall be traceable to the National Institute for Standards and Technology (NIST). Standards for tritium counting will normally be prepared from commercially available NIST-traceable stock solutions. The analysis system shall be calibrated at least annually.

- Three blanks of the same geometry are prepared with DI water and cocktail, and are used for background correction.

- A one-point efficiency is highly accurate and will be used for the calculation of all results showing the Quench Indicating

Parameter result corresponding to the average observed for the calibration standard (within ±10 % relative efficiency or lacking this calibrated range, ±15 of mean H-numbers). Any sample falling outside this range will be calibrated by sample specific addition of a minimum known volume (<200 µL) of NIST-traceable standard. The efficiency from sample specific standard additions is calculated as defined below:

$$\text{Deteff} = \frac{(\text{SSGrCPM} - \text{SmplGrCPM})}{\text{SpkDpm}}$$

In some instances, it may be necessary to prepare a quench curve to establish a relationship between the counting efficiency and the Quench Indicating Parameter (H#). In general, the standards will be prepared by spiking each with a known concentration of the standard and the same volume of cocktail. A quenching agent, such as nitromethane, will be added in increasing increments. The sample specific efficiency will be determined as a function of the H#.

7.5.1 Background calibration (reagent blank) An aliquot of DI water equivalent to the calibration geometry is transferred to a scintillation vial independent of the preparation process and cocktail added such that the calibration geometry is recreated. One reagent blank is submitted for each preparation batch and counted for a time period equal to or greater than the longest sample count. For samples counted in the default calibration geometry (i.e., 10mL water + 10mL cocktail), CPM results (as well as blank ID and count time) of the reagent blank count are entered into a spreadsheet (see below for location of spreadsheets), which tracks the running mean of the last seven reagent blanks, and compares each blank to historical control limits established from the first 30 data points in the population (±3 sigma).

The current running mean of the reagent blank CPM is used as the background in the calculation of associated results for the associated preparation batch. For other beta-emitting analyses which are performed infrequently or for which the "running mean background" mentioned above would not be appropriate, a Reagent Blank should be counted with each batch. The result of the Reagent Blank count will be used as the instrument background for reporting purposes.

Reagent blank spreadsheets are located at R:\inst\lsc\ls6500 or ls6000\prg\: rb_c14.xls, rb_fe55.xls, rb_h3.xls, rb_ni63.xls, rb_tc99.xls, rb_tota.xls, rb_h3_5.xls, and rb_p241.xls.

8. QC MONITORING

8.1 GENERAL

Where EPA drinking water methodologies are required by the client, the LCS and Matrix Spike recovery acceptance criteria shall be ±20%, irrespective of the laboratory's internally derived acceptance criteria.

8.2 DAILY QA CHECKS

Standards for Daily QA Checks consist of unquenched ^{3}H and ^{14}C standards (NIST-traceable), a flame-sealed, vendor-supplied background, and an in-house prepared blank sample.

8.2.1 Place the unquenched ^{3}H calibration standard in position 1, the unquenched ^{14}C calibration standard in position 2, the blank in position 3, and the vendor-supplied background in position 4 of the sample rack labeled "User No. 1", and place the rack in the right front position in the counter. Place the "HALT" (red) rack immediately after the "User No. 1" rack.

8.2.2 Start the Daily checks by pressing "Main Menu", selecting "Automatic Counting" from the menu with the cursor arrows, then pressing "Start" to begin the counting sequence. The QA Check process will initiate a 10 minute count of the ^{3}H standard, the ^{14}C calibration standard, the blank, and the vendor-supplied background. At least 100,000 counts should be acquired for the ^{3}H and ^{14}C check sources.

8.2.3 When the count is complete, enter the count results for the standards and blank in the LSQA spreadsheet (located at R:\inst\ls6000\prg\ lsqa6000.xls or R:\inst\ls6500\prg\lsqa6500.xls) using a network computer. Count results from Window 1 are used for the ^{3}H standard, count results from Window 2 are used for the ^{14}C standard, and count results from Window 1 are used for the blank and vendor-supplied background.

The spreadsheet compares each count result to historical control limits established from the first 30 data points in the population. Control limits are set at ± 3 standard deviations (above and below) the means for the standards and blank. If any of the current data points fall outside the default control limits of ±10% of the mean, re-analyze the QC samples. If the current data points are still outside of control limits, do not operate the instrument until notifying the Supervisor and resolving the problem. *Note that Paragon does not control on the results of the flame sealed vendor-supplied background sample.*

9. CALCULATIONS AND INTERPRETATION OF DATA

9.1 DATA CALCULATIONS

The liquid scintillation instrument calculates sample counts per minute (CPM) for each sample. This "raw" data is provided to an analysis computer, either by

manual entry or by transfer via RS-232 serial protocol. Both data transfer methods provide the user with several full-screen, editable sample information pages to be used for verification of sample and counting data. The "raw" data provided to the analysis and reporting program is modified in several ways to generate final results, as described below.

9.1.1 Sample Result or Activity (A), reported as activity/unit mass or volume.

$$A = \frac{SampleCPM - BlankCPM}{VCEe^{-\lambda t}}$$

where:

V = the sample volume; normally 0.01L

C = the conversion from count rate to activity units; normally 2.22 DPM/pCi. If sample result is desired in Bq, this factor is 1/60 (1 Bq is 1 disintegration per second (DPS))

E = the fractional counting efficiency

$e^{(-\lambda t)}$ = the decay correction from sampling to counting

9.1.2 The counting uncertainty (CU) is reported in units of activity per mass or volume. It is determined for the 1σ level of uncertainty.

$$CU = K\sqrt{SampleCPM \cdot T + BlankCPM \cdot T}$$

where:

T = the time elapsed during sample counting

K = $1/(VTCE\ e^{(-\lambda t)})$

Total Propagated Uncertainty (TPU)at the one sigma level

$$TPU = \sqrt{CU^2 + (IU * A)^2 + (PU * A)^2}$$

where:

A = the sample activity or result

IU = 0.056

PU = the uncertainty propagated by sample preparation (see Test specific Paragon SOPs)

9.1.3 Sample specific Minimum Detectable Concentration (MDC)

$$MDC = K \cdot (2.71 + 4.65 \cdot S_b)$$

where:

K = 1/(VTCE e(-λt))

V = the sample volume

T = the counting time for the background count

C = the conversion from count rate to activity units

E = the fractional counting efficiency

e(-λt) = the decay correction from sampling to counting

Sb = (T*BKG Count Rate)$^{1/2}$

This MDC equation is fundamentally the same as those offered in references (12.3) to (12.4), which represent industry standard methodology for analyses of these types.

9.1.4 Decision Level (DL)

$$DL = 2.33 \cdot S_b \cdot K$$

where:

K = 1/(VTCE e(-λt))

V = the sample volume

T = the counting time for the background count

C = the conversion from count rate to activity units

E = the fractional counting efficiency

e(-λt) = the decay correction from sampling to counting

Sb = (T*BKG Count Rate)$^{1/2}$

9.1.5 The analysis results, along with all of the related sample information, is written to a comprehensive database of analyzed tritium samples. When all of the sample data has been entered into the program and the operator discontinues data entry, the database is searched for all new data entries from the current session. New data is sorted by client for reporting. The reporting software then generates individual reports by client as requested by the operator.

9.2 INTERPRETATION OF DATA

9.2.1 Analysis results should be spot-checked on a monthly basis, with one sample being checked manually for accurate calculation of the result or MDC by the reporting software. This may be aided by the use of a spreadsheet with the appropriate equations, provided the spreadsheet has been validated by the QC Officer. (See SOP 315). The results of the manual calculation should be filed by the analyst for subsequent auditing purposes.

9.2.2 Analysis results should be checked for consistency between results of duplicates, blanks, and spiked samples, and the MDC results should be checked to confirm that the client's required MDC is met. All results must be reviewed according to PAI SOP 715, Review of Radioanalysis Data.

10. DEVIATIONS FROM METHOD

This procedure contains no known deviations from EPA 906.0.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 Normal laboratory safety procedures must be complied with during the conduct of this procedure. No special safety requirements are mandated by this procedure.

11.1.2 High voltage in the range of 1000 volts DC is applied to the photomultiplier tubes in these instruments. This can result in electric shock if the instrument is disassembled with power applied. To minimize the possibility of electric shock, turn off the power and unplug the instrument prior to any disassembly.

11.2 WASTE DISPOSAL

Liquid scintillators contain a solvent and an emulsifying agent to promote mixing with aqueous samples. The solvents used by Paragon are biodegradable, but may not be suitable for sewer disposal. Additionally, the samples may contain concentrations of radioactivity above sewer disposal limits. Contact the Waste Disposal Coordinator and/or Radiological Safety Officer (RSO) for disposal instructions.

12. REFERENCES

12.1 Beckman LS6000 Series Liquid Scintillation System Operators Manual, June 1991.

12.2 Beckman LS6500 Series Liquid Scintillation System Operators Manual.

12.3 Lloyd A. Currie, "Limits for Qualitative Detection and Quantitative Determination", Analytical Chemistry, Volume 40, pages 586-593, March 1968.

12.4 National Council on Radiation Protection and Measurements (NCRP), Report No. 58, page 309, September 1984.

12.5 EPA 520/1-80-012, "Upgrading Environmental Radiation Data", Health Physics Society Committee Report HPSR-1, pages 6-26, August 1980.

TABLE 1

SUMMARY OF INTERNAL QUALITY CONTROL (QC) PROCEDURES AND CORRECTIVE ACTION

QC Check	Frequency	Acceptance Criteria	Corrective Action
Efficiency, Background and Quench Factor Checks	Daily	Within derived control limits.	Recount, re-evaluate, service instrument, if necessary or document why condition is acceptable.
Efficiency Calibration	Yearly	For single point efficiency calibrations, the value must be within ±5% of the previous calibration value. For quench curves, the fitted values shall be within ±5% of the observed value for each point on the curve. Post-calibration method spikes (LSCs) shall meet normal LCS acceptance criteria.	Tag method off-line. Determine and correct problem; verify source activity, recount and/or recalibrate or document why condition is acceptable.
Background Calibration	Continuous	Control limits set from initial calibration run.	Tag method off-line. Determine and correct problem, re-establish limits; or document why condition is acceptable.
Chemical Yield	Each sample, where method allows	Each sample meets current control limits for analysis.	Re-prep; or qualify or narrate why condition is acceptable.
Spectral Interferences	Evaluate each result for spectral interferences	WIND2 count rate within current control limits or interfering activity does not compromise quantitation	Re-prep/recount affected samples; consult with Supervisor or Department Manager; determine and correct problem; or qualify or narrate why condition is acceptable.

NOTE: This SOP and SOP 715 contain acceptance criteria and corrective actions for method blank, laboratory control samples (LCSs), duplicate samples and matrix spike/matrix spike duplicates (MS/MSDs).

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 726 REVISION 4

TITLE: **DETERMINATION OF LEAD-210 IN SOILS, SEDIMENTS, AND WATERS**

FORMS: **302**

APPROVALS:
TECHNICAL MANAGER _____ DATE 12/15/04
QUALITY ASSURANCE MANAGER _____ DATE 12/15/04
LABORATORY MANAGER _____ DATE 12-15-04

HISTORY: Rev0, 11/16/93; Rev1, 5/3/96; Rev2, 4/26/02; Rev3, 4/4/03; Rev4, 12/15/04.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the steps necessary for preparation of environmental soils, sediments, and waters for quantitative measurement of ^{210}Pb.

2. SUMMARY

2.1 Pb in soils and sediments is solubilized using nitric, hydrofluoric and hydrochloric acids.

2.2 Pb is pre-concentrated by passing the sample through a cation exchange column. A chromatographic resin with a high affinity for Pb is used to isolate ^{210}Pb from potentially interfering radionuclides. In nitric acid, Pb is retained on the resin while other unwanted sample constituents are not. Pb is stripped from the resin with hydrochloric acid. The purified solution containing Pb is mixed with liquid scintillation cocktail and counted in a liquid scintillation counter (LSC instrument). Stable Pb, added into the samples at the beginning of the procedure to monitor the chemical recovery, is measured in the sample by ICP AES before and after chemical separation.

2.3 Air filters may be analyzed by using the soil procedure.

2.4 This procedure may also be used for suspended solids deposited on filters. The dried filter may enter the procedure directly at the grinding stage of sample preparation. The sample aliquot weight, in this case, will have to be adjusted to account for the weight of the filter. The adjusted weight should be calculated on a Quality Assurance Summary Sheet (QASS, Form 302) and recorded on the benchsheet as the sample weight. The remainder of the preparation procedure is identical to that for a soil sample.

2.5 The resin also retains Sr, and with some slight modifications, this method can be utilized for a sequential preparation of both Pb and Sr. Pb and Sr are both loaded onto the column in nitric acid. Sr is stripped from the column in dilute nitric acid while Pb is retained. Once the Sr has been removed, Pb is stripped from the column with HCl. Refer to SOP 707 for the preparation of Sr samples.

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2.6 Actinides are not retained on the resin, and will pass through when Pb and Sr are loaded onto the column. Therefore, the column effluent from the load solution and subsequent rinses can be collected and saved for use in actinide separation and purification methods.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.3 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the workorder file information indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.4 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

This SOP is applicable to water and soil samples that do not contain significant concentrations of organically complexed Pb. Organically complexed Pb may not be retained by the cation exchange column. Consequently, samples that are suspected to contain organically complexed Pb should be muffled at 450°C for at least one hour.

5. APPARATUS AND MATERIALS

5.1 Disposable ion exchange columns: 15mL resin volume with attachable funnel to receive 2L bottle (Environmental Express part nos. R1010 and R1030).

5.2 Cation exchange column: Precondition a disposable plastic column with 2-3mL of methanol (the frit at the orifice of the column is hydrophobic). Transfer AG50x8 (or AG50x4) resin to the stem of the column as a slurry with DI water to the 7cm mark. Attach the funnel to the column (make certain that the column and funnel fit tightly).

5.3 Sr Resin™ column: Use a Bio-Rad column (catalog #731-1553) or equivalent and transfer the Sr Resin to the column as a slurry with water. Add resin up to approximately the 1.6mL mark on the column. The Sr Resin is held in place by a layer of clean silica sand on top of the resin bed.

5.4 Eppendorf pipets, or equivalent

5.5 Pipet tips

5.6 Graduated cylinder, 1L

5.7 Disposable plastic bottles, 2L

5.8 Polypropylene beakers with lids, 250mL (8 oz)

5.9 Polypropylene beakers with lids, 100mL

5.10 Balance with 0.01g resolution

5.11 Test tubes, disposable, 15mL

5.12 Plastic graduated cylinder, 25mL

5.13 Disposable glass cups

5.14 Liquid scintillation vials

5.15 Transfer pipets, 7mL polyethylene disposable (VWR Cat. No. 14670-103 or equivalent)

5.16 Parafilm

5.17 Hot Block (Environmental Express or equivalent)

5.18 Steam bath

5.19 Vortex mixer

6. REAGENTS

NOTE: TLV and other hazard information may be given here. Any chemical with a Threshold Limit Value (TLV) below 50ppm must be worked with in a laboratory fume hood. The absence of this information does not imply that the substance is not hazardous. The employee should be familiar with all pertinent MSDSs before proceeding.

6.1 NIST-traceable ^{210}Pb spiking solution.

6.2 Pb carrier, 1.0 mg Pb/mL: Dissolve 1.60g Pb $(NO_3)_2$ in 1000mL of DI water. TLV = 0.05mg/m^3 = 0.006 ppm (TWA).
The Pb carrier reagent must be analyzed by ICP to accurately determine the Pb concentration. This is accomplished by diluting the Pb carrier reagent 1000-fold with ICP diluting solution. Prepare in triplicate and submit to the Metals Lab for

analysis. The preparation and standardization of this reagent must be documented in the Reagent Preparation Logbook.

6.3 Nitric acid 16N, concentrated, reagent grade. TLV = 2ppm (TWA). Irritant, corrosive.

6.4 Hydrofluoric acid, 48% reagent grade. TLV = 3 ppm.

6.5 Hydrochloric acid 12N, reagent grade. TLV = 5 ppm (ceiling). Irritant, corrosive.

6.6 Nitric acid, 8N : Cautiously add 500mL of conc. HNO_3 to approximately 400mL of DI water and dilute to 1 L. See 6.3 for TLV.

6.7 Nitric acid, 0.1N: Add 6.3mL conc. HNO_3 to approximately 900mL DI water and dilute to 1L. See 6.3 for TLV.

6.8 Nitric acid, 0.05N: Add 3.1mL conc. HNO_3 to approximately 900mL DI water and dilute to 1 L. See 6.3 for TLV.

6.9 Nitric acid, 1N: Add 63mL conc. HNO_3 to approximately 900mL DI water and dilute to 1L. See 6.3 for TLV.

6.10 Hydrochloric acid, 6N: Add 500mL of conc. HCL to 400mL of DI water and dilute to 1 L. See 6.5 for TLV.

6.11 Hydrochloric acid, 4N: Cautiously add 330mL conc. HCl to 500mL DI water and dilute to 1L. See 6.5 for TLV.

6.12 Hydrogen Peroxide, ACS grade, 30%. TLV = 1 ppm (TWA).

6.13 ICP diluting solution: Carefully add 10mL of conc. nitric acid and 50mL of hydrochloric acid to 940mL of DI water. See 6.3 and 6.5 for TLVs.

6.14 Cation exchange resin, AG50x8 or AG50x4.

6.15 Sr Resin™ chromatographic resin (particle size 50 - 100 µm). Purchased from Eichrom Industries, Inc. (Darien, IL).

6.16 Radiacwash®.

6.17 Methanol, reagent grade. TLV = 200 ppm (TWA).

6.18 Ultima Gold LLT™ liquid scintillation cocktail.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 It is recommended that samples be preserved at the time of collection by adding enough 1N HNO_3 per liter of sample to bring the pH to 2 (15mL of 1N HNO_3 per liter of sample is usually sufficient). If samples are to be collected without

preservation, they should be brought to the laboratory within 5 days, then preserved (A), and held in the original container for a minimum of 16 hours before analysis or transfer of the sample.

7.2 The container choice should be plastic (rather than glass) to prevent loss due to breakage during transportation and handling.

8. PROCEDURE

8.1 SOIL PREPARATION- Soils/sediments must be prepared through the grinding stages of SOP 721.

NOTE: The acid dissolution procedure for ^{210}Pb in soil is identical to SOP 773 - Dissolution of Solids for Determination of Actinides, *except for the following*:

- Soils that require muffling will be muffled at a maximum temperature of 450°C.
- Conc. HCl is added to the sample when re-dissolving the salts at the end instead of conc. HNO_3.
- Boric acid is not added to the sample when redissolving the salts at the end.

8.1.1 Weigh 2.0g of soil (dry and finely ground) into a 250mL polypropylene beaker. Record weight (W_s) on the benchsheet.

8.1.2 Prepare a blank and blank spike per Section 9.1. If other tests are being prepared sequentially with Pb, the appropriate tracers, spikes and/or carriers should be added at this time.

8.1.3 Add 1.0mL of 1.0mg/mL Pb carrier solution.

NOTE: A replicate 1.0mL aliquot (or similar known volume from a calibrated pipettor) of Pb carrier is diluted by adding 5mL of concentrated HCl and diluting to 1L with DI water. After mixing thoroughly, a 10mL aliquot of this dilution is transferred to a test tube labeled "reference carrier" and submitted with the initial and final tubes for ICP analysis.

8.1.4 Add 25mL conc. HNO_3 to each beaker using a volumetric dispenser.

8.1.5 Using a **plastic** graduated cylinder, add 25mL conc. HF to each beaker (do not allow HF to come into contact with any type of laboratory ware made of glass since HF will dissolve glass).

8.1.6 Add 25mL of conc. HCl to each beaker. Place a 100mL polypropylene beaker as a cover onto the 250mL beaker containing the sample.

8.1.7 Allow the samples to pre-digest at least 1 hour at room temperature to allow any vigorous reaction to subside.

8.1.8 Place the beakers on the steam bath and heat for at least 4 hours.

8.1.9 Uncover the beakers and take to dryness on the steam bath.

8.1.10 For samples with low organic content, skip Section 8.1.13. For samples with significant organic content proceed to Section 8.1.11.

8.1.11 Remove from the steam bath and add 10mL conc. HNO_3. An additional 5mL 30% H_2O_2 can be added to assist with dissolution of difficult matrices. Since the addition of H_2O_2 can result in a vigorous reaction, the samples should be allowed to stand at room temperature for a few minutes. After the reaction has subsided, return the beaker to the steam bath and take to dryness.

8.1.12 Remove from the steam bath and add 10mL conc. HCL and about 140mL DI water to solubilize the solids. Mix well. Return beakers to the steam bath for about 15min. to warm solution and enhance dissolution of salts.

8.1.13 Transfer the sample through a qualitative fluted filter paper into a 1L graduated cylinder. Rinse the beaker two or three times with DI water and transfer the rinsate to the filter.

8.1.14 Dilute to a final volume (V_s) of 1L with DI water and transfer to a clean, labeled 2L plastic bottle.

8.1.15 Mix each sample thoroughly by capping and shaking. Pipet a 10mL aliquot from each sample into a disposable test tube. Cover with Parafilm and label with the sample ID and "initial Pb" (C_i).

8.1.16 Prepare a cation exchange column per Section 5.2. Attach a funnel to the column, making sure they fit tightly to avoid leaking. Condition the column with ~30 mL of 1N HNO_3.

8.1.17 Pass the sample through the column at a rate of about 1-2 mL/min. This is accomplished by inverting the 2L bottle into the funnel that is attached to the top of the cation exchange column. The sample will feed automatically through the column.

8.1.18 After the sample has completely passed through the resin, rinse the column with 10mL of 0.1N HNO_3.

8.1.19 Discard the feed and rinse solutions into the Paragon wastewater treatment facility.

8.1.20 Elute Pb and other cations with 50mL of 8N HNO_3. Collect the solution in a labeled 250mL beaker.

8.1.21 Place on a steam bath and evaporate to dryness.

8.1.22 Extrude the resin from the column and collect in a wide mouth jar labeled "hazardous waste-used acidic resin" in the satellite accumulation area. When the satellite container is full, notify the site Waste Management Officer for further instructions. Soak the empty columns in RadiacWash®, rinse with tap water, and discard into the sanitary trash.

8.1.23 Once dry, dissolve the salts in 5mL of 8N HNO_3 solution. Add the acid to the specimen cup while the sample is still on the steam bath to facilitate complete dissolution of the salt residue.

8.1.24 Proceed to Section 8.3 of this SOP.

8.2 WATER PREPARATION

8.2.1 Using a graduated cylinder, measure the sample to the nearest graduation and transfer into a 2L disposable plastic bottle (usual sample volume = 1L). If the sample is not 1L, dilute with deionized water to 1L. Record the volume on the bench sheet (V_i).

8.2.2 Prepare a blank and blank spike per Section 9.2. If sample is to be run sequentially for other tests, the appropriate tracers, spikes and/or carriers should be added at this time.

8.2.3 Add 1.00mL of 1.0mg Pb/mL carrier (1.0mg Pb) (S).

NOTE: A replicate 1.0mL aliquot (or similar known volume from a calibrated pipettor) of Pb carrier is diluted by adding 5mL of concentrated HCl and diluting to 1L with DI water. After mixing thoroughly, a 10mL aliquot of this dilution is transferred to a test tube labeled "reference carrier" and submitted with the initial and final tubes for ICP analysis.

8.2.4 Mix sample thoroughly by inverting bottle several times and remove a 10mL aliquot (R_i) for ICP determination of Pb. Place aliquot in 15mL test tube, seal with Parafilm and label with sample I.D. and "initial-Pb" (C_i).

8.2.5 Prepare a cation exchange column per Section 5.2. Attach a funnel to the column, making sure they fit tightly to avoid leaking. Condition the

column with ~30 mL of 1N HNO_3. Pass the sample through the column at a rate of about 1-2 mL/min. This is accomplished by inverting the 2L bottle into the funnel that is attached to the top of the cation exchange column. The sample will feed automatically through the column.

8.2.6 After the sample has completely passed through the resin, rinse the column with 10mL of 0.1N HNO_3.

8.2.7 Discard the feed and rinse solutions into the Paragon wastewater treatment facility.

8.2.8 Elute Pb and other cations with 50mL of 8N HNO_3. Collect the solution in a labeled 250mL polypropylene beaker. Place on a steam bath and evaporate to dryness.

8.2.9 See section 8.1.22 above for column and resin disposal.

8.2.10 Dissolve the salts in 5mL of 8N HNO_3 solution. Add the acid to the specimen cup while the sample is still on the steam bath to facilitate complete dissolution of the salt residue.

8.2.11 Proceed to Section 8.3 of this SOP.

8.3 Pb PURIFICATION WITH Sr Resin™

8.3.1 Precondition a Sr Resin™ column (see Section 5.3 for preparation of Sr Resin™ columns) with 5mL of 8N HNO_3, collecting the rinsate in a disposable waste cup.

8.3.2 Transfer the sample solution to the column using a disposable transfer pipet.

8.3.3 Using the disposable transfer pipet, rinse the beaker with 2mL of 8N HNO_3 and add the rinsate to the column. Allow the entire sample solution to pass through the column.

8.3.4 Collect the solution that drains from the column in a disposable waste cup. Repeat this rinse as described in the previous Step two more times for a total of three rinses, allowing each rinse to pass completely through the column before adding the next.

8.3.5 The contents of the waste cup can be discarded into the Paragon wastewater treatment facility via the laboratory sink followed by plenty of cold tap water. The disposable cups may be rinsed with RadiacWash® solution and tap water and re-used for collecting waste column effluent. If the cups are not needed they may be soaked in

RadiacWash®, rinsed with tap water, and discarded into the sanitary trash.

8.3.6 Rinse the column with two 5mL aliquots of 0.05N HNO_3. Collect the solution that drains from the column in the disposable waste cup. Record the date and time to the nearest 10 minutes of the end of the last rinse on the benchsheet. This is the starting time of the ^{210}Bi ingrowth.

8.3.7 The contents of the waste cup from Step 8.3.6 should be discarded into the Pb process waste container provided by the Waste Management Officer.

8.3.8 Elute Pb from the column with 30mL of 6N HCL (V_{Pb}). Collect the eluate in a labeled disposable glass cup.

8.3.9 Add 5mL of 16N nitric acid to the eluate. This will aid in breaking down organic constituents in the column effluent.

8.3.10 Take the samples to dryness by placing the glass cups on a Hot Block set at 100°C.

8.3.11 Once dry, dissolve the residue by adding 1.0mL of 4N HCl. Cap the glass cups and vortex to mix completely. Allow to stand and vortex intermittently several times to be sure all of the Pb is in solution. Add 5.0mL of DI water. Cap and vortex again.

8.3.12 Pipet 0.1mL from the thoroughly-mixed sample and transfer to a test tube labeled with the sample ID and "final-Pb" (C_f). Dilute to 10.0mL by adding 9.9mL of ICP diluting solution. Cap the test tube and invert several times to mix thoroughly.

8.3.13 Submit the "initial" and "final" aliquots to the metals department for ICP determination of Pb for calculation of the chemical yield.

8.3.14 Upon the return of the ICP sample fractions to the lab, and after satisfactory review of the chemical yield data, the ICP fractions may be discharged into the Paragon waste water treatment facility (down the drain in the lab sinks with plenty of cold tap water). The test tubes may be rinsed with RadiacWash® solution, followed with tap water, and discarded into the broken glass receptacle.

8.3.15 From the remaining sample in the glass cups, pipet 5.0mL into a plastic liquid scintillation vial. Add 15mL of Ultima Gold LLT™ cocktail to each vial. Cap and shake well to mix. Since the liquid scintillation vial is an optical surface, all labeling should be done on the cap, not on the vial itself. Wipe each vial down using a kimwipe moistened with methanol.

8.3.16 Relinquish the samples to the instrument lab for counting by liquid scintillation with all appropriate documentation. The LS vials will be analyzed and ultimately disposed of in the manner described in SOP 704.

8.4 PREPARATION OF CALIBRATION STANDARDS

8.4.1 Provide the counting lab with a total of twenty-four liquid scintillation vials consisting of twelve blanks and twelve LCSs with approximately 1000-2500dpm of NIST-traceable ^{210}Pb in each. The blanks and LCSs should be quenched with nitromethane in increments of 15µL.

8.4.2 To accomplish this, label twenty-four 2L disposable plastic bottles. Fill each with 1L of acidified DI water. Add 1mL of Pb carrier to each. Spike the twelve LCSs. Process like water samples, following this SOP (starting with Section 8.2.4). Once samples have been transferred to liquid scintillation vials and cocktail has been added, quench with a range of 0-165µL of nitromethane in 15µL increments for both the blanks and LCSs. Shake to mix and wipe the vials with a kimwipe moistened with methanol. Relinquish to the counting lab with appropriate documentation.

9. CALCULATIONS

The following parameters must be recorded on the benchsheet. The parameters are necessary to calculate chemical recovery and also to provide the instrumentation group with the sample aliquot size to be used in calculating the final results.

9.1 PARAMETERS

9.1.1 Soil Samples

W_s = dry weight of soil (g). Refer to Section 8.1.1.

V_s = final volume of sample (mL). Refer to Section 8.1.14.

C_i = concentration of Pb determined in "initial-Pb" aliquot (µg/mL). Refer to Section 8.1.15.

C_F = concentration of Pb in eluate (µg/mL). Refer to Section 8.3.12.

V_{Pb} = volume of eluate (mL). Refer to Section 8.3.8.

9.1.2 Water Samples

V_i = initial sample volume (mL). Refer to Section 7.2.1.

A = volume of acid added to bring sample to 0.1N acidity (mL). Refer to Section 7.1.

S = volume of Pb carrier solution spiked into sample (mL). Refer to Section 8.2.3.

R_i = volume of solution removed for "initial - Pb" ICP analysis (mL). Refer to Section 8.2.4.

C_i = concentration of Pb determined in "initial - Pb" aliquot (µg/mL). Refer to Section 8.2.4.

V_{Pb} = volume of Pb eluate (mL). Refer to Section 8.3.8.

C_F = concentration of Pb in Pb eluate (µg/mL). Refer to Section 8.3.12.

9.2 CHEMICAL RECOVERY CALCULATIONS
Calculate chemical recovery using the following calculations:

9.2.1 Soil Samples

Pb_i = initial mass of Pb (µg) = $(C_i)(V_s - 10)$

The factor of 10 accounts for the aliquot removed for ICP analysis. Refer to Section 8.1.15.

$Pb_F = (C_F)(V_{pb})(100)$

The factor of 100 accounts for the dilution made prior to ICP analysis. Refer to Section 8.3.11.

% Pb recovery = $(Pb_F / Pb_i)100$

Chemical recovery results must be submitted to instrumentation group.

9.2.2 Water Samples

Pb_i = initial mass of Pb (µg) = $(C_i)(V_i + A + S - R_i)$

Pb_F = final mass of Pb recovered (µg) = $(C_F)(V_{Pb})100$

% Pb recovery = $(Pb_F / Pb_i)(100)$

Chemical recovery results must be submitted to instrumentation group.

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9.3 SAMPLE ALIQUOT SIZE TO BE USED IN FINAL RESULTS CALCULATION

9.3.1 For soils, the sample aliquot mass to be used in calculating the final results must be reduced slightly since two aliquots were removed to determine chemical recovery. This correction is rather insignificant (approximately 2%).

W_c = sample mass used in calculation of final results (g).

$$= W_i \times [(V_s - 10) / (V_s)] \times [(10 - 0.10) / (10)]$$

9.3.2 For waters, the sample aliquot volume to be used in calculating the final results must be reduced slightly since two aliquots were removed to determine chemical recovery. If 1 L of water is used for analysis, this correction is rather insignificant (approximately 2%). The correction becomes more significant for smaller initial sample volumes.

V_c = sample volume used in calculation of final results (mL).

$$= V_i \ [V_i + A + S - R_i) / (V_i + A + S)]$$

9.3.3 W_c and V_c must be submitted to the instrumentation group in order to allow calculation of the final results.

9.4 ACTIVITY CALCULATION

Calculate ^{210}Pb activity in pCi/aliquot as follows:

$$= \frac{(GCPM - BCPM)}{(WcorVc) * 2.22 * ChemicalYield * Pbefficiency * decay}$$

9.5 TPU FACTORS

As defined in SOP 743, the following preparation uncertainty factors should be applied during the final reporting stage of the analysis as a component of the Total Propagated Uncertainty.

9.5.1 Water samples require a preparation uncertainty factor of 0.1033 (1σ). This is based on one gross aliquotting, two quantitative transfers, one volumetric measurement, and one ICP yield determination.

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$$0.1033 = \sqrt{.05^2 + .025^2 + .025^2 + .006^2 + .083^2}$$

9.5.2 Solid samples require a preparation uncertainty factor of 0.1062 (1σ). This is based on one gross aliquotting, three quantitative transfers, one volumetric measurement, and one ICP yield determination.

$$0.1062 = \sqrt{.05^2 + .025^2 + .025^2 + .025^2 + .003^2 + .083^2}$$

9.5.3 In practice, these two TPU factors are not significantly different. To facilitate the use of the radiochemistry reporting software, the greater of the two (0.1062) may be used for both matrices.

10. QUALITY CONTROL

10.1 SOIL SAMPLES

10.1.1 One blank using 2g of quartz sand is run per batch of 20 samples, or at a 5% frequency.

10.1.2 One sample duplicate is run per 10 samples, or at a 10 % frequency.

10.1.3 One laboratory control sample (spiked quartz sand) is run for each batch of 20 samples (5% frequency) with a range of 10 to 30pCi ^{210}Pb/per gram.

10.2 WATER SAMPLES

10.2.1 One blank using 1L containing 5mL of concentrated HCl and 995mL of DI water is run per batch of 20 samples or at a 5% frequency.

10.2.2 One sample duplicate is run per 10 samples or at a 10% frequency.

10.2.3 One laboratory control sample (spiked blank, 1L, containing 5mL of concentrated HCl and 995mL of DI water) is run for each batch of 20 samples (5% frequency) with a range of 10 to 30 pCi ^{210}Pb.

11. SAFETY, HAZARDS, AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

Care should be taken when diluting acids. Always add acids to water, <u>not</u> water to acid.

11.2 WASTE DISPOSAL

11.2.1 Aqueous waste from Sections 8.1.19, 8.2.7 and 8.3.5 can be disposed down the laboratory sink drain.

11.2.2 Solutions collected in Section 8.3.7 should be placed in a waste container provided by the Waste Management Officer.

12. REFERENCES

12.1 E.P. Horwitz, R. Chiarizia, and M. Dietz, "A Novel Strontium- Selective Extraction Chromatographic Resin", Solvent Extraction and Ion Exchange, 10 (2), 313-336 (1992). Note: This reference presents data that shows the strong retention of Pb by the Sr•Spec chromatographic resin. Pb retention exceeds Sr retention by more than two orders of magnitude at certain activities.

12.2 Don Nelson, Argonne National Laboratory, Personal Communication, March 1993.

Analytical Methods

Semivolatile Organic Extractions

3510C/3550B

METHOD 3510C

SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 This method describes a procedure for isolating organic compounds from aqueous samples. The method also describes concentration techniques suitable for preparing the extract for the appropriate determinative methods described in Section 4.3 of Chapter Four.

1.2 This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures.

1.3 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample, usually 1 liter, at a specified pH (see Table 1), is serially extracted with methylene chloride using a separatory funnel.

2.2 The extract is dried, concentrated (if necessary), and, as necessary, exchanged into a solvent compatible with the cleanup or determinative method to be used (see Table 1 for appropriate exchange solvents).

3.0 INTERFERENCES

3.1 Refer to Method 3500.

3.2 The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may dechlorinate, phthalate esters may exchange, and phenols may react to form tannates. These reactions increase with increasing pH, and are decreased by the shorter reaction times available in Method 3510. Method 3510 is preferred over Method 3520 for the analysis of these classes of compounds. However, the recovery of phenols may be optimized by using Method 3520, and performing the initial extraction at the acid pH.

4.0 APPARATUS AND MATERIALS

4.1 Separatory funnel - 2-liter, with polytetrafluoroethylene (PTFE) stopcock.

4.2 Drying column - 20 mm ID Pyrex® chromatographic column with Pyrex® glass wool at bottom and a PTFE stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex® glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus.

4.3.1 Concentrator tube - 10-mL, graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.3.3 Snyder column - Three-ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two-ball micro (Kontes K-569001-0219 or equivalent).

4.3.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

NOTE: The following glassware is recommended for the purpose of solvent recovery during the concentration procedures requiring the use of Kuderna-Danish evaporative concentrators. Incorporation of this apparatus may be required by State or local municipality regulations that govern air emissions of volatile organics. EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program. Solvent recovery is a means to conform with waste minimization and pollution prevention initiatives.

4.4 Solvent vapor recovery system (Kontes K-545000-1006 or K-547300-0000, Ace Glass 6614-30, or equivalent).

4.5 Boiling chips - Solvent-extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.6 Water bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a hood.

4.7 Vials - 2-mL, glass with PTFE-lined screw-caps or crimp tops.

4.8 pH indicator paper - pH range including the desired extraction pH.

4.9 Erlenmeyer flask - 250-mL.

4.10 Syringe - 5-mL.

4.11 Graduated cylinder - 1-liter.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium hydroxide solution (10 N), NaOH. Dissolve 40 g NaOH in organic-free reagent water and dilute to 100 mL. Other concentrations of hydroxide solutions may be used to adjust sample pH, provided that the volume added does not appreciably change (e.g., <1%) the total sample volume.

5.4 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating to 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate. Other concentrations of acid solutions may be used to adjust sample pH, provided that the volume added does not appreciably change (e.g., <1%) the total sample volume.

5.5 Sulfuric acid solution (1:1 v/v), H_2SO_4. Slowly add 50 mL of H_2SO_4 (sp. gr. 1.84) to 50 mL of organic-free reagent water.

5.6 Extraction/exchange solvents - All solvents must be pesticide quality or equivalent.

5.6.1 Methylene chloride, CH_2Cl_2, boiling point 39°C.

5.6.2 Hexane, C_6H_{14}, boiling point 68.7°C.

5.6.3 2-Propanol, $CH_3CH(OH)CH_3$, boiling point 82.3°C.

5.6.4 Cyclohexane, C_6H_{12}, boiling point 80.7°C.

5.6.5 Acetonitrile, CH_3CN, boiling point 81.6°C.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sect. 4.1.

7.0 PROCEDURE

7.1 Using a 1-liter graduated cylinder, measure 1 liter (nominal) of sample. Alternatively, if the entire contents of the sample bottle are to be extracted, mark the level of sample on the outside of the bottle. If high analyte concentrations are anticipated, a smaller sample volume may be taken and diluted to 1-L with organic-free reagent water, or samples may be collected in smaller sample bottles and the whole sample used.

7.2 Pipet 1.0 mL of the surrogate spiking solution into each sample in the graduated cylinder (or sample bottle) and mix well. (See Method 3500 and the determinative method to be used for details on the surrogate standard solution and matrix spiking solution).

7.2.1 For the sample in each batch (see Chapter One) selected for use as a matrix spike sample, add 1.0 mL of the matrix spiking standard.

7.2.2 If Method 3640, Gel-Permeation Cleanup, is to be employed, add twice the volume of the surrogate spiking solution and the matrix spiking standard, since half of the extract is not recovered from the GPC apparatus. (Alternatively, use 1.0 mL of the spiking solutions and concentrate the final extract to half the normal volume, e.g., 0.5 mL instead of 1.0 mL).

7.3 Check the pH of the sample with wide-range pH paper and adjust the pH, if necessary, to the pH indicated in Table 1, using 1:1 (v/v) sulfuric acid or 10 N sodium hydroxide. Lesser strengths of acid or base solution may be employed, provided that they do not result in a significant change (<1%) in the volume of sample extracted (see Secs. 5.3 and 5.5).

7.4 Quantitatively transfer the sample from the graduated cylinder (or sample bottle) to the separatory funnel. Use 60 mL of methylene chloride to rinse the cylinder (or bottle) and transfer this rinse solvent to the separatory funnel. If the sample was transferred directly from the sample bottle, refill the bottle to the mark made in Sec. 7.1 with water and then measure the volume of sample that was in the bottle.

7.5 Seal and shake the separatory funnel vigorously for 1 - 2 minutes with periodic venting to release excess pressure. Alternatively, pour the exchange solvent into the top of the Snyder column while the concentrator remains on the water bath in Sec. 7.11.4.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel should be vented into a hood to avoid exposure of the analyst to solvent vapors.

7.6 Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the solvent extract in an Erlenmeyer flask. If the emulsion cannot be broken (recovery of < 80% of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in Method 3520, Continuous Liquid-Liquid Extraction.

7.7 Repeat the extraction two more times using fresh portions of solvent (Secs. 7.2 through 7.5). Combine the three solvent extracts.

7.8 If further pH adjustment and extraction is required, adjust the pH of the aqueous phase to the desired pH indicated in Table 1. Serially extract three times with 60 mL of methylene chloride, as outlined in Secs. 7.2 through 7.5. Collect and combine the extracts and label the combined extract appropriately.

7.9 If performing GC/MS analysis (Method 8270), the acid/neutral and base extracts may be combined prior to concentration. However, in some situations, separate concentration and analysis of the acid/neutral and base extracts may be preferable (e.g. if for regulatory purposes the presence or absence of specific acid/neutral or base compounds at low concentrations must be determined, separate extract analyses may be warranted).

7.10 Perform the concentration (if necessary) using the Kuderna-Danish Technique (Secs. 7.11.1 through 7.11.6).

7.11 K-D technique

7.11.1 Assemble a Kuderna-Danish (K-D) concentrator (Sec. 4.3) by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

7.11.2 Attach the solvent vapor recovery glassware (condenser and collection device) (Sec. 4.4) to the Snyder column of the K-D apparatus following manufacturer's instructions.

7.11.3 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Rinse the Erlenmeyer flask, which contained the solvent extract, with 20 - 30 mL of methylene chloride and add it to the column to complete the quantitative transfer.

7.11.4 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15 - 20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 - 20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.11.5 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent, a new boiling chip, and reattach the Snyder column. Alternatively, pour the exchange solvent into the top of the Snyder column while the concentrator remains on the water bath in Sec. 7.11.4. Concentrate the extract, as described in Sec. 7.11.4, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.11.6 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1 - 2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Sec. 7.12 or adjusted to 10.0 mL with the solvent last used.

7.12 If further concentration is indicated in Table 1, either the micro-Snyder column technique (7.12.1) or nitrogen blowdown technique (7.12.2) is used to adjust the extract to the final volume required.

7.12.1 Micro-Snyder column technique

If further concentration is indicated in Table 1, add another clean boiling chip to the concentrator tube and attach a two-ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5 - 10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column, rinse the flask and its lower joints into the concentrator tube with 0.2 mL of methylene chloride or the exchange solvent, and adjust the final volume as indicated in Table 1, with solvent.

7.12.2 Nitrogen blowdown technique

7.12.2.1 Place the concentrator tube in a warm bath (35°C) and evaporate the solvent to the final volume indicated in Table 1, using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: New plastic tubing must not be used between the carbon trap and the sample, since it may introduce contaminants.

7.12.2.2 The internal wall of the tube must be rinsed several times with methylene chloride or appropriate solvent during the operation. During evaporation, the tube must be positioned to avoid water condensation (i.e., the solvent level should be below the level of the water bath). Under normal procedures, the extract must not be allowed to become dry.

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.13 The extract may now be analyzed for the target analytes using the appropriate determinative technique(s) (see Sec. 4.3 of this Chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer than 2 days it should be transferred to a vial with a PTFE-lined screw-cap or crimp top, and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks, matrix spikes, or replicate samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

Refer to the determinative methods for performance data.

10.0 REFERENCES

None.

TABLE 1
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative method	Initial extraction pH	Secondary extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)[a]
8041	≤2	none	2-propanol	hexane	1.0	1.0, 0.5[b]
8061	5-7	none	hexane	hexane	2.0	10.0
8070	as received	none	methanol	methylene chloride	2.0	10.0
8081	5-9	none	hexane	hexane	10.0	10.0
8082	5-9	none	hexane	hexane	10.0	10.0
8091	5-9	none	hexane	hexane	2.0	1.0
8100	as received	none	none	cyclohexane	2.0	1.0
8111	as received	none	hexane	hexane	2.0	10.0
8121	as received	none	hexane	hexane	2.0	1.0
8141	as received	none	hexane	hexane	10.0	10.0
8270[c,d]	<2	>11	none	-	-	1.0
8310	as received	none	acetonitrile	-	-	1.0
8321	as received	none	methanol	-	-	1.0
8325	7.0	none	methanol	-	-	1.0
8410	as received	none	methylene chloride	methylene chloride	10.0	0.0 (dry)

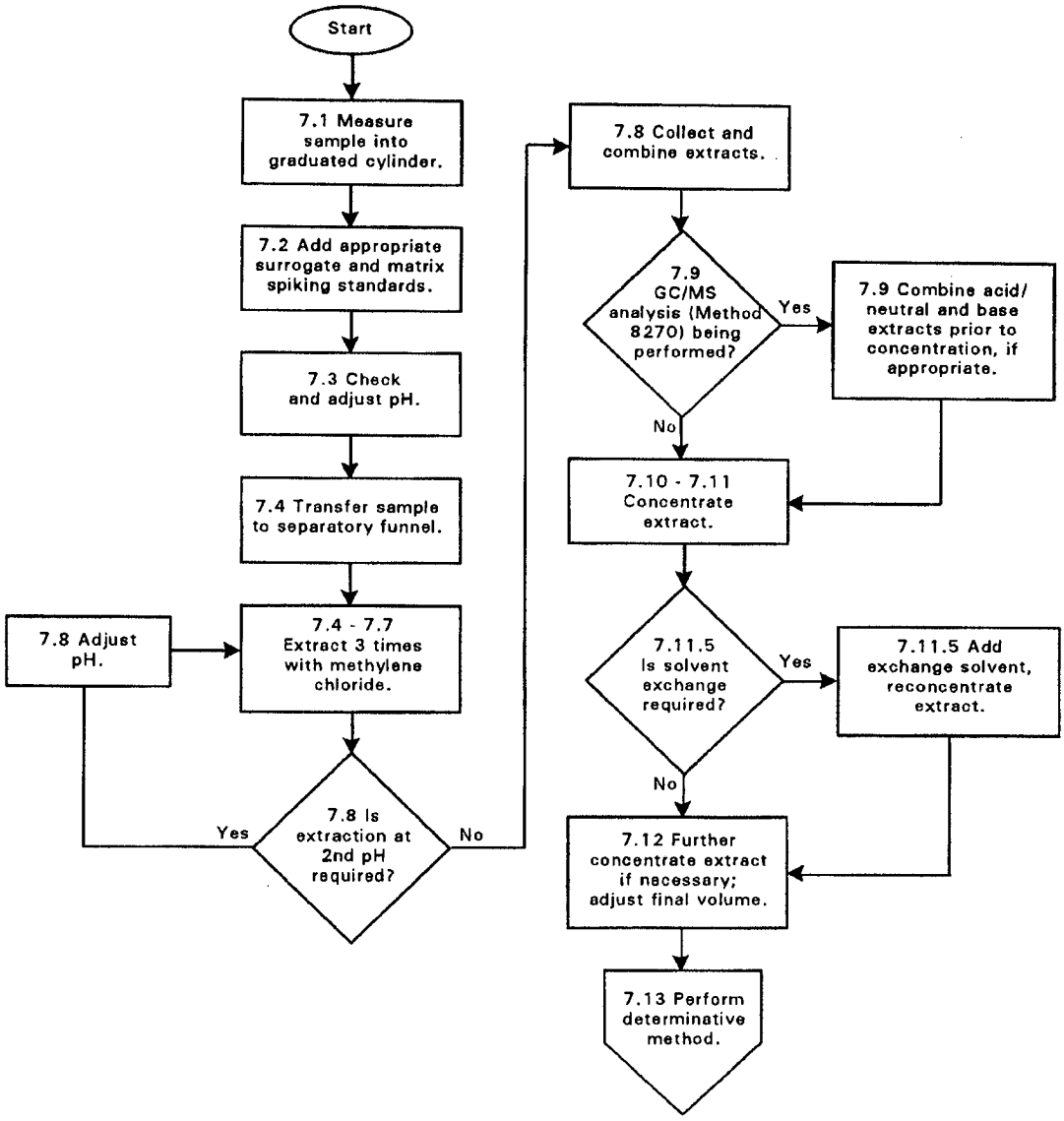
[a] For methods where the suggested final extract volume is 10.0 mL, the volume may be reduced to as low as 1.0 mL to achieve lower detection limits.

[b] Phenols may be analyzed, by Method 8041, using a 1.0 mL 2-propanol extract by GC/FID. Method 8041 also contains an optional derivatization procedure for phenols which results in a 0.5 mL hexane extract to be analyzed by GC/ECD.

[c] The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

[d] Extraction pH sequence may be reversed to better separate acid and neutral waste components. Excessive pH adjustments may result in the loss of some analytes (see Sec. 3.2).

METHOD 3510C
SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION



METHOD 3550B

ULTRASONIC EXTRACTION

See Disclaimer. See manufacturer's specifications for operational settings.

1.0 SCOPE AND APPLICATION

1.1 Method 3550 is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes. The ultrasonic process ensures intimate contact of the sample matrix with the extraction solvent.

1.2 The method is divided into two sections, based on the expected concentration of organics in the sample. The low concentration method (individual organic components of less than or equal to 20 mg/kg) uses a larger sample size and a more rigorous extraction procedure (lower concentrations are more difficult to extract). The medium/high concentration method (individual organic components of greater than 20 mg/kg) is much simpler and therefore faster.

1.3 It is highly recommended that the extracts be cleaned up prior to analysis. See Chapter Four (Cleanup), Sec. 4.2.2, for applicable methods.

1.4 Ultrasonic extraction is not as rigorous as other extraction methods for soils/solids. Therefore, it is critical that the method (including the manufacturer's instructions) be followed explicitly in order to achieve the maximum extraction efficiency. See Sec. 7.0 for the critical aspects of the extraction procedure.

1.5 EPA has not validated Method 3550 for the extraction of organophosphorous compounds from solid matrices. In addition, there are concerns that the ultrasonic energy may lead to breakdown of some organophosphorous compounds (see Reference 3). As a result, this extraction technique should not be used for organophosphorous compounds without extensive validation on real-world samples. Such studies should assess the precision, accuracy, ruggedness, and sensitivity of the technique relative to the appropriate regulatory limits or project-specific concentrations of interest.

1.6 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.7 This method is not appropriate for applications where high extraction efficiencies of analytes at very low concentrations is necessary (e.g., demonstration of effectiveness of corrective action).

2.0 SUMMARY OF METHOD

2.1 Low concentration method - A 30-g sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. This is solvent extracted three times using ultrasonic extraction. The extract is separated from the sample by vacuum filtration or centrifugation. The extract is ready for cleanup and/or analysis following concentration.

2.2 Medium/high concentration method – A 2-g sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. This is solvent extracted once using ultrasonic extraction. A portion of the extract is removed for cleanup and/or analysis.

3.0 INTERFERENCES

Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Apparatus for grinding dry waste samples.

4.2 Ultrasonic preparation - A horn-type device equipped with a titanium tip, or a device that will give equivalent performance, shall be used.

4.2.1 Ultrasonic Disrupter - The disrupter must have a minimum power wattage of 300 watts, with pulsing capability. A device designed to reduce the cavitation sound is recommended. Follow the manufacturers instructions for preparing the disrupter for extraction of samples with low and medium/high concentration.

4.2.2 Use a 3/4" horn for the low concentration method and a 1/8" tapered microtip attached to a 1/2" horn for the medium/high concentration method.

4.3 Sonabox - Recommended with above disrupters for decreasing cavitation sound (Heat Systems - Ultrasonics, Inc., Model 432B or equivalent).

4.4 Apparatus for determining percent dry weight.

4.4.1 Drying oven - capable of maintaining 105°C.

4.4.2 Desiccator.

4.4.3 Crucibles - Porcelain or disposable aluminum.

4.5 Pasteur glass pipets - 1-mL, disposable.

4.6 Beakers - 400-mL.

4.7 Vacuum or pressure filtration apparatus.

4.7.1 Buchner funnel.

4.7.2 Filter paper - Whatman No. 41 or equivalent.

4.8 Kuderna-Danish (K-D) apparatus.

4.8.1 Concentrator tube - 10-mL, graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.

4.8.2 Evaporation flask - 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent

4.8.3 Snyder column - Three-ball macro (Kontes K-503000-0121 or equivalent).

4.8.4 Snyder column - Two-ball micro (Kontes K-569001-0219 or equivalent).

4.8.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

NOTE The following glassware is recommended for the purpose of solvent recovery during the concentration procedures requiring the use of Kuderna-Danish evaporative concentrators. Incorporation of this apparatus may be required by State or local municipality regulations that govern air emissions of volatile organics. EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program. Solvent recovery is a means to conform with waste minimization and pollution prevention initiatives.

4.9 Solvent vapor recovery system (Kontes K-545000-1006 or K-547300-0000, Ace Glass 6614-30, or equivalent)

4.10 Boiling chips - Solvent-extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.11 Water bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The batch should be used in a hood.

4.12 Balance - Top-loading, capable of accurately weighing to the nearest 0.01 g.

4.13 Vials - 2-mL, for GC autosampler, with polytetrafluoroethylene (PTFE)-lined screw caps or crimp tops.

4.14 Glass scintillation vials - 20-mL, with PTFE-lined screw caps.

4.15 Spatula - Stainless steel or PTFE.

4.16 Drying column - 20-mm ID Pyrex chromatographic column with Pyrex glass wool at bottom.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.17 Syringe - 5-mL.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise specified, it is intended that all inorganic reagents shall conform to the specifications of the Committee on

Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.4 Extraction solvents

Samples should be extracted using a solvent system that gives optimum, reproducible recovery of the analytes of interest from the sample matrix. Table 1 provides recovery data for selected semivolatile organic compounds extracted from an NIST SRM. The following sections provide guidance on the choice of solvents for various classes of analytes. All solvents must be pesticide quality or equivalent.

5.4.1 Semivolatile organics may be extracted with acetone/methylene chloride (1:1, v/v), CH_3COCH_3/CH_2Cl_2 or acetone/hexane (1:1, v/v), CH_3COCH_3/C_6H_{14}.

5.4.2 Organochlorine pesticides may be extracted with acetone/hexane (1:1, v/v) CH_3COCH_3/C_6H_{14} or acetone/methylene chloride (1:1,v/v), CH_3COCH_3/CH_2Cl_2.

5.4.3 PCBs may be extracted with acetone/hexane (1:1, v/v), CH_3COCH_3/C_6H_{14}, acetone/methylene chloride (1:1, v/v), CH_3COCH_3/CH_2Cl_2 or hexane, C_6H_{14}.

5.4.4 Other solvent systems may be employed, provided that the analyst can demonstrate adequate performance for the analytes of interest in the sample matrix (see Method 3500, Sec. 8.0).

5.5 Exchange solvents - All solvents must be pesticide quality or equivalent.

5.5.1 Hexane, C_6H_{14}.

5.5.2 2-Propanol, $(CH_3)_2CHOH$.

5.5.3 Cyclohexane, C_6H_{12}.

5.5.4 Acetonitrile, CH_3CN.

5.5.5 Methanol, CH_3OH.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

As noted in Sec. 1.4, ultrasonic extraction is not as rigorous a method as other extraction methods for soils/solids. Therefore, it is critical that the method be followed explicitly (including the manufacturer's instructions) to achieve the maximum extraction efficiency. At a minimum, successful use of this technique requires that:

- The extraction device must have a minimum of 300 watts of power and be equipped with appropriate size disrupter horns (see Sec. 4.2).
- The horn must be properly maintained, including tuning according to the manufacturer's instructions prior to use, and inspection of the horn tip for excessive wear.
- The samples must be properly prepared by thorough mixing with sodium sulfate so that it forms a free-flowing powder prior to the addition of the solvent.
- The extraction horns used for the low concentration and high concentration protocols (Sec. 7.3 and Sec. 7.4, respectively) are not interchangeable. Results indicate that the use of the 3/4" horn is inappropriate for the high concentration method, particularly for extraction of very non-polar organic compounds such as PCBs, which are strongly adsorbed to the soil matrix.
- Three extractions are performed with the appropriate solvent, the extraction is performed in the specified pulse mode, and the horn tip is positioned just below the surface of the solvent yet above the sample.
- Very active mixing of the sample and the solvent must occur when the ultrasonic pulse is activated. The analyst must observe such mixing at some point during the extraction process.

7.1 Sample handling

7.1.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.1.2 Waste samples - Samples consisting of multiple phases must be prepared by the phase separation method in Chapter Two before extraction. This extraction procedure is for solids only.

7.1.3 Dry waste samples amenable to grinding - Grind or otherwise subdivide the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 10 g after grinding.

7.1.4 Gummy, fibrous, or oily materials not amenable to grinding should be cut, shredded, or otherwise reduced in size to allow mixing and maximum exposure of the sample surfaces for the extraction. The addition of anhydrous sodium sulfate to the sample (1:1) may make the mixture amenable to grinding.

7.2 Determination of percent dry weight - When sample results are to be calculated on a dry weight basis, a second portion of sample should be weighed out at the same time as the portion used for analytical determination.

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from drying a heavily contaminated sample.

Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Dry this aliquot overnight at 105°C. Allow to cool in a desiccator before weighing. Calculate the % dry weight as follows:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

7.3 Extraction method for samples expected to contain low concentrations of organics and pesticides (less than or equal to 20 mg/kg):

7.3.1 The following steps should be performed rapidly to avoid loss of the more volatile extractables.

7.3.1.1 Weigh approximately 30 g of sample into a 400-mL beaker. Record the weight to the nearest 0.1 g.

7.3.1.2 Nonporous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture must be mixed with 60 g of anhydrous sodium sulfate, using a spatula. If required, more sodium sulfate may be added. After addition of sodium sulfate, the sample should be free flowing.

7.3.1.3 Add 1.0 mL of the surrogate standard solution to all samples, spiked samples, QC samples, and blanks. Consult Method 3500, Secs. 5.0 and 8.0 for guidance on the appropriate choice of surrogate compounds and concentrations.

7.3.1.4 For the sample in each batch selected for spiking, add 1.0 mL of the matrix spiking solution. Consult Method 3500, Secs. 5.0 and 8.0 for guidance on the appropriate choice of matrix spiking compounds and concentrations.

7.3.1.5 If gel permeation cleanup (Method 3640) is to be employed, the analyst should either add twice the volume of the surrogate spiking solution (and matrix spiking solution, where applicable), or concentrate the final extract to half the normal volume, to compensate for the half of the extract that is lost due to loading of the GPC column.

7.3.1.6 Immediately add 100 mL of the appropriate/recommended extraction solvent or solvent mixture (see Sec. 5.4 and Table 1).

7.3.2 Place the bottom surface of the tip of the #207 (or equivalent) 3/4 inch disrupter horn about 1/2 inch below the surface of the solvent, but above the sediment layer.

NOTE: Be sure the horn is properly tuned according to the manufacturer's instructions.

7.3.3 Extract ultrasonically for 3 minutes, with output control knob set at 10 (full power) and with mode switch on Pulse (pulsing energy rather than continuous energy) and percent-duty cycle knob set at 50% (energy on 50% of time and off 50% of time). Do not use microtip probe.

7.3.4 Decant the extract and filter it through Whatman No. 41 filter paper (or equivalent) in a Buchner funnel that is attached to a clean 500-mL filtration flask. Alternatively, decant the extract into a centrifuge bottle and centrifuge at low speed to remove particles.

7.3.5 Repeat the extraction two or more times with two additional 100 mL portions of solvent. Decant off the solvent after each ultrasonic extraction. On the final ultrasonic extraction, pour the entire sample into the Buchner funnel and rinse with extraction solvent. Apply a vacuum to the filtration flask, and collect the solvent extract. Continue filtration until all visible solvent is removed from the funnel, but do not attempt to completely dry the sample, as the continued application of a vacuum may result in the loss of some analytes. Alternatively, if centrifugation is used in Sec. 7.3.4, transfer the entire sample to the centrifuge bottle. Centrifuge at low speed, and then decant the solvent from the bottle.

7.3.6 Assemble a Kuderna-Danish (K-D) concentrator (if necessary) by attaching a 10-mL concentrator tube to a 500-mL evaporator flask. Attach the solvent vapor recovery glassware (condenser and collection device) to the Snyder column of the Kuderna-Danish apparatus following manufacturer's instructions. Transfer filtered extract to a 500-mL evaporator flask and proceed to the next section.

7.3.7 Add one to two clean boiling chips to the evaporation flask, and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (80 - 90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10 - 15 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.3.8 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent and a new boiling chip, and re-attach the Snyder column. Concentrate the extract as described in Sec. 7.3.10, raising the temperature of the water bath, if necessary, to maintain proper distillation. When the apparent volume again reaches 1 - 2 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

7.3.9 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1 - 2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Sec. 7.3.10 or adjusted to 10.0 mL with the solvent last used.

7.3.10 If further concentration is indicated in Table 1, either micro Snyder column technique (Sec. 7.3.10.1) or nitrogen blowdown technique (Sec. 7.3.10.2) may be used to adjust the extract to the final volume required.

7.3.10.1 Micro Snyder column technique

7.3.10.1.1 Add a clean boiling chip and attach a two-ball micro Snyder column to the concentrator tube. Prewet the column by adding approximately 0.5 mL of methylene chloride or exchange solvent through the top. Place the apparatus in the hot water bath. Adjust the vertical position and the

water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the liquid reaches an apparent volume of approximately 0.5 mL, remove the apparatus from the water bath and allow to drain and cool for at least 10 minutes. Remove the micro Snyder column and rinse its lower joint with approximately 0.2 mL of appropriate solvent and add to the concentrator tube. Adjust the final volume to the volume required for cleanup or for the determinative method (see Table 1).

7.3.10.2 Nitrogen blowdown technique

7.3.10.2.1 Place the concentrator tube in a warm water bath (approximately 35°C) and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: Do not use plasticized tubing between the carbon trap and the sample, since it may introduce contaminants.

7.3.10.2.2 The internal wall of the tube must be rinsed down several times with the appropriate solvent during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry.

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.4 Extraction method for samples expected to contain high concentrations of organics (greater than 20 mg/kg):

7.4.1 Transfer approximately 2 g (record weight to the nearest 0.1 g) of sample to a 20-mL vial. Wipe the mouth of the vial with a tissue to remove any sample material. Record the exact weight of sample taken. Cap the vial before proceeding with the next sample to avoid any cross contamination.

7.4.2 Add 2 g of anhydrous sodium sulfate to sample in the 20-mL vial and mix well.

7.4.3 Surrogates are added to all samples, spikes, and blanks (see Method 3500 for details on the surrogate spiking solution and on the matrix spike solution).

7.4.3.1 Add 1.0 mL of surrogate spiking solution to sample mixture.

7.4.3.2 For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard.

7.4.3.3 If gel permeation cleanup (Method 3640) is to be employed, the analyst should either add twice the volume of the surrogate spiking solution (and matrix spiking solution, where applicable), or concentrate the final extract to half the normal volume, to compensate for the half of the extract that is lost due to loading of the GPC column.

7.4.4 Immediately add whatever volume of solvent is necessary to bring the final volume to 10.0 mL considering the added volume of surrogates and matrix spikes. Disrupt the sample with the 1/8 in. tapered microtip ultrasonic probe for 2 minutes at output control setting 5 and with mode switch on pulse and percent duty cycle at 50%. Extraction solvents are:

7.4.4.1 For nonpolar compounds (i.e., organochlorine pesticides and PCBs), use hexane or appropriate solvent.

7.4.4.2 For other semivolatile organics, use methylene chloride.

7.4.5 Loosely pack a disposable Pasteur pipette with 2 to 3 cm of glass wool. Filter the sample extract through the glass wool and collect the extract in a suitable container. The entire 10 mL of extraction solvent cannot be recovered from the sample. Therefore, the analyst should collect a volume appropriate for the sensitivity of the determinative method. For instance, for methods that do not require that the extract be concentrated further (e.g., Method 8081 typically employs a final extract volume of 10 mL), the extract may be collected in a scintillation vial or other sealable container. For extracts that will require further concentration, it is advisable to collect a standard volume for all such samples in order to simplify the calculation of the final sample results. For instance, collect 5.0 mL of extract in a clean concentrator tube. This volume represents exactly half of the total volume of the original sample extract. As necessary, account for the "loss" of half of the extract in the final sample calculations, or concentrate the final extract to one-half the nominal final volume (e.g., 0.5 mL vs. 1.0 mL) to compensate for the loss.

7.4.6 The extract is ready for cleanup or analysis, depending on the extent of interfering co-extractives.

7.5 If analysis of the extract will not be performed immediately, stopper the concentrator tube and refrigerate. If the extract will be stored longer than 2 days, it should be transferred to a vial with a PTFE-lined cap and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks, matrix spike, and replicate samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA. Interlaboratory Comparison Study: Methods for Volatile and Semi-Volatile Compounds, Environmental Monitoring Systems Laboratory, Office of Research and Development, Las Vegas, NV, EPA 600/4-84-027, 1984.

2. Christopher S. Hein, Paul J. Marsden, Arthur S. Shurtleff, "Evaluation of Methods 3540 (Soxhlet) and 3550 (Sonication) for Evaluation of Appendix IX Analytes from Solid Samples", S-CUBED, Report for EPA Contract 68-03-33-75, Work Assignment No. 03, Document No. SSS-R-88-9436, October 1988.

3. Kotronarou, A., et al., "Decomposition of Parathion in Aqueous Solution by Ultrasonic Irradiation," *ES&T*, 1992, Vol. 26, 1460-1462.

TABLE 1
EFFICIENCIES OF VARIOUS EXTRACTION SOLVENT SYSTEMS[a]

Compound	CAS No.[b]	ABN[c]	Solvent System[d] A %R	A SD	B %R	B SD	C %R	C SD	D %R	D SD	E %R	E SD
4-Bromophenyl phenyl ether	101-55-3	N	84.2	6.5	56.4	0.5	86.7	1.9	84.5	0.4	73.4	1.0
4-Chloro-3-methylphenol	59-50-7	A	66.7	6.4	74.3	2.8	97.4	3.4	89.4	3.8	84.1	1.6
Bis(2-chloroethoxy)methane	111-91-1	N	71.2	4.5	58.3	5.4	69.3	2.4	74.8	4.3	37.5	5.8
Bis(2-chloroethyl) ether	111-44-4	N	42.0	4.8	17.2	3.1	41.2	8.4	61.3	11.7	4.8	1.0
2-Chloronaphthalene	91-58-7	N	86.4	8.8	78.9	3.2	100.8	3.2	83.0	4.6	57.0	2.2
4-Chlorophenyl phenyl ether	7005-72-3	N	68.2	8.1	63.0	2.5	96.6	2.5	80.7	1.0	67.8	1.0
1,2-Dichlorobenzene	95-50-1	N	33.3	4.5	15.8	2.0	27.8	6.5	53.2	10.1	2.0	1.2
1,3-Dichlorobenzene	541-73-1	N	29.3	4.8	12.7	1.7	20.5	6.2	46.8	10.5	0.6	0.6
Diethyl phthalate	84-66-2	N	24.8	1.6	23.3	0.3	121.1	3.3	99.0	4.5	94.8	2.9
4,6-Dinitro-o-cresol	534-52-1	A	66.1	8.0	63.8	2.5	74.2	3.5	55.2	5.6	63.4	2.0
2,4-Dinitrotoluene	121-14-2	N	68.9	1.6	65.6	4.9	85.6	1.7	68.4	3.0	64.9	2.3
2,6-Dinitrotoluene	606-20-2	N	70.0	7.6	68.3	0.7	88.3	4.0	65.2	2.0	59.8	0.8
Heptachlor epoxide	1024-57-3	N	65.5	7.8	58.7	1.0	86.7	1.0	84.8	2.5	77.0	0.7
Hexachlorobenzene	118-74-1	N	82.1	8.8	56.5	1.2	95.8	2.5	89.3	1.2	78.1	4.4
Hexachlorobutadiene	87-68-3	N	55.8	8.3	41.0	2.7	63.4	4.1	76.9	8.4	12.5	4.6
Hexachlorocyclopentadiene	77-47-4	N	26.8	3.3	19.3	1.8	35.5	6.5	46.6	4.7	9.2	1.7
Hexachloroethane	67-72-1	N	28.4	3.8	15.5	1.6	31.1	7.4	57.9	10.4	1.4	1.2
5-Nitro-o-toluidine	99-55-8	B	52.6	26.7	64.6	4.7	74.7	4.7	27.9	4.0	34.0	4.0
Nitrobenzene	98-95-3	N	59.8	7.0	38.7	5.5	46.9	6.3	60.6	6.3	13.6	3.2
Phenol	108-95-2	A	51.6	2.4	52.0	3.3	65.6	3.4	65.5	2.1	50.0	8.1
1,2,4-Trichlorobenzene	120-82-1	N	66.7	5.5	49.9	4.0	73.4	3.6	84.0	7.0	20.0	3.2

[a] Percent recovery of analytes spiked at 200 mg/kg into NIST sediment SRM 1645
[b] Chemical Abstracts Service Registry Number
[c] Compound Type: A = Acid, B = Base, N = neutral
[d] Solvent system A = Methylene chloride
Solvent system B = Methylene chloride/Acetone (1/1)
Solvent system C = Hexane/Acetone (1/1)
Solvent system D = Methyl t-butyl ether
Solvent system E = Methyl t-butyl ether/Methanol (2/1)

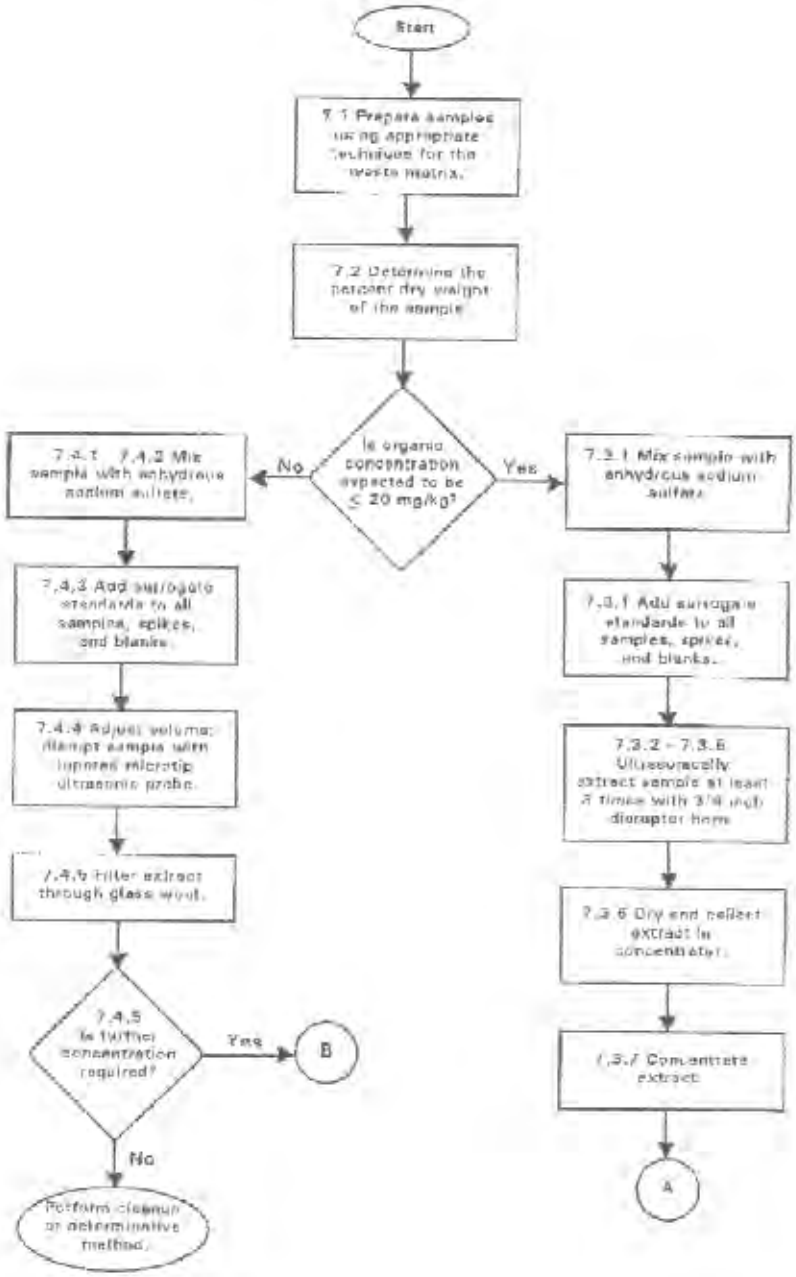
TABLE 2
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

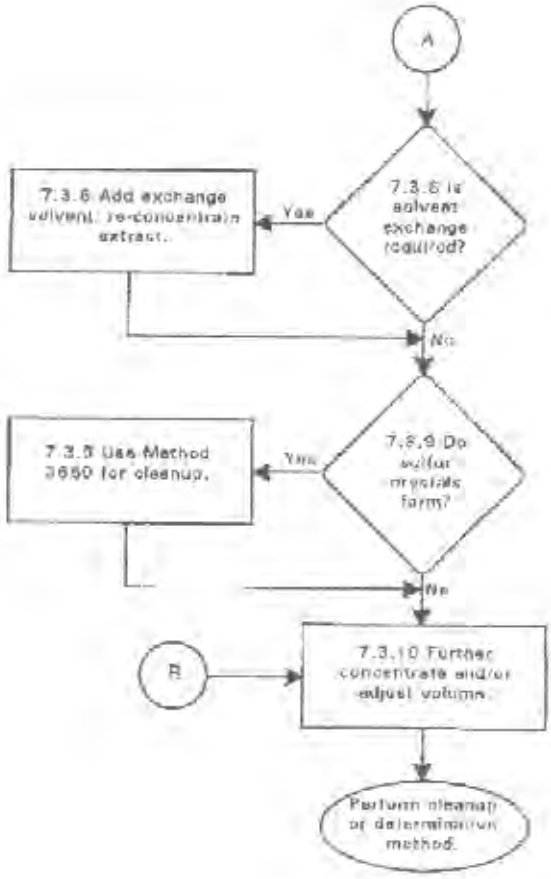
Determinative method	Extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)[a]
8041	as received	2-propanol	hexane	1.0	1.0, 0.5[b]
8061	as received	hexane	hexane	2.0	10.0
8070	as received	methanol	methylene chloride	2.0	10.0
8081	as received	hexane	hexane	10.0	10.0
8091	as received	hexane	hexane	2.0	1.0
8100	as received	none	cyclohexane	2.0	1.0
8111	as received	hexane	hexane	2.0	10.0
8121	as received	hexane	hexane	2.0	1.0
8141	as received	hexane	hexane	10.0	10.0
8270[c]	as received	none	-	-	1.0
8310	as received	acetonitrile	-	-	1.0
8321	as received	methanol	-	-	1.0
8325	as received	methanol	-	-	1.0
8410	as received	methylene chloride	methylene chloride	10.0	0.0 (dry)

[a] For methods where the suggested final extract volume is 10.0 mL, the volume may be reduced to as low as 1.0 mL to achieve lower detection limits.

[b] Phenols may be analyzed by Method 8041, using a 1.0-mL 2-propanol extract by GC/FID. Method 8041 also contains an optional derivatization procedure for phenols which results in a 0.5-mL hexane extract to be analyzed by GC/ECD.

[c] The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.


Start
7.1 Prepare samples using appropriate techniques for the waste matrix.
7.2 Determine the percent dry weight of the sample.
Is organic concentration expected to be ≤ 20 mg/kg?
No
Yes
7.4.1 - 7.4.2 Mix sample with anhydrous sodium sulfate.
7.4.3 Add surrogate standards to all samples, spikes, and blanks.
7.4.4 Adjust volume; disrupt sample with (optional) ultrasonic probe.
7.4.5 Filter extract through glass wool.
7.4.5 Is further concentration required?
Yes
B
No
Perform cleanup or determinative method.
7.3.1 Mix sample with anhydrous sodium sulfate.
7.3.1 Add surrogate standards to all samples, spikes, and blanks.
7.3.2 - 7.3.6 Ultrasonically extract sample at least 3 times with 3/4 inch disrupter horn.
7.3.6 Dry and collect extract (a concentrator).
7.3.7 Concentrate extract.
A


A
7.3.6 Is solvent exchange required?
Yes
7.3.6 Add exchange solvent, re-concentrate extract.
No
7.3.8 Do sulfur crystals form?
Yes
7.3.5 Use Method 3660 for cleanup.
No
B
7.3.10 Further concentrate and/or adjust volume.
Perform cleanup or determinative method.

Analytical Methods

Semivolatile Organics

8270C

SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

1.0 SCOPE AND APPLICATION

1.1 Method 8270 is used to determine the concentration of semivolatile organic compounds in extracts prepared from many types of solid waste matrices, soils, air sampling media and water samples. Direct injection of a sample may be used in limited applications. The following compounds can be determined by this method:

		Appropriate Preparation Techniques[b]				
Compounds	CAS No[a]	3510	3520	3540/ 3541	3550	3580
Acenaphthene	83-32-9	X	X	X	X	X
Acenaphthene-d_{10} (IS)		X	X	X	X	X
Acenaphthylene	208-96-8	X	X	X	X	X
Acetophenone	98-86-2	X	ND	ND	ND	X
2-Acetylaminofluorene	53-96-3	X	ND	ND	ND	X
1-Acetyl-2-thiourea	591-08-2	LR	ND	ND	ND	LR
Aldrin	309-00-2	X	X	X	X	X
2-Aminoanthraquinone	117-79-3	X	ND	ND	ND	X
Aminoazobenzene	60-09-3	X	ND	ND	ND	X
4-Aminobiphenyl	92-67-1	X	ND	ND	ND	X
3-Amino-9-ethylcarbazole	132-32-1	X	X	ND	ND	ND
Anilazine	101-05-3	X	ND	ND	ND	X
Aniline	62-53-3	X	X	ND	X	X
o-Anisidine	90-04-0	X	ND	ND	ND	X
Anthracene	120-12-7	X	X	X	X	X
Aramite	140-57-8	HS(43)	ND	ND	ND	X
Aroclor 1016	12674-11-2	X	X	X	X	X
Aroclor 1221	11104-28-2	X	X	X	X	X
Aroclor 1232	11141-16-5	X	X	X	X	X
Aroclor 1242	53469-21-9	X	X	X	X	X
Aroclor 1248	12672-29-6	X	X	X	X	X
Aroclor 1254	11097-69-1	X	X	X	X	X
Aroclor 1260	11096-82-5	X	X	X	X	X
Azinphos-methyl	86-50-0	HS(62)	ND	ND	ND	X
Barban	101-27-9	LR	ND	ND	ND	LR
Benzidine	92-87-5	CP	CP	CP	CP	CP
Benzoic acid	65-85-0	X	X	ND	X	X
Benz(a)anthracene	56-55-3	X	X	X	X	X
Benzo(b)fluoranthene	205-99-2	X	X	X	X	X
Benzo(k)fluoranthene	207-08-9	X	X	X	X	X
Benzo(g,h,i)perylene	191-24-2	X	X	X	X	X
Benzo(a)pyrene	50-32-8	X	X	X	X	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b] 3510	3520	3540/ 3541	3550	3580
p-Benzoquinone	106-51-4	OE	ND	ND	ND	X
Benzyl alcohol	100-51-6	X	X	ND	X	X
α-BHC	319-84-6	X	X	X	X	X
β-BHC	319-85-7	X	X	X	X	X
δ-BHC	319-86-8	X	X	X	X	X
γ-BHC (Lindane)	58-89-9	X	X	X	X	X
Bis(2-chloroethoxy)methane	111-91-1	X	X	X	X	X
Bis(2-chloroethyl) ether	111-44-4	X	X	X	X	X
Bis(2-chloroisopropyl) ether	108-60-1	X	X	X	X	X
Bis(2-ethylhexyl) phthalate	117-81-7	X	X	X	X	X
4-Bromophenyl phenyl ether	101-55-3	X	X	X	X	X
Bromoxynil	1689-84-5	X	ND	ND	ND	X
Butyl benzyl phthalate	85-68-7	X	X	X	X	X
Captafol	2425-06-1	HS(55)	ND	ND	ND	X
Captan	133-06-2	HS(40)	ND	ND	ND	X
Carbaryl	63-25-2	X	ND	ND	ND	X
Carbofuran	1563-66-2	X	ND	ND	ND	X
Carbophenothion	786-19-6	X	ND	ND	ND	X
Chlordane (NOS)	57-74-9	X	X	X	X	X
Chlorfenvinphos	470-90-6	X	ND	ND	ND	X
4-Chloroaniline	106-47-8	X	ND	ND	ND	X
Chlorobenzilate	510-15-6	X	ND	ND	ND	X
5-Chloro-2-methylaniline	95-79-4	X	ND	ND	ND	X
4-Chloro-3-methylphenol	59-50-7	X	X	X	X	X
3-(Chloromethyl)pyridine hydrochloride	6959-48-4	X	ND	ND	ND	X
1-Chloronaphthalene	90-13-1	X	X	X	X	X
2-Chloronaphthalene	91-58-7	X	X	X	X	X
2-Chlorophenol	95-57-8	X	X	X	X	X
4-Chloro-1,2-phenylenediamine	95-83-0	X	X	ND	ND	ND
4-Chloro-1,3-phenylenediamine	5131-60-2	X	X	ND	ND	ND
4-Chlorophenyl phenyl ether	7005-72-3	X	X	X	X	X
Chrysene	218-01-9	X	X	X	X	X
Chrysene-d_{12} (IS)		X	X	X	X	X
Coumaphos	56-72-4	X	ND	ND	ND	X
p-Cresidine	120-71-8	X	ND	ND	ND	X
Crotoxyphos	7700-17-6	X	ND	ND	ND	X
2-Cyclohexyl-4,6-dinitro-phenol	131-89-5	X	ND	ND	ND	LR
4,4'-DDD	72-54-8	X	X	X	X	X
4,4'-DDE	72-55-9	X	X	X	X	X
4,4'-DDT	50-29-3	X	X	X	X	X
Demeton-O	298-03-3	HS(68)	ND	ND	ND	X
Demeton-S	126-75-0	X	ND	ND	ND	X
Diallate (cis or trans)	2303-16-4	X	ND	ND	ND	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b] 3510	3520	3540/ 3541	3550	3580
2,4-Diaminotoluene	95-80-7	DC,0E(42)	ND	ND	ND	X
Dibenz(a,j)acridine	224-42-0	X	ND	ND	ND	X
Dibenz(a,h)anthracene	53-70-3	X	X	X	X	X
Dibenzofuran	132-64-9	X	X	ND	X	X
Dibenzo(a,e)pyrene	192-65-4	ND	ND	ND	ND	X
1,2-Dibromo-3-chloropropane	96-12-8	X	X	ND	ND	ND
Di-n-butyl phthalate	84-74-2	X	X	X	X	X
Dichlone	117-80-6	OE	ND	ND	ND	X
1,2-Dichlorobenzene	95-50-1	X	X	X	X	X
1,3-Dichlorobenzene	541-73-1	X	X	X	X	X
1,4-Dichlorobenzene	106-46-7	X	X	X	X	X
1,4-Dichlorobenzene-d_4 (IS)		X	X	X	X	X
3,3'-Dichlorobenzidine	91-94-1	X	X	X	X	X
2,4-Dichlorophenol	120-83-2	X	X	X	X	X
2,6-Dichlorophenol	87-65-0	X	ND	ND	ND	X
Dichlorovos	62-73-7	X	ND	ND	ND	X
Dicrotophos	141-66-2	X	ND	ND	ND	X
Dieldrin	60-57-1	X	X	X	X	X
Diethyl phthalate	84-66-2	X	X	X	X	X
Diethylstilbestrol	56-53-1	AW,0S(67)	ND	ND	ND	X
Diethyl sulfate	64-67-5	LR	ND	ND	ND	LR
Dihydrosaffrole	56312-13-1	ND	ND	ND	ND	ND
Dimethoate	60-51-5	HE,HS(31)	ND	ND	ND	X
3,3'-Dimethoxybenzidine	119-90-4	X	ND	ND	ND	LR
Dimethylaminoazobenzene	60-11-7	X	ND	ND	ND	X
7,12-Dimethylbenz(a)-anthracene	57-97-6	CP(45)	ND	ND	ND	CP
3,3'-Dimethylbenzidine	119-93-7	X	ND	ND	ND	X
α,α-Dimethylphenethylamine	122-09-8	ND	ND	ND	ND	X
2,4-Dimethylphenol	105-67-9	X	X	X	X	X
Dimethyl phthalate	131-11-3	X	X	X	X	X
1,2-Dinitrobenzene	528-29-0	X	ND	ND	ND	X
1,3-Dinitrobenzene	99-65-0	X	ND	ND	ND	X
1,4-Dinitrobenzene	100-25-4	HE(14)	ND	ND	ND	X
4,6-Dinitro-2-methylphenol	534-52-1	X	X	X	X	X
2,4-Dinitrophenol	51-28-5	X	X	X	X	X
2,4-Dinitrotoluene	121-14-2	X	X	X	X	X
2,6-Dinitrotoluene	606-20-2	X	X	X	X	X
Dinocap	39300-45-3	CP,HS(28)	ND	ND	ND	CP
Dinoseb	88-85-7	X	ND	ND	ND	X
Dioxathion	78-34-2	ND	ND	ND	ND	ND
Diphenylamine	122-39-4	X	X	X	X	X
5,5-Diphenylhydantoin	57-41-0	X	ND	ND	ND	X
1,2-Diphenylhydrazine	122-66-7	X	X	X	X	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b] 3510	3520	3540/ 3541	3550	3580
Di-n-octyl phthalate	117-84-0	X	X	X	X	X
Disulfoton	298-04-4	X	ND	ND	ND	X
Endosulfan I	959-98-8	X	X	X	X	X
Endosulfan II	33213-65-9	X	X	X	X	X
Endosulfan sulfate	1031-07-8	X	X	X	X	X
Endrin	72-20-8	X	X	X	X	X
Endrin aldehyde	7421-93-4	X	X	X	X	X
Endrin ketone	53494-70-5	X	X	ND	X	X
EPN	2104-64-5	X	ND	ND	ND	X
Ethion	563-12-2	X	ND	ND	ND	X
Ethyl carbamate	51-79-6	DC(28)	ND	ND	ND	X
Ethyl methanesulfonate	62-50-0	X	ND	ND	ND	X
Famphur	52-85-7	X	ND	ND	ND	X
Fensulfothion	115-90-2	X	ND	ND	ND	X
Fenthion	55-38-9	X	ND	ND	ND	X
Fluchloralin	33245-39-5	X	ND	ND	ND	X
Fluoranthene	206-44-0	X	X	X	X	X
Fluorene	86-73-7	X	X	X	X	X
2-Fluorobiphenyl (surr)	321-60-8	X	X	X	X	X
2-Fluorophenol (surr)	367-12-4	X	X	X	X	X
Heptachlor	76-44-8	X	X	X	X	X
Heptachlor epoxide	1024-57-3	X	X	X	X	X
Hexachlorobenzene	118-74-1	X	X	X	X	X
Hexachlorobutadiene	87-68-3	X	X	X	X	X
Hexachlorocyclopentadiene	77-47-4	X	X	X	X	X
Hexachloroethane	67-72-1	X	X	X	X	X
Hexachlorophene	70-30-4	AW,CP(62)	ND	ND	ND	CP
Hexachloropropene	1888-71-7	X	ND	ND	ND	X
Hexamethylphosphoramide	680-31-9	X	ND	ND	ND	X
Hydroquinone	123-31-9	ND	ND	ND	ND	X
Indeno(1,2,3-cd)pyrene	193-39-5	X	X	X	X	X
Isodrin	465-73-6	X	ND	ND	ND	X
Isophorone	78-59-1	X	X	X	X	X
Isosafrole	120-58-1	DC(46)	ND	ND	ND	X
Kepone	143-50-0	X	ND	ND	ND	X
Leptophos	21609-90-5	X	ND	ND	ND	X
Malathion	121-75-5	HS(5)	ND	ND	ND	X
Maleic anhydride	108-31-6	HE	ND	ND	ND	X
Mestranol	72-33-3	X	ND	ND	ND	X
Methapyrilene	91-80-5	X	ND	ND	ND	X
Methoxychlor	72-43-5	X	ND	ND	ND	X
3-Methylcholanthrene	56-49-5	X	ND	ND	ND	X
4,4'-Methylenebis (2-chloroaniline)	101-14-4	OE,OS(0)	ND	ND	ND	LR

Compounds	CAS No[a]	Appropriate Preparation Techniques[b] 3510	3520	3540/ 3541	3550	3580
4,4'-Methylenebis (N,N-dimethylaniline)	101-61-1	X	X	ND	ND	ND
Methyl methanesulfonate	66-27-3	X	ND	ND	ND	X
2-Methylnaphthalene	91-57-6	X	X	ND	X	X
Methyl parathion	298-00-0	X	ND	ND	ND	X
2-Methylphenol	95-48-7	X	ND	ND	ND	X
3-Methylphenol	108-39-4	X	ND	ND	ND	X
4-Methylphenol	106-44-5	X	ND	ND	ND	X
Mevinphos	7786-34-7	X	ND	ND	ND	X
Mexacarbate	315-18-4	HE,HS(68)	ND	ND	ND	X
Mirex	2385-85-5	X	ND	ND	ND	X
Monocrotophos	6923-22-4	HE	ND	ND	ND	X
Naled	300-76-5	X	ND	ND	ND	X
Naphthalene	91-20-3	X	X	X	X	X
Naphthalene-d_8 (IS)		X	X	X	X	X
1,4-Naphthoquinone	130-15-4	X	ND	ND	ND	X
1-Naphthylamine	134-32-7	OS(44)	ND	ND	ND	X
2-Naphthylamine	91-59-8	X	ND	ND	ND	X
Nicotine	54-11-5	DE(67)	ND	ND	ND	X
5-Nitroacenaphthene	602-87-9	X	ND	ND	ND	X
2-Nitroaniline	88-74-4	X	X	ND	X	X
3-Nitroaniline	99-09-2	X	X	ND	X	X
4-Nitroaniline	100-01-6	X	X	ND	X	X
5-Nitro-o-anisidine	99-59-2	X	ND	ND	ND	X
Nitrobenzene	98-95-3	X	X	X	X	X
Nitrobenzene-d_5 (surr)		X	X	X	X	X
4-Nitrobiphenyl	92-93-3	X	ND	ND	ND	X
Nitrofen	1836-75-5	X	ND	ND	ND	X
2-Nitrophenol	88-75-5	X	X	X	X	X
4-Nitrophenol	100-02-7	X	X	X	X	X
5-Nitro-o-toluidine	99-55-8	X	X	ND	ND	X
Nitroquinoline-1-oxide	56-57-5	X	ND	ND	ND	X
N-Nitrosodi-n-butylamine	924-16-3	X	ND	ND	ND	X
N-Nitrosodiethylamine	55-18-5	X	ND	ND	ND	X
N-Nitrosodimethylamine	62-75-9	X	X	X	X	X
N-Nitrosomethylethylamine	10595-95-6	X	ND	ND	ND	X
N-Nitrosodiphenylamine	86-30-6	X	X	X	X	X
N-Nitrosodi-n-propylamine	621-64-7	X	X	X	X	X
N-Nitrosomorpholine	59-89-2	ND	ND	ND	ND	X
N-Nitrosopiperidine	100-75-4	X	ND	ND	ND	X
N-Nitrosopyrrolidine	930-55-2	X	ND	ND	ND	X
Octamethyl pyrophosphoramide	152-16-9	LR	ND	ND	ND	LR
4,4'-Oxydianiline	101-80-4	X	ND	ND	ND	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b] 3510	3520	3540/ 3541	3550	3580
Parathion	56-38-2	X	X	ND	ND	X
Pentachlorobenzene	608-93-5	X	ND	ND	ND	X
Pentachloronitrobenzene	82-68-8	X	ND	ND	ND	X
Pentachlorophenol	87-86-5	X	X	X	X	X
Perylene-d_{12} (IS)		X	X	X	X	X
Phenacetin	62-44-2	X	ND	ND	ND	X
Phenanthrene	85-01-8	X	X	X	X	X
Phenanthrene-d_{10} (IS)		X	X	X	X	X
Phenobarbital	50-06-6	X	ND	ND	ND	X
Phenol	108-95-2	DC(28)	X	X	X	X
Phenol-d_6 (surr)		DC(28)	X	X	X	X
1,4-Phenylenediamine	106-50-3	X	ND	ND	ND	X
Phorate	298-02-2	X	ND	ND	ND	X
Phosalone	2310-17-0	HS(65)	ND	ND	ND	X
Phosmet	732-11-6	HS(15)	ND	ND	ND	X
Phosphamidon	13171-21-6	HE(63)	ND	ND	ND	X
Phthalic anhydride	85-44-9	CP,HE(1)	ND	ND	ND	CP
2-Picoline (2-Methylpyridine)	109-06-8	X	X	ND	ND	ND
Piperonyl sulfoxide	120-62-7	X	ND	ND	ND	X
Pronamide	23950-58-5	X	ND	ND	ND	X
Propylthiouracil	51-52-5	LR	ND	ND	ND	LR
Pyrene	129-00-0	X	X	X	X	X
Pyridine	110-86-1	ND	ND	ND	ND	ND
Resorcinol	108-46-3	DC,OE(10)	ND	ND	ND	X
Safrole	94-59-7	X	ND	ND	ND	X
Strychnine	57-24-9	AW,0S(55)	ND	ND	ND	X
Sulfallate	95-06-7	X	ND	ND	ND	X
Terbufos	13071-79-9	X	ND	ND	ND	X
Terphenyl-d_{14}(surr)	1718-51-0	X	X	ND	X	X
1,2,4,5-Tetrachlorobenzene	95-94-3	X	ND	ND	ND	X
2,3,4,6-Tetrachlorophenol	58-90-2	X	ND	ND	ND	X
Tetrachlorvinphos	961-11-5	X	ND	ND	ND	X
Tetraethyl dithiopyrophosphate	3689-24-5	X	X	ND	ND	ND
Tetraethyl pyrophosphate	107-49-3	X	ND	ND	ND	X
Thionazine	297-97-2	X	ND	ND	ND	X
Thiophenol (Benzenethiol)	108-98-5	X	ND	ND	ND	X
Toluene diisocyanate	584-84-9	HE(6)	ND	ND	ND	X
o-Toluidine	95-53-4	X	ND	ND	ND	X
Toxaphene	8001-35-2	X	X	X	X	X
2,4,6-Tribromophenol (surr)	118-79-6	X	X	X	X	X
1,2,4-Trichlorobenzene	120-82-1	X	X	X	X	X
2,4,5-Trichlorophenol	95-95-4	X	X	ND	X	X
2,4,6-Trichlorophenol	88-06-2	X	X	X	X	X
Trifluralin	1582-09-8	X	ND	ND	ND	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b] 3510	3520	3540/ 3541	3550	3580
2,4,5-Trimethylaniline	137-17-7	X	ND	ND	ND	X
Trimethyl phosphate	512-56-1	HE(60)	ND	ND	ND	X
1,3,5-Trinitrobenzene	99-35-4	X	ND	ND	ND	X
Tris(2,3-dibromopropyl) phosphate	126-72-7	X	ND	ND	ND	LR
Tri-p-tolyl phosphate	78-32-0	X	ND	ND	ND	X
O,O,O-Triethyl phosphorothioate	126-68-1	X	ND	ND	ND	X

[a] Chemical Abstract Service Registry Number
[b] See Sec. 1.2 for other acceptable preparation methods.

KEY TO ANALYTE LIST

IS = This compound may be used as an internal standard.
surr = This compound may be used as a surrogate.
AW = Adsorption to walls of glassware during extraction and storage.
CP = Nonreproducible chromatographic performance.
DC = Unfavorable distribution coefficient (number in parenthesis is percent recovery).
HE = Hydrolysis during extraction accelerated by acidic or basic conditions (number in parenthesis is percent recovery).
HS = Hydrolysis during storage (number in parenthesis is percent stability).
LR = Low response.
ND = Not determined.
OE = Oxidation during extraction accelerated by basic conditions (number in parenthesis is percent recovery).
OS = Oxidation during storage (number in parenthesis is percent stability).
X = Greater than 70 percent recovery by this technique.

1.2 In addition to the sample preparation methods listed in the above analyte list, Method 3542 describes sample preparation for semivolatile organic compounds in air sampled by Method 0010 (Table 11 contains surrogate performance data), Method 3545 describes an automated solvent extraction device for semivolatiles in solids (Table 12 contains performance data), and Method 3561 describes a supercritical fluid extraction of solids for PAHs (see Tables 13, 14, and 15 for performance data).

1.3 Method 8270 can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted, without derivatization, as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. See Table 1 for a list of compounds and their characteristic ions that have been evaluated.

In most cases, Method 8270 is not appropriate for the quantitation of multicomponent analytes, e.g., Aroclors, Toxaphene, Chlordane, etc., because of limited sensitivity for those analytes. When these analytes have been identified by another technique, Method 8270 is appropriate for confirmation of the presence of these analytes when concentration in the extract permits. Refer to Sec. 7.0 of Methods 8081 and 8082 for guidance on calibration and quantitation of multicomponent analytes such as the Aroclors, Toxaphene, and Chlordane.

1.4 The following compounds may require special treatment when being determined by this method:

1.4.1 Benzidine may be subject to oxidative losses during solvent concentration and its chromatographic behavior is poor.

1.4.2 Under the alkaline conditions of the extraction step from aqueous matrices, α-BHC, γ-BHC, Endosulfan I and II, and Endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected.

1.4.3 Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.

1.4.4 N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described.

1.4.5 N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine.

1.4.6 Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, benzoic acid, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

1.4.7 Pyridine may perform poorly at the GC injection port temperatures listed in the method. Lowering the injection port temperature may reduce the amount of degradation. The analyst needs to use caution if modifying the injection port temperature as the performance of other analytes may be adversely affected.

1.4.8 Toluene diisocyanate rapidly hydrolyses in water (half-life of less then 30 min.). Therefore, recoveries of this compound from aqueous matrices should not be expected. In addition, in solid matrices, toluene diisocyanate often reacts with alcohols and amines to produce urethane and ureas and consequently cannot usually coexist in a solution containing these materials.

1.4.9 In addition, analytes in the list provided above are flagged when there are limitations caused by sample preparation and/or chromatographic problems.

1.5 The estimated quantitation limit (EQL) of Method 8270 for determining an individual compound is approximately 660 µg/kg (wet weight) for soil/sediment samples, 1-200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 µg/L for ground water samples (see Table 2). EQLs will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 The samples are prepared for analysis by gas chromatography/mass spectrometry (GC/MS) using the appropriate sample preparation (refer to Method 3500) and, if necessary, sample cleanup procedures (refer to Method 3600).

2.2 The semivolatile compounds are introduced into the GC/MS by injecting the sample extract into a gas chromatograph (GC) with a narrow-bore fused-silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected to the gas chromatograph.

2.3 Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration curve.

2.4 The method includes specific calibration and quality control steps that supersede the general requirements provided in Method 8000.

3.0 INTERFERENCES

3.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

3.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between sample injections. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross-contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph/mass spectrometer system

4.1.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

4.1.2 Column - 30 m x 0.25 mm ID (or 0.32 mm ID) 1 µm film thickness silicone-coated fused-silica capillary column (J&W Scientific DB-5 or equivalent).

4.1.3 Mass spectrometer

4.1.3.1 Capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets the criteria in Table 3 when 1 µL of the GC/MS tuning standard is injected through the GC (50 ng of DFTPP).

4.1.3.2 An ion trap mass spectrometer may be used if it is capable of axial modulation to reduce ion-molecule reactions and can produce electron impact-like spectra that match those in the EPA/NIST Library. The mass spectrometer must be capable of producing a mass spectrum for DFTPP which meets the criteria in Table 3 when 5 or 50 ng are introduced.

4.1.4 GC/MS interface - Any GC-to-MS interface may be used that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria. For a narrow-bore capillary column, the interface is usually capillary-direct into the mass spectrometer source.

4.1.5 Data system - A computer system should be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer should have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software should also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

4.1.6 Guard column (optional) - (J&W Deactivated Fused Silica, 0.25 mm ID x 6 m, or equivalent) between the injection port and the analytical column joined with column joiners (Hewlett-Packard Catalog No. 5062-3556, or equivalent).

4.2 Syringe - 10-µL.

4.3 Volumetric flasks, Class A - Appropriate sizes with ground-glass stoppers.

4.4 Balance - Analytical, capable of weighing 0.0001 g.

4.5 Bottles - glass with polytetrafluoroethylene (PTFE)-lined screw caps or crimp tops.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Stock standard solutions (1000 mg/L) - Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.3.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially-prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.2 Transfer the stock standard solutions into bottles with PTFE-lined screw-caps. Store, protected from light, at -10°C or less or as recommended by the standard manufacturer. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.3.3 Stock standard solutions must be replaced after 1 year or sooner if comparison with quality control check samples indicates a problem.

5.3.4 It is recommended that nitrosamine compounds be placed together in a separate calibration mix and not combined with other calibration mixes. When using a premixed certified standard, consult the manufacturer's instructions for additional guidance.

5.3.5 Mixes with hydrochloride salts may contain hydrochloric acid, which can cause analytical difficulties. When using a premixed certified standard, consult the manufacturer's instructions for additional guidance.

5.4 Internal standard solutions - The internal standards recommended are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12} (see Table 5). Other compounds may be used as internal standards as long as the requirements given in Sec. 7.3.2 are met.

5.4.1 Dissolve 0.200 g of each compound with a small volume of carbon disulfide. Transfer to a 50 mL volumetric flask and dilute to volume with methylene chloride so that the final solvent is approximately 20% carbon disulfide. Most of the compounds are also soluble in small volumes of methanol, acetone, or toluene, except for perylene-d_{12}. The resulting solution will contain each standard at a concentration of 4,000 ng/µL. Each 1 mL sample extract undergoing analysis should be spiked with 10 µL of the internal standard solution, resulting in a concentration of 40 ng/µL of each internal standard. Store at -10°C or less when not in use. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

5.4.2 If a more sensitive mass spectrometer is employed to achieve lower detection levels, a more dilute internal standard solution may be required. Area counts of the internal standard peaks should be between 50-200% of the area of the target analytes in the mid-point calibration analysis.

5.5 GC/MS tuning standard - A methylene chloride solution containing 50 ng/µL of decafluorotriphenylphosphine (DFTPP) should be prepared. The standard should also contain 50 ng/µL each of 4,4'-DDT, pentachlorophenol, and benzidine to verify injection port inertness and GC column performance. Store at -10°C or less when not in use. If a more sensitive mass spectrometer is employed to achieve lower detection levels, a more dilute tuning solution may be necessary. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

5.6 Calibration standards - A minimum of five calibration standards should be prepared at five different concentrations. At least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining standards should correspond to the range of concentrations found in actual samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method.

5.6.1 It is the intent of EPA that all target analytes for a particular analysis be included in the calibration standard(s). These target analytes may not include the entire list of analytes (Sec. 1.1) for which the method has been demonstrated. However, the laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s).

5.6.2 Each 1-mL aliquot of calibration standard should be spiked with 10 µL of the internal standard solution prior to analysis. All standards should be stored at -10°C or less, and should be freshly prepared once a year, or sooner if check standards indicate a problem. The calibration verification standard should be prepared weekly and stored at 4°C. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

5.7 Surrogate standards - The recommended surrogates are phenol-d_5, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d_5, 2-fluorobiphenyl, and p-terphenyl-d_{14}. See Method 3500 for instructions on preparing the surrogate solutions.

5.7.1 Surrogate Standard Check: Determine what the appropriate concentration should be for the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards. It is recommended that this check be done whenever a new surrogate spiking solution is prepared.

NOTE: Method 3561 (SFE Extraction of PAHs) recommends the use of bromobenzene and p-quaterphenyl to better cover the range of PAHs listed in the method.

5.7.2 If a more sensitive mass spectrometer is employed to achieve lower detection levels, a more dilute surrogate solution may be necessary.

5.8 Matrix spike and laboratory control standards - See Method 3500 for instructions on preparing the matrix spike standard. The same standard may be used as the laboratory control standard (LCS).

5.8.1 Matrix Spike Check: Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery. It is recommended that this check be done whenever a new matrix spiking solution is prepared.

5.8.2 If a more sensitive mass spectrometer is employed to achieve lower detection levels, a more dilute matrix and LCS spiking solution may be necessary.

5.8.3 Some projects may require the spiking of the specific compounds of interest, since the spiking compounds listed in Method 3500 would not be representative of the compounds of interest required for the project. When this occurs, the matrix and LCS spiking

standards should be prepared in methanol, with each compound present at a concentration appropriate for the project.

5.9 Acetone, hexane, methylene chloride, isooctane, carbon disulfide, toluene, and other appropriate solvents - All solvents should be pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

6.2 Store the sample extracts at -10°C, protected from light, in sealed vials (e.g., screw-cap vials or crimp-capped vials) equipped with unpierced PTFE-lined septa.

7.0 PROCEDURE

7.1 Sample preparation

7.1.1 Samples are normally prepared by one of the following methods prior to GC/MS analysis.

Matrix	Methods
Air	3542
Water	3510, 3520, 3535
Soil/sediment	3540, 3541, 3545, 3550, 3560, 3561
Waste	3540, 3541, 3545, 3550, 3560, 3561, 3580

7.1.2 In very limited applications, direct injection of the sample into the GC/MS system with a 10-µL syringe may be appropriate. The detection limit is very high (approximately 10,000 µg/L). Therefore, it is only permitted where concentrations in excess of 10,000 µg/L are expected.

7.2 Extract cleanup - Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

Analytes of interest	Methods
Aniline & aniline derivatives	3620
Phenols	3630, 3640, 8041[a]
Phthalate esters	3610, 3620, 3640
Nitrosamines	3610, 3620, 3640
Organochlorine pesticides & PCBs	3610, 3620, 3630, 3660, 3665
Nitroaromatics and cyclic ketones	3620, 3640
Polynuclear aromatic hydrocarbons	3611, 3630, 3640
Haloethers	3620, 3640
Chlorinated hydrocarbons	3620, 3640
Organophosphorus pesticides	3620

Analytes of interest	Methods
Petroleum waste	3611, 3650
All base, neutral, and acid priority pollutants	3640

[a] Method 8041 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered on GC/FID.

7.3 Initial calibration

Establish the GC/MS operating conditions, using the following recommendations as guidance.

Mass range:	35-500 amu
Scan time:	1 sec/scan
Initial temperature:	40°C, hold for 4 minutes
Temperature program:	40-270°C at 10°C/min
Final temperature:	270°C, hold until benzo[g,h,i]perylene elutes
Injector temperature:	250-300°C
Transfer line temperature:	250-300°C
Source temperature:	According to manufacturer's specifications
Injector:	Grob-type, splitless
Injection volume:	1-2 µL
Carrier gas:	Hydrogen at 50 cm/sec or helium at 30 cm/sec
Ion trap only:	Set axial modulation, manifold temperature, and emission current to manufacturer's recommendations

Split injection is allowed if the sensitivity of the mass spectrometer is sufficient.

7.3.1 The GC/MS system must be hardware-tuned using a 50 ng injection of DFTPP. Analyses must not begin until the tuning criteria are met.

7.3.1.1 In the absence of specific recommendations on how to acquire the mass spectrum of DFTPP from the instrument manufacturer, the following approach has been shown to be useful: Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak.

7.3.1.2 Use the DFTPP mass intensity criteria in Table 3 as tuning acceptance criteria. Alternatively, other documented tuning criteria may be used (e.g. CLP, Method 525, or manufacturer's instructions), provided that method performance is not adversely affected.

NOTE: All subsequent standards, samples, MS/MSDs, and blanks associated with a DFTPP analysis must use the identical mass spectrometer instrument conditions.

7.3.1.3 The GC/MS tuning standard solution should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD

should not exceed 20%. (See Sec. 8.0 of Method 8081 for the percent breakdown calculation). Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible.

7.3.1.4 If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning. It may also be necessary to break off the first 6-12 in. of the capillary column. The use of a guard column (Sec. 4.1.6) between the injection port and the analytical column may help prolong analytical column performance.

7.3.2 The internal standards selected in Sec. 5.4 should permit most of the components of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 1). If interferences are noted, use the next most intense ion as the quantitation ion (i.e. for 1,4-dichlorobenzene-d_4, use 152 m/z for quantitation).

7.3.3 Analyze 1-2 µL of each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each target analyte (as indicated in Table 1). A set of at least five calibration standards is necessary (see Sec. 5.6 and Method 8000). The injection volume must be the same for all standards and sample extracts. Figure 1 shows a chromatogram of a calibration standard containing base/neutral and acid analytes.

Calculate response factors (RFs) for each target analyte relative to one of the internal standards as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Peak area (or height) of the analyte or surrogate.
A_{is} = Peak area (or height) of the internal standard.
C_s = Concentration of the analyte or surrogate, in µg/L.
C_{is} = Concentration of the internal standard, in µg/L.

7.3.4 System performance check compounds (SPCCs)

7.3.4.1 A system performance check must be performed to ensure that minimum average RFs are met before the calibration curve is used. For semivolatiles, the System Performance Check Compounds (SPCCs) are: N-nitroso-di-n-propylamine; hexachlorocyclopentadiene; 2,4-dinitrophenol; and 4-nitrophenol.

7.3.4.2 The minimum acceptable average RF for these compounds is 0.050. These SPCCs typically have very low RFs (0.1-0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

7.3.4.3 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

7.3.5 Calibration check compounds (CCCs)

7.3.5.1 The purpose of the CCCs are to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. Meeting the CCC criteria is not a substitute for successful calibration of the target analytes using one of the approaches described in Section 7.0 of Method 8000.

7.3.5.2 Calculate the mean response factor and the relative standard deviation (RSD) of the response factors for each target analyte. The RSD should be less than or equal to 15% for each target analyte. However, the RSD for each individual CCC (see Table 4) must be less than or equal to 30%.

$$\text{mean RF} = \overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n}$$

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (RF_i - \overline{RF})^2}{n-1}}$$

$$RSD = \frac{SD}{\overline{RF}} \times 100$$

7.3.5.3 If the RSD of any CCC is greater than 30%, then the chromatographic system is too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the calibration procedure beginning with Sec. 7.3.

7.3.5.4 If the CCCs are not included in the list of analytes for a project, and therefore not included in the calibration standards, refer to Sec. 7.0 of Method 8000.

7.3.6 Evaluation of retention times - The relative retention time (RRT) of each target analyte in each calibration standard should agree within 0.06 RRT units. Late-eluting target analytes usually have much better agreement.

7.3.7 Linearity of target analytes - If the RSD of any target analytes is 15% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation (Sec. 7.6.2).

7.3.7.1 If the RSD of any target analyte is greater than 15%, refer to Sec. 7.0 in Method 8000 for additional calibration options. One of the options must be applied to GC/MS calibration in this situation, or a new initial calibration must be performed.

NOTE: Method 8000 designates a linearity criterion of 20% RSD. That criterion pertains to GC and HPLC methods other than GC/MS. Method 8270 requires 15% RSD as evidence of sufficient linearity to employ an average response factor.

7.3.7.2 When the RSD exceeds 15%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc.

7.4 GC/MS calibration verification - Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

7.4.1 Prior to the analysis of samples or calibration standards, inject 50 ng of the DFTPP standard into the GC/MS system. The resultant mass spectrum for DFTPP must meet the criteria given in Table 3 before sample analysis begins. These criteria must be demonstrated each 12-hour shift during which samples are analyzed.

7.4.2 The initial calibration (Sec. 7.3) for each compound of interest should be verified once every 12 hours prior to sample analysis, using the introduction technique and conditions used for samples. This is accomplished by analyzing a calibration standard at a concentration near the midpoint concentration for the calibrating range of the GC/MS. The results from the calibration standard analysis should meet the verification acceptance criteria provided in Secs. 7.4.4 through 7.4.7.

NOTE: The DFTPP and calibration verification standard may be combined into a single standard as long as both tuning and calibration verification acceptance criteria for the project can be met without interferences.

7.4.3 A method blank should be analyzed after the calibration standard, or at any other time during the analytical shift, to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples. See Sec. 8.0 of Method 8000B for method blank performance criteria.

7.4.4 System performance check compounds (SPCCs)

7.4.4.1 A system performance check must be made during every 12-hour analytical shift. Each SPCC in the calibration verification standard must meet a minimum response factor of 0.050. This is the same check that is applied during the initial calibration.

7.4.4.2 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

7.4.5 Calibration check compounds (CCCs)

7.4.5.1 After the system performance check is met, the CCCs listed in Table 4 are used to check the validity of the initial calibration. Use percent difference when performing the average response factor model calibration. Use percent drift when calibrating using a regression fit model. Refer to Sec. 7.0 of Method 8000 for guidance on calculating percent difference and drift.

7.4.5.2 If the percent difference for each CCC is less than or equal to 20%, then the initial calibration is assumed to be valid. If the criterion is not met (i.e., greater than 20% difference or drift) for any one CCC, then corrective action must be taken prior to the analysis of samples. If the CCCs are not included in the list of analytes for a project,

and therefore not included in the calibration standards, then all analytes must meet the 20% difference or drift criterion.

7.4.5.3 Problems similar to those listed under SPCCs could affect the CCCs. If the problem cannot be corrected by other measures, a new initial calibration must be generated. The CCC criteria must be met before sample analysis begins.

7.4.6 Internal standard retention time - The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.4.7 Internal standard response - If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to +100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.5 GC/MS analysis of samples

7.5.1 It is highly recommended that sample extracts be screened on a GC/FID or GC/PID using the same type of capillary column used in the GC/MS system. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

7.5.2 Allow the sample extract to warm to room temperature. Just prior to analysis, add 10 µL of the internal standard solution to the 1-mL concentrated sample extract obtained from sample preparation.

7.5.3 Inject a 1-2 µL aliquot of the sample extract into the GC/MS system, using the same operating conditions that were used for the calibration (Sec. 7.3). The volume to be injected should contain 100 ng of base/neutral and 200 ng of acid surrogates (assuming 100% recovery), unless a more sensitive GC/MS system is being used and the surrogate solution is less concentrated then that listed in Sec. 5.7. The injection volume must be the same volume used for the calibration standards.

7.5.4 If the response for any quantitation ion exceeds the initial calibration range of the GC/MS system, the sample extract must be diluted and reanalyzed. Additional internal standard must be added to the diluted extract to maintain the same concentration as in the calibration standards (40 ng/µL, unless a more sensitive GC/MS system is being used).

NOTE: It may be a useful diagnostic tool to monitor internal standard retention times and responses (area counts) in all samples, spikes, blanks, and standards to effectively check drifting method performance, poor injection execution, and anticipate the need for system inspection and/or maintenance.

7.5.5 The use of selected ion monitoring (SIM) is acceptable for applications requiring detection limits below the normal range of electron impact mass spectrometry. However, SIM

may provide a lesser degree of confidence in the compound identification unless multiple ions are monitored for each compound.

7.6 Qualitative analysis

7.6.1 The qualitative identification of compounds determined by this method is based on retention time and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity, if less than three such ions occur in the reference spectrum. Compounds are identified when the following criteria are met.

7.6.1.1 The intensities of the characteristic ions of a compound must maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.6.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

7.6.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.6.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. Diastereomeric pairs (e.g., Aramite and Isosafrol) that may be separable by the GC should be identified, quantitated and reported as the sum of both compounds by the GC.

7.6.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

7.6.1.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.6.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the

analyses being conducted. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Guidelines for tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%.)

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

7.7 Quantitative analysis

7.7.1 Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance of the primary characteristic ion from the EICP.

7.7.2 If the RSD of a compound's response factor is 15% or less, then the concentration in the extract may be determined using the average response factor (RF) from initial calibration data (Sec. 7.3.5). See Method 8000, Sec. 7.0, for the equations describing internal standard calibration and either linear or non-linear calibrations.

7.7.3 Where applicable, the concentration of any non-target analytes identified in the sample (Sec. 7.6.2) should be estimated. The same formulae should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1.

7.7.4 The resulting concentration should be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.7.5 Quantitation of multicomponent compounds (e.g., Toxaphene, Aroclors, etc.) is beyond the scope of Method 8270. Normally, quantitation is performed using a GC/ECD, by Methods 8081 or 8082. However, Method 8270 may be used to confirm the identification of these compounds, when the concentrations are at least 10 ng/µL in the concentrated sample extract.

7.7.6 Structural isomers that produce very similar mass spectra should be quantitated as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are quantitated as isomeric pairs. Diastereomeric pairs (e.g., Aramite and Isosafrol) that may be separable by the GC should be summed and reported as the sum of both compounds.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation and/or sample introduction techniques can be found in Method 3500. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Sec. 7.0 of Method 8000 and include calibration verification and chromatographic analysis of samples. In addition, instrument QC requirements may be found in the following sections of Method 8270:

8.2.1 The GC/MS system must be tuned to meet the DFTPP criteria listed in Secs. 7.3.1 and 7.4.1.

8.2.2 There must be an initial calibration of the GC/MS system as described in Sec. 7.3.

8.2.3 The GC/MS system must meet the calibration verification acceptance criteria in Sec. 7.4, each 12 hours.

8.2.4 The RRT of the sample component must fall within the RRT window of the standard component provided in Sec. 7.6.1.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

8.4.1 Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a method blank should be analyzed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

8.4.2 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

8.4.3 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.4.4 See Method 8000, Sec. 8.0 for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0 for information on evaluating surrogate data and developing and updating surrogate limits.

8.6 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the calibration verification standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g., the column changed, a septum is changed), see the guidance in Sec 8.2 of Method 8000 regarding whether recalibration of the system must take place.

8.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 Method 8250 (the packed column version of Method 8270) was tested by 15 laboratories using organic-free reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations ranging from 5 to 1,300 µg/L. Single operator accuracy and precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 7. These values are presented as guidance only and are not intended as absolute acceptance criteria. Laboratories should generate their own acceptance criteria for capillary column method performance. (See Method 8000.)

9.2 Chromatograms from calibration standards analyzed with Day 0 and Day 7 samples were compared to detect possible deterioration of GC performance. These recoveries (using Method 3510 extraction) are presented in Table 8.

9.3 Method performance data (using Method 3541 Automated Soxhlet extraction) are presented in Table 9. Single laboratory accuracy and precision data were obtained for semivolatile organics in a clay soil by spiking at a concentration of 6 mg/kg for each compound. The spiking solution was mixed into the soil during addition and then allowed to equilibrate for approximately 1 hour prior to extraction. The spiked samples were then extracted by Method 3541 (Automated Soxhlet). Three determinations were performed and each extract was analyzed by gas chromatography/ mass spectrometry following Method 8270. The low recovery of the more volatile compounds is probably due to volatilization losses during equilibration. These data are listed in Table 10 and were taken from Reference 7.

9.4 Surrogate precision and accuracy data are presented in Table 11 from a field dynamic spiking study based on air sampling by Method 0010. The trapping media were prepared for analysis by Method 3542 and subsequently analyzed by Method 8270.

9.5 Single laboratory precision and bias data (using Method 3545 Accelerated Solvent Extraction) for semivolatile organic compounds are presented in Table 12. The samples were conditioned spiked samples prepared and certified by a commercial supplier that contained 57 semivolatile organics at three concentrations (250, 2500, and 12,500 µg/kg) on three types of soil (clay, loam and sand). Spiked samples were extracted both by the Dionex Accelerated Solvent Extraction system and by Perstorp Environmental Soxtec™ (automated Soxhlet). The data presented in Table 12 represents seven replicate extractions and analyses for each individual sample and were taken from reference 9. The average recoveries from the three matrices for all analytes and all replicates relative to the automated Soxhlet data are as follows: clay 96.8%, loam 98.7% and sand 102.1%. The average recoveries from the three concentrations also relative to the automated Soxhlet data are as follows: low-101.2%, mid-97.2% and high-99.2%.

9.6 Single laboratory precision and bias data (using Method 3561 SFE Extraction of PAHs with a variable restrictor and solid trapping material) were obtained for the method analytes by the extraction of two certified reference materials (one, EC-1, a lake sediment from Environment Canada and the other, HS-3, a marine sediment from the National Science and Engineering Research Council of Canada, both naturally-contaminated with PAHs). The SFE instrument used for these extractions was a Hewlett-Packard Model 7680. Analysis was by GC/MS. Average recoveries from six replicate extractions range from 85 to 148% (overall average of 100%) based on the certified value (or a Soxhlet value if a certified value was unavailable for a specific analyte) for the lake sediment. Average recoveries from three replicate extractions range from 73 to 133% (overall average of 92%) based on the certified value for the marine sediment. The data are found in Tables 13 and 14 and were taken from Reference 10.

9.7 Single laboratory precision and accuracy data (using Method 3561 SFE Extraction of PAHs with a fixed restrictor and liquid trapping) were obtained for twelve of the method analytes by the extraction of a certified reference material (a soil naturally contaminated with PAHs). The SFE instrument used for these extractions was a Dionex Model 703-M. Analysis was by GC/MS. Average recoveries from four replicate extractions range from 60 to 122% (overall average of 89%) based on the certified value. Following are the instrument conditions that were utilized to extract a 3.4 g sample: Pressure - 300 atm; Time - 60 min.; Extraction fluid - CO_2; Modifier - 10% 1:1 (v/v) methanol/methylene chloride; Oven temperature - 80°C; Restrictor temperature - 120°C; and, Trapping fluid - chloroform (methylene chloride has also been used). The data are found in Table 15 and were taken from Reference 11.

10.0 REFERENCES

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TABLE 1

CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
2-Picoline	3.75[a]	93	66,92
Aniline	5.68	93	66,65
Phenol	5.77	94	65,66
Bis(2-chloroethyl) ether	5.82	93	63,95
2-Chlorophenol	5.97	128	64,130
1,3-Dichlorobenzene	6.27	146	148,111
1,4-Dichlorobenzene-d_4 (IS)	6.35	152	150,115
1,4-Dichlorobenzene	6.40	146	148,111
Benzyl alcohol	6.78	108	79,77
1,2-Dichlorobenzene	6.85	146	148,111
N-Nitrosomethylethylamine	6.97	88	42,43,56
Bis(2-chloroisopropyl) ether	7.22	45	77,121
Ethyl carbamate	7.27	62	44,45,74
Thiophenol (Benzenethiol)	7.42	110	66,109,84
Methyl methanesulfonate	7.48	80	79,65,95
N-Nitrosodi-n-propylamine	7.55	70	42,101,130
Hexachloroethane	7.65	117	201,199
Maleic anhydride	7.65	54	98,53,44
Nitrobenzene	7.87	77	123,65
Isophorone	8.53	82	95,138
N-Nitrosodiethylamine	8.70	102	42,57,44,56
2-Nitrophenol	8.75	139	109,65
2,4-Dimethylphenol	9.03	122	107,121
p-Benzoquinone	9.13	108	54,82,80
Bis(2-chloroethoxy)methane	9.23	93	95,123
Benzoic acid	9.38	122	105,77
2,4-Dichlorophenol	9.48	162	164,98
Trimethyl phosphate	9.53	110	79,95,109,140
Ethyl methanesulfonate	9.62	79	109,97,45,65
1,2,4-Trichlorobenzene	9.67	180	182,145
Naphthalene-d_8 (IS)	9.75	136	68
Naphthalene	9.82	128	129,127
Hexachlorobutadiene	10.43	225	223,227
Tetraethyl pyrophosphate	11.07	99	155,127,81,109
Diethyl sulfate	11.37	139	45,59,99,111,125
4-Chloro-3-methylphenol	11.68	107	144,142
2-Methylnaphthalene	11.87	142	141
2-Methylphenol	12.40	107	108,77,79,90
Hexachloropropene	12.45	213	211,215,117,106,141
Hexachlorocyclopentadiene	12.60	237	235,272

TABLE 1
(continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
N-Nitrosopyrrolidine	12.65	100	41,42,68,69
Acetophenone	12.67	105	71,51,120
4-Methylphenol	12.82	107	108,77,79,90
2,4,6-Trichlorophenol	12.85	196	198,200
o-Toluidine	12.87	106	107,77,51,79
3-Methylphenol	12.93	107	108,77,79,90
2-Chloronaphthalene	13.30	162	127,164
N-Nitrosopiperidine	13.55	114	42,55,56,41
1,4-Phenylenediamine	13.62	108	80,53,54,52
1-Chloronaphthalene	13.65[a]	162	127,164
2-Nitroaniline	13.75	65	92,138
5-Chloro-2-methylaniline	14.28	106	141,140,77,89
Dimethyl phthalate	14.48	163	194,164
Acenaphthylene	14.57	152	151,153
2,6-Dinitrotoluene	14.62	165	63,89
Phthalic anhydride	14.62	104	76,50,148
o-Anisidine	15.00	108	80,123,52
3-Nitroaniline	15.02	138	108,92
Acenaphthene-d_{10} (IS)	15.05	164	162,160
Acenaphthene	15.13	154	153,152
2,4-Dinitrophenol	15.35	184	63,154
2,6-Dinitrophenol	15.47	162	164,126,98,63
4-Chloroaniline	15.50	127	129,65,92
Isosafrole	15.60	162	131,104,77,51
Dibenzofuran	15.63	168	139
2,4-Diaminotoluene	15.78	121	122,94,77,104
2,4-Dinitrotoluene	15.80	165	63,89
4-Nitrophenol	15.80	139	109,65
2-Naphthylamine	16.00[a]	143	115,116
1,4-Naphthoquinone	16.23	158	104,102,76,50,130
p-Cresidine	16.45	122	94,137,77,93
Dichlorovos	16.48	109	185,79,145
Diethyl phthalate	16.70	149	177,150
Fluorene	16.70	166	165,167
2,4,5-Trimethylaniline	16.70	120	135,134,91,77
N-Nitrosodi-n-butylamine	16.73	84	57,41,116,158
4-Chlorophenyl phenyl ether	16.78	204	206,141
Hydroquinone	16.93	110	81,53,55
4,6-Dinitro-2-methylphenol	17.05	198	51,105
Resorcinol	17.13	110	81,82,53,69
N-Nitrosodiphenylamine	17.17	169	168,167
Safrole	17.23	162	104,77,103,135

TABLE 1
(continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Hexamethyl phosphoramide	17.33	135	44,179,92,42
3-(Chloromethyl)pyridine hydrochloride	17.50	92	127,129,65,39
Diphenylamine	17.54[a]	169	168,167
1,2,4,5-Tetrachlorobenzene	17.97	216	214,179,108,143,218
1-Naphthylamine	18.20	143	115,89,63
1-Acetyl-2-thiourea	18.22	118	43,42,76
4-Bromophenyl phenyl ether	18.27	248	250,141
Toluene diisocyanate	18.42	174	145,173,146,132,91
2,4,5-Trichlorophenol	18.47	196	198,97,132,99
Hexachlorobenzene	18.65	284	142,249
Nicotine	18.70	84	133,161,162
Pentachlorophenol	19.25	266	264,268
5-Nitro-o-toluidine	19.27	152	77,79,106,94
Thionazine	19.35	107	96,97,143,79,68
4-Nitroaniline	19.37	138	65,108,92,80,39
Phenanthrene-d_{10} (IS)	19.55	188	94,80
Phenanthrene	19.62	178	179,176
Anthracene	19.77	178	176,179
1,4-Dinitrobenzene	19.83	168	75,50,76,92,122
Mevinphos	19.90	127	192,109,67,164
Naled	20.03	109	145,147,301,79,189
1,3-Dinitrobenzene	20.18	168	76,50,75,92,122
Diallate (cis or trans)	20.57	86	234,43,70
1,2-Dinitrobenzene	20.58	168	50,63,74
Diallate (trans or cis)	20.78	86	234,43,70
Pentachlorobenzene	21.35	250	252,108,248,215,254
5-Nitro-o-anisidine	21.50	168	79,52,138,153,77
Pentachloronitrobenzene	21.72	237	142,214,249,295,265
4-Nitroquinoline-1-oxide	21.73	174	101,128,75,116
Di-n-butyl phthalate	21.78	149	150,104
2,3,4,6-Tetrachlorophenol	21.88	232	131,230,166,234,168
Dihydrosaffrole	22.42	135	64,77
Demeton-O	22.72	88	89,60,61,115,171
Fluoranthene	23.33	202	101,203
1,3,5-Trinitrobenzene	23.68	75	74,213,120,91,63
Dicrotophos	23.82	127	67,72,109,193,237
Benzidine	23.87	184	92,185
Trifluralin	23.88	306	43,264,41,290
Bromoxynil	23.90	277	279,88,275,168
Pyrene	24.02	202	200,203
Monocrotophos	24.08	127	192,67,97,109
Phorate	24.10	75	121,97,93,260

TABLE 1
(continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Sulfallate	24.23	188	88,72,60,44
Demeton-S	24.30	88	60,81,89,114,115
Phenacetin	24.33	108	180,179,109,137,80
Dimethoate	24.70	87	93,125,143,229
Phenobarbital	24.70	204	117,232,146,161
Carbofuran	24.90	164	149,131,122
Octamethyl pyrophosphoramide	24.95	135	44,199,286,153,243
4-Aminobiphenyl	25.08	169	168,170,115
Dioxathion	25.25	97	125,270,153
Terbufos	25.35	231	57,97,153,103
α,α-Dimethylphenylamine	25.43	58	91,65,134,42
Pronamide	25.48	173	175,145,109,147
Aminoazobenzene	25.72	197	92,120,65,77
Dichlone	25.77	191	163,226,228,135,193
Dinoseb	25.83	211	163,147,117,240
Disulfoton	25.83	88	97,89,142,186
Fluchloralin	25.88	306	63,326,328,264,65
Mexacarbate	26.02	165	150,134,164,222
4,4'-Oxydianiline	26.08	200	108,171,80,65
Butyl benzyl phthalate	26.43	149	91,206
4-Nitrobiphenyl	26.55	199	152,141,169,151
Phosphamidon	26.85	127	264,72,109,138
2-Cyclohexyl-4,6-Dinitrophenol	26.87	231	185,41,193,266
Methyl parathion	27.03	109	125,263,79,93
Carbaryl	27.17	144	115,116,201
Dimethylaminoazobenzene	27.50	225	120,77,105,148,42
Propylthiouracil	27.68	170	142,114,83
Benz(a)anthracene	27.83	228	229,226
Chrysene-d_{12} (IS)	27.88	240	120,236
3,3'-Dichlorobenzidine	27.88	252	254,126
Chrysene	27.97	228	226,229
Malathion	28.08	173	125,127,93,158
Kepone	28.18	272	274,237,178,143,270
Fenthion	28.37	278	125,109,169,153
Parathion	28.40	109	97,291,139,155
Anilazine	28.47	239	241,143,178,89
Bis(2-ethylhexyl) phthalate	28.47	149	167,279
3,3'-Dimethylbenzidine	28.55	212	106,196,180
Carbophenothion	28.58	157	97,121,342,159,199
5-Nitroacenaphthene	28.73	199	152,169,141,115
Methapyrilene	28.77	97	50,191,71
Isodrin	28.95	193	66,195,263,265,147

TABLE 1
(continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Captan	29.47	79	149,77,119,117
Chlorfenvinphos	29.53	267	269,323,325,295
Crotoxyphos	29.73	127	105,193,166
Phosmet	30.03	160	77,93,317,76
EPN	30.11	157	169,185,141,323
Tetrachlorvinphos	30.27	329	109,331,79,333
Di-n-octyl phthalate	30.48	149	167,43
2-Aminoanthraquinone	30.63	223	167,195
Barban	30.83	222	51,87,224,257,153
Aramite	30.92	185	191,319,334,197,321
Benzo(b)fluoranthene	31.45	252	253,125
Nitrofen	31.48	283	285,202,139,253
Benzo(k)fluoranthene	31.55	252	253,125
Chlorobenzilate	31.77	251	139,253,111,141
Fensulfothion	31.87	293	97,308,125,292
Ethion	32.08	231	97,153,125,121
Diethylstilbestrol	32.15	268	145,107,239,121,159
Famphur	32.67	218	125,93,109,217
Tri-p-tolyl phosphate[b]	32.75	368	367,107,165,198
Benzo(a)pyrene	32.80	252	253,125
Perylene-d_{12} (IS)	33.05	264	260,265
7,12-Dimethylbenz(a)anthracene	33.25	256	241,239,120
5,5-Diphenylhydantoin	33.40	180	104,252,223,209
Captafol	33.47	79	77,80,107
Dinocap	33.47	69	41,39
Methoxychlor	33.55	227	228,152,114,274,212
2-Acetylaminofluorene	33.58	181	180,223,152
4,4'-Methylenebis(2-chloroaniline)	34.38	231	266,268,140,195
3,3'-Dimethoxybenzidine	34.47	244	201,229
3-Methylcholanthrene	35.07	268	252,253,126,134,113
Phosalone	35.23	182	184,367,121,379
Azinphos-methyl	35.25	160	132,93,104,105
Leptophos	35.28	171	377,375,77,155,379
Mirex	35.43	272	237,274,270,239,235
Tris(2,3-dibromopropyl) phosphate	35.68	201	137,119,217,219,199
Dibenz(a,j)acridine	36.40	279	280,277,250
Mestranol	36.48	277	310,174,147,242
Coumaphos	37.08	362	226,210,364,97,109
Indeno(1,2,3-cd)pyrene	39.52	276	138,227
Dibenz(a,h)anthracene	39.82	278	139,279
Benzo(g,h,i)perylene	41.43	276	138,277
1,2:4,5-Dibenzopyrene	41.60	302	151,150,300

TABLE 1
(continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Strychnine	45.15	334	334,335,333
Piperonyl sulfoxide	46.43	162	135,105,77
Hexachlorophene	47.98	196	198,209,211,406,408
Aldrin	–	66	263,220
Aroclor 1016	–	222	260,292
Aroclor 1221	–	190	224,260
Aroclor 1232	–	190	224,260
Aroclor 1242	–	222	256,292
Aroclor 1248	–	292	362,326
Aroclor 1254	–	292	362,326
Aroclor 1260	–	360	362,394
α-BHC	–	183	181,109
β-BHC	–	181	183,109
δ-BHC	–	183	181,109
γ-BHC (Lindane)	–	183	181,109
4,4'-DDD	–	235	237,165
4,4'-DDE	–	246	248,176
4,4'-DDT	–	235	237,165
Dieldrin	–	79	263,279
1,2-Diphenylhydrazine	–	77	105,182
Endosulfan I	–	195	339,341
Endosulfan II	–	337	339,341
Endosulfan sulfate	–	272	387,422
Endrin	–	263	82,81
Endrin aldehyde	–	67	345,250
Endrin ketone	–	317	67,319
2-Fluorobiphenyl (surr)	–	172	171
2-Fluorophenol (surr)	–	112	64
Heptachlor	–	100	272,274
Heptachlor epoxide	–	353	355,351
Nitrobenzene-d_5 (surr)	–	82	128,54
N-Nitrosodimethylamine	–	42	74,44
Phenol-d_6 (surr)	–	99	42,71
Terphenyl-d_{14} (surr)	–	244	122,212
2,4,6-Tribromophenol (surr)	–	330	332,141
Toxaphene	–	159	231,233

IS = internal standard
surr = surrogate
[a]Estimated retention times
[b]Substitute for the non-specific mixture, tricresyl phosphate

TABLE 2

ESTIMATED QUANTITATION LIMITS (EQLs) FOR SEMIVOLATILE ORGANICS

Compound	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[b] µg/kg
Acenaphthene	10	660
Acenaphthylene	10	660
Acetophenone	10	ND
2-Acetylaminofluorene	20	ND
1-Acetyl-2-thiourea	1000	ND
2-Aminoanthraquinone	20	ND
Aminoazobenzene	10	ND
4-Aminobiphenyl	20	ND
Anilazine	100	ND
o-Anisidine	10	ND
Anthracene	10	660
Aramite	20	ND
Azinphos-methyl	100	ND
Barban	200	ND
Benz(a)anthracene	10	660
Benzo(b)fluoranthene	10	660
Benzo(k)fluoranthene	10	660
Benzoic acid	50	3300
Benzo(g,h,i)perylene	10	660
Benzo(a)pyrene	10	660
p-Benzoquinone	10	ND
Benzyl alcohol	20	1300
Bis(2-chloroethoxy)methane	10	660
Bis(2-chloroethyl) ether	10	660
Bis(2-chloroisopropyl) ether	10	660
4-Bromophenyl phenyl ether	10	660
Bromoxynil	10	ND
Butyl benzyl phthalate	10	660
Captafol	20	ND
Captan	50	ND
Carbaryl	10	ND
Carbofuran	10	ND
Carbophenothion	10	ND
Chlorfenvinphos	20	ND
4-Chloroaniline	20	1300
Chlorobenzilate	10	ND
5-Chloro-2-methylaniline	10	ND
4-Chloro-3-methylphenol	20	1300
3-(Chloromethyl)pyridine hydrochloride	100	ND
2-Chloronaphthalene	10	660

TABLE 2 (cont.)

Compound	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[b] µg/kg
2-Chlorophenol	10	660
4-Chlorophenyl phenyl ether	10	660
Chrysene	10	660
Coumaphos	40	ND
p-Cresidine	10	ND
Crotoxyphos	20	ND
2-Cyclohexyl-4,6-dinitrophenol	100	ND
Demeton-O	10	ND
Demeton-S	10	ND
Diallate (cis or trans)	10	ND
Diallate (trans or cis)	10	ND
2,4-Diaminotoluene	20	ND
Dibenz(a,j)acridine	10	ND
Dibenz(a,h)anthracene	10	660
Dibenzofuran	10	660
Dibenzo(a,e)pyrene	10	ND
Di-n-butyl phthalate	10	ND
Dichlone	NA	ND
1,2-Dichlorobenzene	10	660
1,3-Dichlorobenzene	10	660
1,4-Dichlorobenzene	10	660
3,3'-Dichlorobenzidine	20	1300
2,4-Dichlorophenol	10	660
2,6-Dichlorophenol	10	ND
Dichlorovos	10	ND
Dicrotophos	10	ND
Diethyl phthalate	10	660
Diethylstilbestrol	20	ND
Diethyl sulfate	100	ND
Dimethoate	20	ND
3,3'-Dimethoxybenzidine	100	ND
Dimethylaminoazobenzene	10	ND
7,12-Dimethylbenz(a)anthracene	10	ND
3,3'-Dimethylbenzidine	10	ND
a,a-Dimethylphenethylamine	ND	ND
2,4-Dimethylphenol	10	660
Dimethyl phthalate	10	660
1,2-Dinitrobenzene	40	ND
1,3-Dinitrobenzene	20	ND
1,4-Dinitrobenzene	40	ND
4,6-Dinitro-2-methylphenol	50	3300
2,4-Dinitrophenol	50	3300

TABLE 2 (cont.)

Compound	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[b] µg/kg
2,4-Dinitrotoluene	10	660
2,6-Dinitrotoluene	10	660
Dinocap	100	ND
Dinoseb	20	ND
5,5-Diphenylhydantoin	20	ND
Di-n-octyl phthalate	10	660
Disulfoton	10	ND
EPN	10	ND
Ethion	10	ND
Ethyl carbamate	50	ND
Bis(2-ethylhexyl) phthalate	10	660
Ethyl methanesulfonate	20	ND
Famphur	20	ND
Fensulfothion	40	ND
Fenthion	10	ND
Fluchloralin	20	ND
Fluoranthene	10	660
Fluorene	10	660
Hexachlorobenzene	10	660
Hexachlorobutadiene	10	660
Hexachlorocyclopentadiene	10	660
Hexachloroethane	10	660
Hexachlorophene	50	ND
Hexachloropropene	10	ND
Hexamethylphosphoramide	20	ND
Hydroquinone	ND	ND
Indeno(1,2,3-cd)pyrene	10	660
Isodrin	20	ND
Isophorone	10	660
Isosafrole	10	ND
Kepone	20	ND
Leptophos	10	ND
Malathion	50	ND
Maleic anhydride	NA	ND
Mestranol	20	ND
Methapyrilene	100	ND
Methoxychlor	10	ND
3-Methylcholanthrene	10	ND
4,4'-Methylenebis(2-chloroaniline)	NA	ND
Methyl methanesulfonate	10	ND
2-Methylnaphthalene	10	660
Methyl parathion	10	ND
2-Methylphenol	10	660
3-Methylphenol	10	ND

TABLE 2 (cont.)

Compound	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[c] µg/kg
4-Methylphenol	10	660
Mevinphos	10	ND
Mexacarbate	20	ND
Mirex	10	ND
Monocrotophos	40	ND
Naled	20	ND
Naphthalene	10	660
1,4-Naphthoquinone	10	ND
1-Naphthylamine	10	ND
2-Naphthylamine	10	ND
Nicotine	20	ND
5-Nitroacenaphthene	10	ND
2-Nitroaniline	50	3300
3-Nitroaniline	50	3300
4-Nitroaniline	20	ND
5-Nitro-o-anisidine	10	ND
Nitrobenzene	10	660
4-Nitrobiphenyl	10	ND
Nitrofen	20	ND
2-Nitrophenol	10	660
4-Nitrophenol	50	3300
5-Nitro-o-toluidine	10	ND
4-Nitroquinoline-1-oxide	40	ND
N-Nitrosodi-n-butylamine	10	ND
N-Nitrosodiethylamine	20	ND
N-Nitrosodiphenylamine	10	660
N-Nitroso-di-n-propylamine	10	660
N-Nitrosopiperidine	20	ND
N-Nitrosopyrrolidine	40	ND
Octamethyl pyrophosphoramide	200	ND
4,4'-Oxydianiline	20	ND
Parathion	10	ND
Pentachlorobenzene	10	ND
Pentachloronitrobenzene	20	ND
Pentachlorophenol	50	3300
Phenacetin	20	ND
Phenanthrene	10	660
Phenobarbital	10	ND
Phenol	10	660
1,4-Phenylenediamine	10	ND
Phorate	10	ND
Phosalone	100	ND
Phosmet	40	ND
Phosphamidon	100	ND

TABLE 2 (cont.)

Compound	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[b] µg/kg
Phthalic anhydride	100	ND
2-Picoline	ND	ND
Piperonyl sulfoxide	100	ND
Pronamide	10	ND
Propylthiouracil	100	ND
Pyrene	10	660
Pyridine	ND	ND
Resorcinol	100	ND
Safrole	10	ND
Strychnine	40	ND
Sulfallate	10	ND
Terbufos	20	ND
1,2,4,5-Tetrachlorobenzene	10	ND
2,3,4,6-Tetrachlorophenol	10	ND
Tetrachlorvinphos	20	ND
Tetraethyl pyrophosphate	40	ND
Thionazine	20	ND
Thiophenol (Benzenethiol)	20	ND
o-Toluidine	10	ND
1,2,4-Trichlorobenzene	10	660
2,4,5-Trichlorophenol	10	660
2,4,6-Trichlorophenol	10	660
Trifluralin	10	ND
2,4,5-Trimethylaniline	10	ND
Trimethyl phosphate	10	ND
1,3,5-Trinitrobenzene	10	ND
Tris(2,3-dibromopropyl) phosphate	200	ND
Tri-p-tolyl phosphate(h)	10	ND
O,O,O-Triethyl phosphorothioate	NT	ND

[a] Sample EQLs are highly matrix-dependent. The EQLs listed here are provided for guidance and may not always be achievable.

[b] EQLs listed for soil/sediment are based on wet weight. Normally, data are reported on a dry weight basis, therefore, EQLs will be higher based on the % dry weight of each sample. These EQLs are based on a 30-g sample and gel permeation chromatography cleanup.

ND = Not Determined
NA = Not Applicable
NT = Not Tested

Other Matrices	Factor[c]
High-concentration soil and sludges by ultrasonic extractor	7.5
Non-water miscible waste	75

[c] EQL = (EQL for Low Soil/Sediment given above in Table 2) x (Factor)

TABLE 3

DFTPP KEY IONS AND ION ABUNDANCE CRITERIA[a,b]

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	40-60% of mass 198
197	< 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	> 40% of mass 198
443	17-23% of mass 442

[a] Data taken from Reference 3.
[b] Alternate tuning criteria may be used, (e.g., CLP, Method 525, or manufacturers' instructions), provided that method performance is not adversely affected.

TABLE 4

CALIBRATION CHECK COMPOUNDS (CCC)

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
Diphenylamine	Phenol
Di-n-octyl phthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

TABLE 5

SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}
Aniline	Acetophenone	Acenaphthene
Benzyl alcohol	Benzoic acid	Acenaphthylene
Bis(2-chloroethyl) ether	Bis(2-chloroethoxy)methane	1-Chloronaphthalene
Bis(2-chloroisopropyl) ether	4-Chloroaniline	2-Chloronaphthalene
2-Chlorophenol	4-Chloro-3-methylphenol	4-Chlorophenyl phenyl ether
1,3-Dichlorobenzene	2,4-Dichlorophenol	Dibenzofuran
1,4-Dichlorobenzene	2,6-Dichlorophenol	Diethyl phthalate
1,2-Dichlorobenzene	α,α-Dimethyl-phenethylamine	Dimethyl phthalate
Ethyl methanesulfonate	2,4-Dimethylphenol	2,4-Dinitrophenol
2-Fluorophenol (surr)	Hexachlorobutadiene	2,4-Dinitrotoluene
Hexachloroethane	Isophorone	2,6-Dinitrotoluene
Methyl methanesulfonate	2-Methylnaphthalene	Fluorene
2-Methylphenol	Naphthalene	2-Fluorobiphenyl (surr)
4-Methylphenol	Nitrobenzene	Hexachlorocyclo-pentadiene
N-Nitrosodimethylamine	Nitrobenzene-d_5 (surr)	1-Naphthylamine
N-Nitroso-di-n-propyl-amine	2-Nitrophenol	2-Naphthylamine
Phenol	N-Nitrosodi-n-butylamine	2-Nitroaniline
Phenol-d_6 (surr)	N-Nitrosopiperidine	3-Nitroaniline
2-Picoline	1,2,4-Trichlorobenzene	4-Nitroaniline
		4-Nitrophenol
		Pentachlorobenzene
		1,2,4,5-Tetra-chlorobenzene
		2,3,4,6-Tetra-chlorophenol
		2,4,6-Tribromo-phenol (surr)
		2,4,6-Trichloro-phenol
		2,4,5-Trichloro-phenol

(surr) = surrogate

TABLE 5
(continued)

Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
4-Aminobiphenyl	Benzidine	Benzo(b)fluor-anthene
Anthracene	Benzo(a)anthracene	Benzo(k)fluor-anthene
4-Bromophenyl phenyl ether	Bis(2-ethylhexyl) phthalate	Benzo(g,h,i)-perylene
Di-n-butyl phthalate	Butyl benzyl phthalate	Benzo(a)pyrene
4,6-Dinitro-2-methyl-phenol	Chrysene	Dibenz(a,j)acridine
Diphenylamine	3,3'-Dichlorobenzidine	Dibenz(a,h)-anthracene
Fluoranthene	p-Dimethylaminoazobenzene	
Hexachlorobenzene	Pyrene	
N-Nitrosodiphenylamine	Terphenyl-d_{14} (surr)	
Pentachlorophenol	7,12-Dimethylbenz-(a)anthracene	
Pentachloronitrobenzene	Di-n-octyl phthalate	
Phenacetin	Indeno(1,2,3-cd) pyrene	
Phenanthrene	3-Methylchol-anthrene	
Pronamide		

(surr) = surrogate

TABLE 6

MULTILABORATORY PERFORMANCE DATA[a]

Compound	Test conc. (µg/L)	Limit for s (µg/L)	Range for $\bar{x}$ (µg/L)	Range P_t, P_s (%)
Acenaphthene	100	27.6	60.1-132.3	47-145
Acenaphthylene	100	40.2	53.5-126.0	33-145
Aldrin	100	39.0	7.2-152.2	D-166
Anthracene	100	32.0	43.4-118.0	27-133
Benz(a)anthracene	100	27.6	41.8-133.0	33-143
Benzo(b)fluoranthene	100	38.8	42.0-140.4	24-159
Benzo(k)fluoranthene	100	32.3	25.2-145.7	11-162
Benzo(a)pyrene	100	39.0	31.7-148.0	17-163
Benzo(g,h,i)perylene	100	58.9	D-195.0	D-219
Benzyl butyl phthalate	100	23.4	D-139.9	D-152
β-BHC	100	31.5	41.5-130.6	24-149
δ-BHC	100	21.6	D-100.0	D-110
Bis(2-chloroethyl) ether	100	55.0	42.9-126.0	12-158
Bis(2-chloroethoxy)methane	100	34.5	49.2-164.7	33-184
Bis(2-chloroisopropyl) ether	100	46.3	62.8-138.6	36-166
Bis(2-ethylhexyl) phthalate	100	41.1	28.9-136.8	8-158
4-Bromophenyl phenyl ether	100	23.0	64.9-114.4	53-127
2-Chloronaphthalene	100	13.0	64.5-113.5	60-118
4-Chlorophenyl phenyl ether	100	33.4	38.4-144.7	25-158
Chrysene	100	48.3	44.1-139.9	17-168
4,4'-DDD	100	31.0	D-134.5	D-145
4,4'-DDE	100	32.0	19.2-119.7	4-136
4,4'-DDT	100	61.6	D-170.6	D-203
Dibenzo(a,h)anthracene	100	70.0	D-199.7	D-227
Di-n-butyl phthalate	100	16.7	8.4-111.0	1-118
1,2-Dichlorobenzene	100	30.9	48.6-112.0	32-129
1,3-Dichlorobenzene	100	41.7	16.7-153.9	D-172
1,4-Dichlorobenzene	100	32.1	37.3-105.7	20-124
3,3'-Dichlorobenzidine	100	71.4	8.2-212.5	D-262
Dieldrin	100	30.7	44.3-119.3	29-136
Diethyl phthalate	100	26.5	D-100.0	D-114
Dimethyl phthalate	100	23.2	D-100.0	D-112
2,4-Dinitrotoluene	100	21.8	47.5-126.9	39-139
2,6-Dinitrotoluene	100	29.6	68.1-136.7	50-158
Di-n-octyl phthalate	100	31.4	18.6-131.8	4-146
Endosulfan sulfate	100	16.7	D-103.5	D-107
Endrin aldehyde	100	32.5	D-188.8	D-209
Fluoranthene	100	32.8	42.9-121.3	26-137
Fluorene	100	20.7	71.6-108.4	59-121
Heptachlor	100	37.2	D-172.2	D-192

TABLE 6
(continued)

Compound	Test conc. (µg/L)	Limit for s (µg/L)	Range for $\bar{x}$ (µg/L)	Range p, p_s (%)
Heptachlor epoxide	100	54.7	70.9-109.4	26-155
Hexachlorobenzene	100	24.9	7.8-141.5	D-152
Hexachlorobutadiene	100	26.3	37.8-102.2	24-116
Hexachloroethane	100	24.5	55.2-100.0	40-113
Indeno(1,2,3-cd)pyrene	100	44.6	D-150.9	D-171
Isophorone	100	63.3	46.6-180.2	21-196
Naphthalene	100	30.1	35.6-119.6	21-133
Nitrobenzene	100	39.3	54.3-157.6	35-180
N-Nitrosodi-n-propylamine	100	55.4	13.6-197.9	D-230
Aroclor 1260	100	54.2	19.3-121.0	D-164
Phenanthrene	100	20.6	65.2-108.7	54-120
Pyrene	100	25.2	69.6-100.0	52-115
1,2,4-Trichlorobenzene	100	28.1	57.3-129.2	44-142
4-Chloro-3-methylphenol	100	37.2	40.8-127.9	22-147
2-Chlorophenol	100	28.7	36.2-120.4	23-134
2,4-Chlorophenol	100	26.4	52.5-121.7	39-135
2,4-Dimethylphenol	100	26.1	41.8-109.0	32-119
2,4-Dinitrophenol	100	49.8	D-172.9	D-191
2-Methyl-4,6-dinitrophenol	100	93.2	53.0-100.0	D-181
2-Nitrophenol	100	35.2	45.0-166.7	29-182
4-Nitrophenol	100	47.2	13.0-106.5	D-132
Pentachlorophenol	100	48.9	38.1-151.8	14-176
Phenol	100	22.6	16.6-100.0	5-112
2,4,6-Trichlorophenol	100	31.7	52.4-129.2	37-144

s = Standard deviation of four recovery measurements, in µg/L

$\bar{x}$ = Average recovery for four recovery measurements, in µg/L

p, p_s = Measured percent recovery

D = Detected; result must be greater than zero

* Criteria from 40 CFR Part 136 for Method 625, using a packed GC column. These criteria are based directly on the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7. These values are for guidance only. Appropriate derivation of acceptance criteria for capillary columns should result in much narrower ranges. See Method 8000 for information on developing and updating acceptance criteria for method performance.

TABLE 7

METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Compound	Accuracy, as recovery, x' (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S' (µg/L)
Acenaphthene	0.96C+0.19	0.15$\bar{x}$-0.12	0.21$\bar{x}$-0.67
Acenaphthylene	0.89C+0.74	0.24$\bar{x}$-1.06	0.26$\bar{x}$-0.54
Aldrin	0.78C+1.66	0.27$\bar{x}$-1.28	0.43$\bar{x}$+1.13
Anthracene	0.80C+0.68	0.21$\bar{x}$-0.32	0.27$\bar{x}$-0.64
Benz(a)anthracene	0.88C-0.60	0.15$\bar{x}$+0.93	0.26$\bar{x}$-0.21
Benzo(b)fluoranthene	0.93C-1.80	0.22$\bar{x}$+0.43	0.29$\bar{x}$+0.96
Benzo(k)fluoranthene	0.87C-1.56	0.19$\bar{x}$+1.03	0.35$\bar{x}$+0.40
Benzo(a)pyrene	0.90C-0.13	0.22$\bar{x}$+0.48	0.32$\bar{x}$+1.35
Benzo(g,h,i)perylene	0.98C-0.86	0.29$\bar{x}$+2.40	0.51$\bar{x}$-0.44
Benzyl butyl phthalate	0.66C-1.68	0.18$\bar{x}$+0.94	0.53$\bar{x}$+0.92
β-BHC	0.87C-0.94	0.20$\bar{x}$-0.58	0.30$\bar{x}$+1.94
δ-BHC	0.29C-1.09	0.34$\bar{x}$+0.86	0.93$\bar{x}$-0.17
Bis(2-chloroethyl) ether	0.86C-1.54	0.35$\bar{x}$-0.99	0.35$\bar{x}$+0.10
Bis(2-chloroethoxy)methane	1.12C-5.04	0.16$\bar{x}$+1.34	0.26$\bar{x}$+2.01
Bis(2-chloroisopropyl) ether	1.03C-2.31	0.24$\bar{x}$+0.28	0.25$\bar{x}$+1.04
Bis(2-ethylhexyl) phthalate	0.84C-1.18	0.26$\bar{x}$+0.73	0.36$\bar{x}$+0.67
4-Bromophenyl phenyl ether	0.91C-1.34	0.13$\bar{x}$+0.66	0.16$\bar{x}$+0.66
2-Chloronaphthalene	0.89C+0.01	0.07$\bar{x}$+0.52	0.13$\bar{x}$+0.34
4-Chlorophenyl phenyl ether	0.91C+0.53	0.20$\bar{x}$-0.94	0.30x-0.46
Chrysene	0.93C-1.00	0.28$\bar{x}$+0.13	0.33$\bar{x}$-0.09
4,4'-DDD	0.56C-0.40	0.29$\bar{x}$-0.32	0.66$\bar{x}$-0.96
4,4'-DDE	0.70C-0.54	0.26$\bar{x}$-1.17	0.39$\bar{x}$-1.04
4,4'-DDT	0.79C-3.28	0.42$\bar{x}$+0.19	0.65$\bar{x}$-0.58
Dibenzo(a,h)anthracene	0.88C+4.72	0.30$\bar{x}$+8.51	0.59$\bar{x}$+0.25
Di-n-butyl phthalate	0.59C+0.71	0.13$\bar{x}$+1.16	0.39$\bar{x}$+0.60
1,2-Dichlorobenzene	0.80C+0.28	0.20$\bar{x}$+0.47	0.24$\bar{x}$+0.39
1,3-Dichlorobenzene	0.86C-0.70	0.25$\bar{x}$+0.68	0.41$\bar{x}$+0.11
1,4-Dichlorobenzene	0.73C-1.47	0.24$\bar{x}$+0.23	0.29$\bar{x}$+0.36
3,3'-Dichlorobenzidine	1.23C-12.65	0.28$\bar{x}$+7.33	0.47$\bar{x}$+3.45
Dieldrin	0.82C-0.16	0.20$\bar{x}$-0.16	0.26$\bar{x}$-0.07
Diethyl phthalate	0.43C+1.00	0.28$\bar{x}$+1.44	0.52$\bar{x}$+0.22
Dimethyl phthalate	0.20C+1.03	0.54$\bar{x}$+0.19	1.05$\bar{x}$-0.92
2,4-Dinitrotoluene	0.92C-4.81	0.12$\bar{x}$+1.06	0.21$\bar{x}$+1.50
2,6-Dinitrotoluene	1.06C-3.60	0.14$\bar{x}$+1.26	0.19$\bar{x}$+0.35
Di-n-octyl phthalate	0.76C-0.79	0.21$\bar{x}$+1.19	0.37$\bar{x}$+1.19
Endosulfan sulfate	0.39C+0.41	0.12$\bar{x}$+2.47	0.63$\bar{x}$-1.03
Endrin aldehyde	0.76C-3.86	0.18$\bar{x}$+3.91	0.73$\bar{x}$-0.62
Fluoranthene	0.81C+1.10	0.22$\bar{x}$-0.73	0.28$\bar{x}$-0.60
Fluorene	0.90C-0.00	0.12$\bar{x}$+0.26	0.13$\bar{x}$+0.61
Heptachlor	0.87C-2.97	0.24$\bar{x}$-0.56	0.50$\bar{x}$-0.23
Heptachlor epoxide	0.92C-1.87	0.33$\bar{x}$-0.46	0.28$\bar{x}$+0.64

TABLE 7
(continued)

Compound	Accuracy, as recovery, x' (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S' (µg/L)
Hexachlorobenzene	0.74C+0.66	0.18$\bar{x}$-0.10	0.43$\bar{x}$-0.52
Hexachlorobutadiene	0.71C-1.01	0.19$\bar{x}$+0.92	0.26$\bar{x}$+0.49
Hexachloroethane	0.73C-0.83	0.17$\bar{x}$+0.67	0.17$\bar{x}$+0.80
Indeno(1,2,3-cd)pyrene	0.78C-3.10	0.29$\bar{x}$+1.46	0.50$\bar{x}$-0.44
Isophorone	1.12C+1.41	0.27$\bar{x}$+0.77	0.33$\bar{x}$+0.26
Naphthalene	0.76C+1.58	0.21$\bar{x}$-0.41	0.30$\bar{x}$-0.68
Nitrobenzene	1.09C-3.05	0.19$\bar{x}$+0.92	0.27$\bar{x}$+0.21
N-Nitrosodi-n-propylamine	1.12C-6.22	0.27$\bar{x}$+0.68	0.44$\bar{x}$+0.47
Aroclor 1260	0.81C-10.86	0.35$\bar{x}$+3.61	0.43$\bar{x}$+1.82
Phenanthrene	0.87C+0.06	0.12$\bar{x}$+0.57	0.15$\bar{x}$+0.25
Pyrene	0.84C-0.16	0.16$\bar{x}$+0.06	0.15$\bar{x}$+0.31
1,2,4-Trichlorobenzene	0.94C-0.79	0.15$\bar{x}$+0.85	0.21$\bar{x}$+0.39
4-Chloro-3-methylphenol	0.84C+0.35	0.23$\bar{x}$+0.75	0.29$\bar{x}$+1.31
2-Chlorophenol	0.78C+0.29	0.18$\bar{x}$+1.46	0.28$\bar{x}$+0.97
2,4-Dichlorophenol	0.87C-0.13	0.15$\bar{x}$+1.25	0.21$\bar{x}$+1.28
2,4-Dimethylphenol	0.71C+4.41	0.16$\bar{x}$+1.21	0.22$\bar{x}$+1.31
2,4-Dinitrophenol	0.81C-18.04	0.38$\bar{x}$+2.36	0.42$\bar{x}$+26.29
2-Methyl-4,6-dinitrophenol	1.04C-28.04	0.10$\bar{x}$+42.29	0.26$\bar{x}$+23.10
2-Nitrophenol	0.07C-1.15	0.16$\bar{x}$+1.94	0.27$\bar{x}$+2.60
4-Nitrophenol	0.61C-1.22	0.38$\bar{x}$+2.57	0.44$\bar{x}$+3.24
Pentachlorophenol	0.93C+1.99	0.24$\bar{x}$+3.03	0.30$\bar{x}$+4.33
Phenol	0.43C+1.26	0.26$\bar{x}$+0.73	0.35$\bar{x}$+0.58
2,4,6-Trichlorophenol	0.91C-0.18	0.16$\bar{x}$+2.22	0.22$\bar{x}$+1.81

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in µg/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{x}$, in µg/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{x}$, in µg/L.

C = True value for the concentration, in µg/L.

$\bar{x}$ = Average recovery found for measurements of samples containing a concentration of C, in µg/L.

* Criteria from 40 CFR Part 136 for Method 625, using a packed GC column. These criteria are based directly on the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7. These values are for guidance only. Appropriate derivation of acceptance criteria for capillary columns should result in much narrower ranges. See Method 8000 for information on developing and updating acceptance criteria for method performance.

TABLE 8

EXTRACTION EFFICIENCY AND AQUEOUS STABILITY RESULTS

Compound	Percent Recovery on Day 0		Percent Recovery on Day 7	
	Mean	RSD	Mean	RSD
3-Amino-9-ethylcarbazole	80	8	73	3
4-Chloro-1,2-phenylenediamine	91	1	108	4
4-Chloro-1,3-phenylenediamine	84	3	70	3
1,2-Dibromo-3-chloropropane	97	2	98	5
Dinoseb	99	3	97	6
Parathion	100	2	103	4
4,4'-Methylenebis(N,N-dimethylaniline)	108	4	90	4
5-Nitro-o-toluidine	99	10	93	4
2-Picoline	80	4	83	4
Tetraethyl dithiopyrophosphate	92	7	70	1

Data taken from Reference 6.

TABLE 9

MEAN PERCENT RECOVERIES AND PERCENT RSD VALUES FOR SEMIVOLATILE ORGANICS FROM SPIKED CLAY SOIL AND TOPSOIL BY AUTOMATED SOXHLET EXTRACTION (METHOD 3541) WITH HEXANE-ACETONE (1:1)[a]

Compound	Clay Soil		Topsoil	
	Mean Recovery	RSD	Mean Recovery	RSD
1,3-Dichlorobenzene	0	–	0	–
1,2-Dichlorobenzene	0	–	0	–
Nitrobenzene	0	–	0	–
Benzal chloride	0	–	0	–
Benzotrichloride	0	–	0	–
4-Chloro-2-nitrotoluene	0	–	0	–
Hexachlorocyclopentadiene	4.1	15	7.8	23
2,4-Dichloronitrobenzene	35.2	7.6	21.2	15
3,4-Dichloronitrobenzene	34.9	15	20.4	11
Pentachlorobenzene	13.7	7.3	14.8	13
2,3,4,5-Tetrachloronitrobenzene	55.9	6.7	50.4	6.0
Benefin	62.6	4.8	62.7	2.9
alpha-BHC	58.2	7.3	54.8	4.8
Hexachlorobenzene	26.9	13	25.1	5.7
delta-BHC	95.8	4.6	99.2	1.3
Heptachlor	46.9	9.2	49.1	6.3
Aldrin	97.7	12	102	7.4
Isopropalin	102	4.3	105	2.3
Heptachlor epoxide	90.4	4.4	93.6	2.4
trans-Chlordane	90.1	4.5	95.0	2.3
Endosulfan I	96.3	4.4	101	2.2
Dieldrin	129	4.7	104	1.9
2,5-Dichlorophenyl-4-nitrophenyl ether	110	4.1	112	2.1
Endrin	102	4.5	106	3.7
Endosulfan II	104	4.1	105	0.4
p,p'-DDT	134	2.1	111	2.0
2,3,6-Trichlorophenyl-4'-nitrophenyl ether	110	4.8	110	2.8
2,3,4-Trichlorophenyl-4'-nitrophenyl ether	112	4.4	112	3.3
Mirex	104	5.3	108	2.2

[a] The operating conditions for the Soxtec apparatus were as follows: immersion time 45 min; extraction time 45 min; the sample size was 10 g; the spiking concentration was 500 ng/g, except for the surrogate compounds at 1000 ng/g, 2,5-Dichlorophenyl-4-nitrophenyl ether, 2,3,6-Trichlorophenyl-4-nitrophenyl ether, and 2,3,4-Trichlorophenyl-4-nitrophenyl ether at 1500 ng/g, Nitrobenzene at 2000 ng/g, and 1,3-Dichlorobenzene and 1,2-Dichlorobenzene at 5000 ng/g.

TABLE 10

SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR THE EXTRACTION OF SEMIVOLATILE ORGANICS FROM SPIKED CLAY BY AUTOMATED SOXHLET (METHOD 3541)[a]

Compound	Mean Recovery	RSD
Phenol	47.8	5.6
Bis(2-chloroethyl)ether	25.4	13
2-Chlorophenol	42.7	4.3
Benzyl alcohol	55.9	7.2
2-Methylphenol	17.6	6.6
Bis(2-chloroisopropyl)ether	15.0	15
4-Methylphenol	23.4	6.7
N-Nitroso-di-n-propylamine	41.4	6.2
Nitrobenzene	28.2	7.7
Isophorone	56.1	4.2
2-Nitrophenol	36.0	6.5
2,4-Dimethylphenol	50.1	5.7
Benzoic acid	40.6	7.7
Bis(2-chloroethoxy)methane	44.1	3.0
2,4-Dichlorophenol	55.6	4.6
1,2,4-Trichlorobenzene	18.1	31
Naphthalene	26.2	15
4-Chloroaniline	55.7	12
4-Chloro-3-methylphenol	65.1	5.1
2-Methylnaphthalene	47.0	8.6
Hexachlorocyclopentadiene	19.3	19
2,4,6-Trichlorophenol	70.2	6.3
2,4,5-Trichlorophenol	26.8	2.9
2-Chloronaphthalene	61.2	6.0
2-Nitroaniline	73.8	6.0
Dimethyl phthalate	74.6	5.2
Acenaphthylene	71.6	5.7
3-Nitroaniline	77.6	5.3
Acenaphthene	79.2	4.0
2,4-Dinitrophenol	91.9	8.9
4-Nitrophenol	62.9	16
Dibenzofuran	82.1	5.9
2,4-Dinitrotoluene	84.2	5.4
2,6-Dinitrotoluene	68.3	5.8
Diethyl phthalate	74.9	5.4
4-Chlorophenyl-phenyl ether	67.2	3.2
Fluorene	82.1	3.4
4-Nitroaniline	79.0	7.9

TABLE 10
(continued)

Compound	Mean Recovery	RSD
4,6-Dinitro-2-methylphenol	63.4	6.8
N-Nitrosodiphenylamine	77.0	3.4
4-Bromophenyl-phenyl ether	62.4	3.0
Hexachlorobenzene	72.6	3.7
Pentachlorophenol	62.7	6.1
Phenanthrene	83.9	5.4
Anthracene	96.3	3.9
Di-n-butyl phthalate	78.3	40
Fluoranthene	87.7	6.9
Pyrene	102	0.8
Butyl benzyl phthalate	66.3	5.2
3,3'-Dichlorobenzidine	25.2	11
Benzo(a)anthracene	73.4	3.8
Bis(2-ethylhexyl) phthalate	77.2	4.8
Chrysene	76.2	4.4
Di-n-octyl phthalate	83.1	4.8
Benzo(b)fluoranthene	82.7	5.0
Benzo(k)fluoranthene	71.7	4.1
Benzo(a)pyrene	71.7	4.1
Indeno(1,2,3-cd)pyrene	72.2	4.3
Dibenzo(a,h)anthracene	66.7	6.3
Benzo(g,h,i)perylene	63.9	8.0
1,2-Dichlorobenzene	0	--
1,3-Dichlorobenzene	0	--
1,4-Dichlorobenzene	0	--
Hexachloroethane	0	--
Hexachlorobutadiene	0	--

* Number of determinations was three. The operating conditions for the Soxtec apparatus were as follows: immersion time 45 min; extraction time 45 min; the sample size was 10 g clay soil; the spike concentration was 6 mg/kg per compound. The sample was allowed to equilibrate 1 hour after spiking.

Data taken from Reference 7

TABLE 11

PRECISION AND BIAS VALUES FOR METHOD 3542[1]

Compound	Mean Recovery	Standard Deviation	Relative Standard Deviation Percent
2-Fluorophenol	74.6	28.6	38.3
Phenol-d_5	77.8	27.7	35.6
Nitrobenzene-d_5	65.6	32.5	49.6
2-Fluorobiphenyl	75.9	30.3	39.9
2,4,6-Tribromophenol	67.0	34.0	50.7
Terphenyl-d_{14}	78.6	32.4	41.3

[1] The surrogate values shown in Table 11 represent mean recoveries for surrogates in all Method 0010 matrices in a field dynamic spiking study.

TABLE 12

ACCELERATED SOLVENT EXTRACTION (METHOD 3545) RECOVERY VALUES
AS PERCENT OF SOXTEC™

COMPOUND	CLAY			LOAM			SAND			AVE
	LOW	MID	HIGH	LOW	MID	HIGH	LOW	MID	HIGH	
Phenol	93.3	78.7	135.9	73.9	82.8	124.8	108.8	130.6	89.7	**102.0**
Bis(2-chloroethyl) ether	102.1	65.1	109.1	96.0	88.0	103.8	122.3	119.9	90.8	**101.9**
2-Chlorophenol	100.8	82.6	115.0	93.8	88.9	111.1	115.0	115.3	91.9	**101.6**
1,3-Dichlorobenzene	127.7	129.7	110.0	*384.2	129.9	119.0	*241.3	*163.7	107.1	**120.6**
1,4-Dichlorobenzene	127.9	127.0	110.5	*385.9	127.8	116.4	*309.6	*164.1	105.8	**119.2**
1,2-Dichlorobenzene	116.8	115.8	101.3	*159.2	113.4	105.5	*189.3	134.0	100.4	**112.5**
2-Methylphenol	98.9	82.1	119.7	87.6	89.4	111.0	133.2	128.0	92.1	**104.7**
Bis(2-chloroisopropyl)ether	109.4	71.5	108.0	81.8	81.0	88.6	118.1	148.3	94.8	**100.2**
o-Toluidine	100.0	89.7	117.2	100.0	*152.5	120.3	100.0	*199.5	102.7	**110.3**
N-Nitroso-di-n-propylamine	103.0	79.1	107.7	83.9	86.1	96.2	109.9	123.3	91.4	**98.1**
Hexachloroethane	97.1	125.1	111.0	*245.4	117.1	128.1	*568.7	147.9	103.7	**118.6**
Nitrobenzene	104.8	82.4	106.6	86.8	84.6	101.7	119.7	122.1	93.3	**100.2**
Isophorone	100.0	86.4	98.2	87.1	87.5	109.7	135.5	118.4	92.7	**101.7**
2,4-Dimethylphenol	100.0	104.5	140.0	100.0	114.4	123.1	100.0	*180.6	96.3	**109.8**
2-Nitrophenol	80.7	80.5	107.9	91.4	86.7	103.2	122.1	107.1	87.0	**96.3**
Bis(chloroethoxy)methane	94.4	80.8	94.7	86.5	84.4	99.6	130.6	110.7	93.2	**97.2**
2,4-Dichlorophenol	88.9	87.8	111.4	85.9	87.6	103.5	123.3	107.0	92.1	**98.6**
1,2,4-Trichlorobenzene	98.0	97.8	98.8	123.0	93.7	94.5	137.0	99.4	95.3	**104.2**
Naphthalene	101.7	97.2	123.6	113.2	102.9	129.5	*174.5	114.0	89.8	**106.1**
4-Chloroaniline	100.0	*150.2	*162.4	100.0	125.5	*263.6	100.0	*250.8	114.9	**108.1**
Hexachlorobutadiene	101.1	98.7	102.2	124.1	90.3	98.0	134.9	98.1	96.8	**104.7**
4-Chlom-3-methylphenol	90.4	80.2	114.7	79.0	85.2	109.8	131.6	116.2	90.1	**99.7**
2-Methylnaphthalene	93.2	89.9	94.6	104.1	92.2	105.9	146.2	99.1	93.3	**102.1**
Hexachlorocyclopentadiene	100.0	100.0	0.0	100.0	100.0	6.8	100.0	100.0	*238.3	**75.8**
2,4,6-Trichlorophenol	94.6	90.0	112.0	84.2	91.2	103.6	101.6	95.9	89.8	**95.9**
2,4,5-Trichlorophenol	84.4	91.9	109.6	96.1	80.7	103.6	108.9	83.9	87.9	**94.1**
2-Chloronaphthalene	100.0	91.3	93.6	97.6	93.4	98.3	106.6	93.0	92.0	**96.2**
2-Nitroaniline	90.0	83.4	97.4	71.3	88.4	89.9	112.1	113.3	87.7	**92.6**
2,6-Dinitrotoluene	83.1	90.6	91.6	86.4	90.6	90.3	104.3	84.7	90.9	**90.3**
Acenaphthylene	104.9	95.9	100.5	99.0	97.9	108.8	118.5	97.8	92.0	**101.7**
3-Nitroaniline	*224.0	115.6	97.6	100.0	111.8	107.8	0.0	111.7	99.0	**92.9**
Acenaphthene	102.1	92.6	97.6	97.2	96.9	104.4	114.2	92.0	89.0	**98.4**
4-Nitrophenol	0.0	93.2	121.5	18.1	87.1	116.6	69.1	90.5	84.5	**75.6**
2,4-Dinitrotoluene	73.9	91.9	100.2	84.7	93.8	98.9	100.9	84.3	87.3	**90.7**

TABLE 12 (cont.)

ACCELERATED SOLVENT EXTRACTION (METHOD 3545) RECOVERY VALUES
AS PERCENT OF SOXTEC™

COMPOUND	CLAY			LOAM			SAND			AVE
	LOW	MID	HIGH	LOW	MID	HIGH	LOW	MID	HIGH	
Dibenzofuran	89.5	91.7	109.3	98.5	92.2	111.4	113.8	92.7	90.4	**98.8**
4-Chlorophenyl phenyl ether	83.0	94.5	98.7	95.7	94.3	94.2	111.4	87.7	90.3	**94.4**
Fluorene	85.2	94.9	89.2	102.0	95.5	93.8	121.3	85.7	90.9	**95.4**
4-Nitroaniline	77.8	114.8	94.5	129.6	103.6	95.4	*154.1	89.3	87.5	**99.1**
N-Nitrosodiphenylamine	82.6	96.7	93.8	92.9	93.4	116.4	97.5	110.9	86.7	**96.8**
4-Bromophenyl phenyl ether	85.6	92.9	92.8	91.1	107.6	89.4	118.0	97.5	87.1	**95.8**
Hexachlorobenzene	95.4	91.7	92.3	95.4	93.6	83.7	106.6	94.3	90.0	**93.7**
Pentachlorophenol	68.2	85.9	107.7	53.2	89.8	88.1	96.6	59.8	81.3	**81.2**
Phenanthrene	92.1	93.7	93.3	100.0	97.8	113.3	124.4	101.0	89.9	**100.6**
Anthracene	101.6	95.0	93.5	92.5	101.8	118.4	123.0	94.5	90.6	**101.2**
Carbazole	94.4	99.3	96.6	105.5	96.7	111.4	115.7	83.2	88.9	**99.1**
Fluoranthene	109.9	101.4	94.3	111.6	96.6	109.6	123.2	85.4	92.7	**102.7**
Pyrene	106.5	105.8	107.6	116.7	90.7	127.5	103.4	95.5	93.2	**105.2**
3,3'-Dichlorobenzidine	100.0	*492.3	131.4	100.0	*217.6	*187.6	100.0	*748.8	100.0	**116.5**
Benzo(a)anthracene	98.1	107.0	98.4	119.3	98.6	104.0	105.0	93.4	89.3	**101.5**
Chrysene	100.0	108.5	100.2	116.8	93.0	117.0	106.7	93.6	90.2	**102.9**
Benzo(b)fluoranthene	106.8	109.9	75.8	121.7	100.7	93.9	106.9	81.9	93.6	**99.0**
Benzo(k)fluoranthene	102.4	105.2	88.4	125.5	99.4	95.1	144.7	89.2	78.1	**103.1**
Benzo(a)pyrene	107.9	105.5	80.8	122.3	97.7	104.6	101.7	86.2	92.0	**99.9**
Indeno(1,2,3-cd)pyrene	95.1	105.7	93.8	126.0	105.2	90.4	133.6	82.6	91.9	**102.7**
Dibenz(a,h)anthracene	85.0	102.6	82.0	118.8	100.7	91.9	142.3	71.0	93.1	**98.6**
Benzo(g,h,i)perylene	98.0	0.0	81.2	0.0	33.6	78.6	128.7	83.0	94.2	**66.4**
Average	**95.1**	**94.3**	**101.0**	**95.5**	**96.5**	**104.1**	**113.0**	**100.9**	**92.5**	

* Values greater than 150% were not used to determine the averages, but the 0% values were used.

TABLE 13

SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs FROM A CERTIFIED REFERENCE SEDIMENT EC-1, USING METHOD 3561 (SFE - SOLID TRAP)

Compound	Certified Value (mg/kg)	SFE Value[a] (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	(27.9)[b]	41.3 ± 3.6	(148)	8.7
Acenaphthylene	(0.8)	0.9 ± 0.1	(112)	11.1
Acenaphthene	(0.2)	0.2 ± 0.01	(100)	0.05
Fluorene	(15.3)	15.6 ± 1.8	(102)	11.5
Phenanthrene	15.8 ± 1.2	16.1 ± 1.8	102	11.2
Anthracene	(1.3)	1.1 ± 0.2	(88)	18.2
Fluoranthene	23.2 ± 2.0	24.1 ± 2.1	104	8.7
Pyrene	16.7 ± 2.0	17.2 ± 1.9	103	11.0
Benz(a)anthracene	8.7 ± 0.8	8.8 ± 1.0	101	11.4
Chrysene	(9.2)	7.9 ± 0.9	(86)	11.4
Benzo(b)fluoranthene	7.9 ± 0.9	8.5 ± 1.1	108	12.9
Benzo(k)fluoranthene	4.4 ± 0.5	4.1 ± 0.5	91	12.2
Benzo(a)pyrene	5.3 ± 0.7	5.1 ± 0.6	96	11.8
Indeno(1,2,3-cd)pyrene	5.7 ± 0.6	5.2 ± 0.6	91	11.5
Benzo(g,h,i)perylene	4.9 ± 0.7	4.3 ± 0.5	88	11.6
Dibenz(a,h)anthracene	(1.3)	1.1 ± 0.2	(85)	18.2

[a] Relative standard deviations for the SFE values are based on six replicate extractions.

[b] Values in parentheses were obtained from, or compared to, Soxhlet extraction results which were not certified.

Data are taken from Reference 10.

TABLE 14

SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs FROM A CERTIFIED REFERENCE SEDIMENT HS-3, USING METHOD 3561 (SFE - SOLID TRAP)

Compound	Certified Value (mg/kg)	SFE Value[a] (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	9.0 ± 0.7	7.4 ± 0.6	82	8.1
Acenaphthylene	0.3 ± 0.1	0.4 ± 0.1	133	25.0
Acenaphthene	4.5 ± 1.5	3.3 ± 0.3	73	9.0
Fluorene	13.6 ± 3.1	10.4 ± 1.3	77	12.5
Phenanthrene	85.0 ± 20.0	86.2 ± 9.5	101	11.0
Anthracene	13.4 ± 0.5	12.1 ± 1.5	90	12.4
Fluoranthene	60.0 ± 9.0	54.0 ± 6.1	90	11.3
Pyrene	39.0 ± 9.0	32.7 ± 3.7	84	11.3
Benz(a)anthracene	14.6 ± 2.0	12.1 ± 1.3	83	10.7
Chrysene	14.1 ± 2.0	12.0 ± 1.3	85	10.8
Benzo(b)fluoranthene	7.7 ± 1.2	8.4 ± 0.9	109	10.7
Benzo(k)fluoranthene	2.8 ± 2.0	3.2 ± 0.5	114	15.6
Benzo(a)pyrene	7.4 ± 3.6	6.6 ± 0.8	89	12.1
Indeno(1,2,3-cd)pyrene	5.0 ± 2.0	4.5 ± 0.6	90	13.3
Benzo(g,h,i)perylene	5.4 ± 1.3	4.4 ± 0.6	82	13.6
Dibenz(a,h)anthracene	1.3 ± 0.5	1.1 ± 0.3	85	27.3

[a] Relative standard deviations for the SFE values are based on three replicate extractions.

Data are taken from Reference 10.

TABLE 15

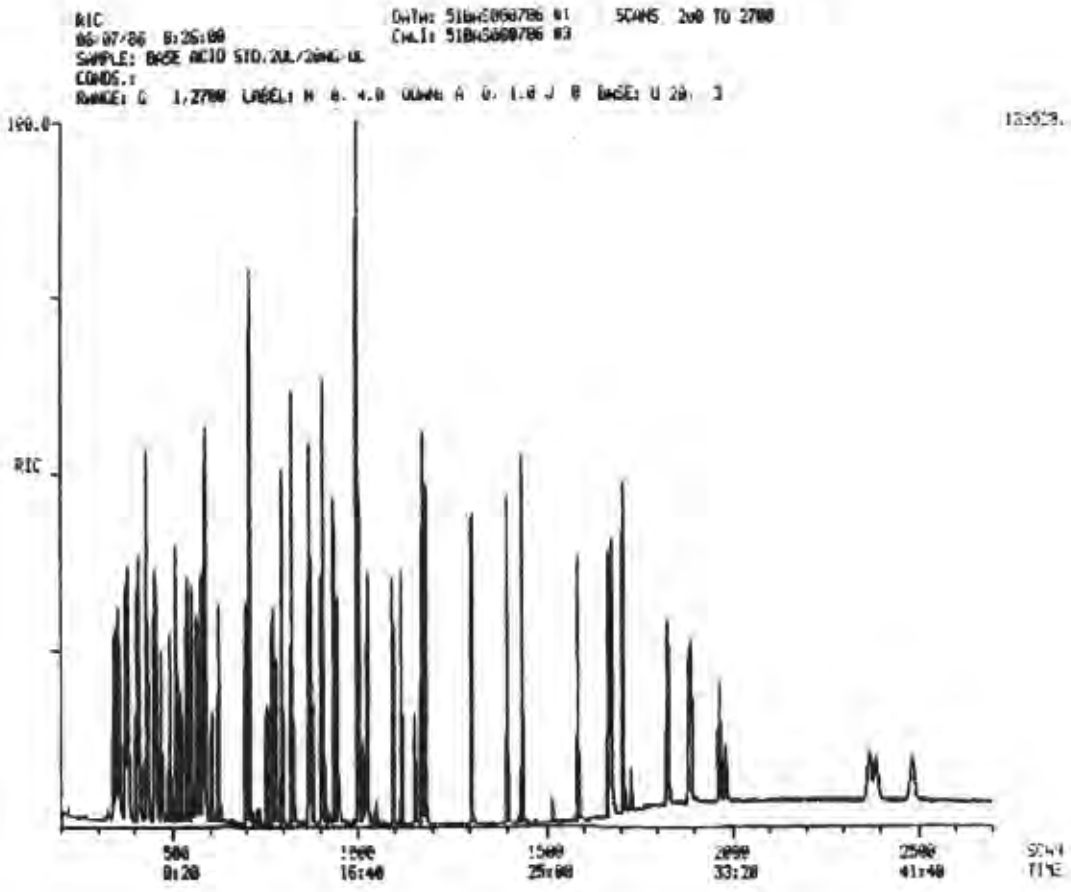
SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs FROM A CERTIFIED REFERENCE SOIL SRS103-100, USING METHOD 3561 (SFE - LIQUID TRAP)

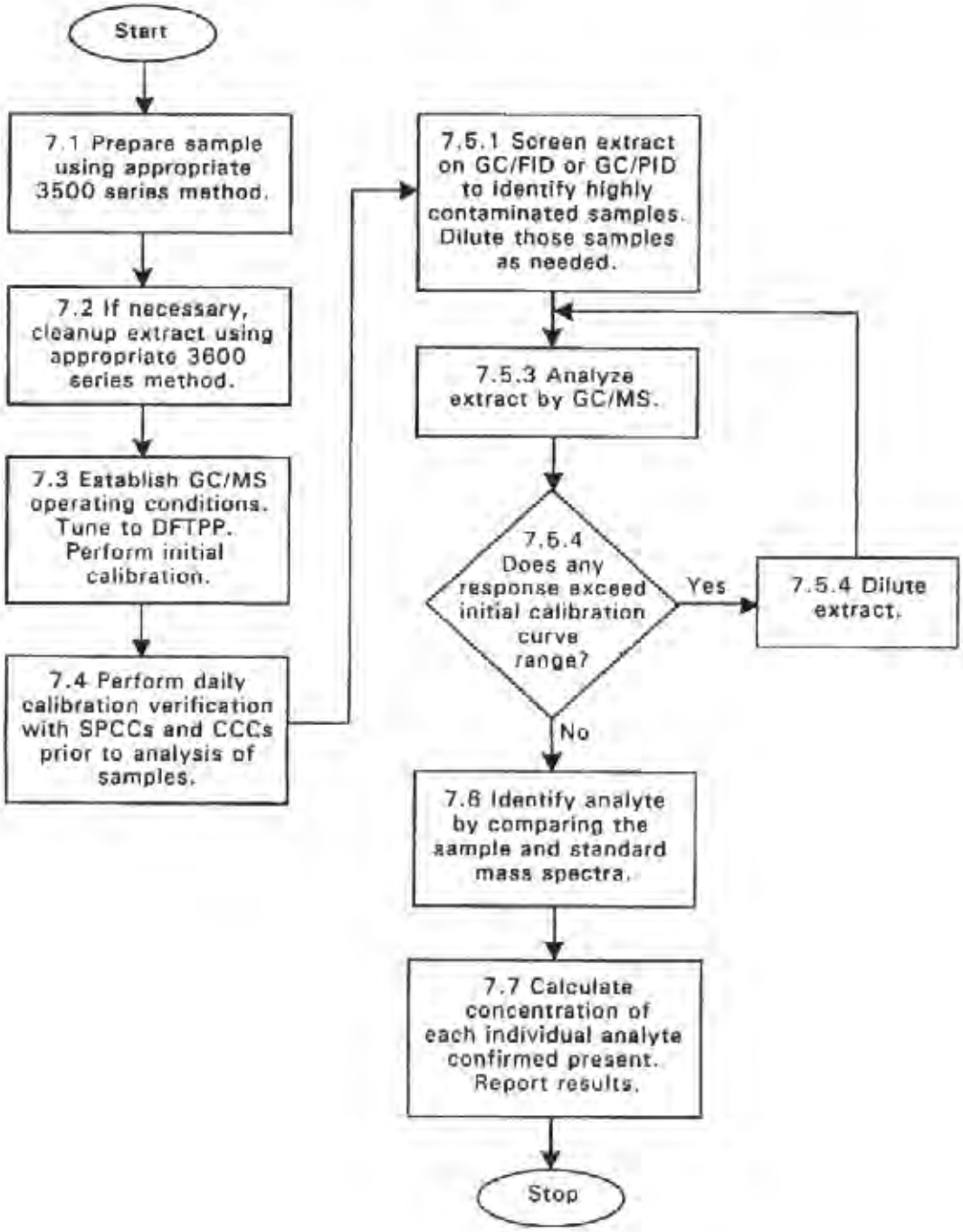
Compound	Certified Value (mg/kg)			SFE Value[a] (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	32.4	±	8.2	29.55	91	10.5
2-Methylnaphthalene	62.1	±	11.5	76.13	122	2.0
Acenaphthene	632	±	105	577.28	91	2.9
Dibenzofuran	307	±	49	302.25	98	4.1
Fluorene	492	±	78	427.15	87	3.0
Phenanthrene	1618	±	340	1278.03	79	3.4
Anthracene	422	±	49	400.80	95	2.6
Fluoranthene	1280	±	220	1019.13	80	4.5
Pyrene	1033	±	285	911.82	88	3.1
Benz(a)anthracene	252	±	38	225.50	89	4.8
Chrysene	297	±	26	283.00	95	3.8
Benzo(b)fluoranthene + Benzo(k)fluoranthene	153	±	22	130.88	86	10.7
Benzo(a)pyrene	97.2	±	17.1	58.28	60	6.5

[a] Relative standard deviations for the SFE values are based on four replicate extractions.

Data are taken from Reference 11.

FIGURE 1
GAS CHROMATOGRAM OF BASE/NEUTRAL AND ACID CALIBRATION STANDARD




Start
7.1 Prepare sample using appropriate 3500 series method.
7.2 If necessary, cleanup extract using appropriate 3600 series method.
7.3 Establish GC/MS operating conditions. Tune to DFTPP. Perform initial calibration.
7.4 Perform daily calibration verification with SPCCs and CCCs prior to analysis of samples.
7.5.1 Screen extract on GC/FID or GC/PID to identify highly contaminated samples. Dilute those samples as needed.
7.5.3 Analyze extract by GC/MS.
7.5.4 Does any response exceed initial calibration curve range?
Yes
7.5.4 Dilute extract.
No
7.6 Identify analyte by comparing the sample and standard mass spectra.
7.7 Calculate concentration of each individual analyte confirmed present. Report results.
Stop

Analytical Methods

Total Organic Carbon

415.1

ORGANIC CARBON, TOTAL

Method 415.1 (Combustion or Oxidation)

STORET NO. Total 00680
Dissolved 00681

1. Scope and Application
   1.1 This method includes the measurement of organic carbon in drinking, surface and saline waters, domestic and industrial wastes. Exclusions are noted under Definitions and Interferences.
   1.2 The method is most applicable to measurement of organic carbon above 1 mg/1.
2. Summary of Method
   2.1 Organic carbon in a sample is converted to carbon dioxide (CO_2) by catalytic combustion or wet chemical oxidation. The CO_2 formed can be measured directly by an infrared detector or converted to methane (CH_4) and measured by a flame ionization detector. The amount of CO_2 or CH_4 is directly proportional to the concentration of carbonaceous material in the sample.
3. Definitions
   3.1 The carbonaceous analyzer measures all of the carbon in a sample. Because of various properties of carbon-containing compounds in liquid samples, preliminary treatment of the sample prior to analysis dictates the definition of the carbon as it is measured. Forms of carbon that are measured by the method are:
      A) soluble, nonvolatile organic carbon; for instance, natural sugars.
      B) soluble, volatile organic carbon; for instance, mercaptans.
      C) insoluble, partially volatile carbon; for instance, oils.
      D) insoluble, particulate carbonaceous materials, for instance; cellulose fibers.
      E) soluble or insoluble carbonaceous materials adsorbed or entrapped on insoluble inorganic suspended matter; for instance, oily matter adsorbed on silt particles.
   3.2 The final usefulness of the carbon measurement is in assessing the potential oxygen-demanding load of organic material on a receiving stream. This statement applies whether the carbon measurement is made on a sewage plant effluent, industrial waste, or on water taken directly from the stream. In this light, carbonate and bicarbonate carbon are not a part of the oxygen demand in the stream and therefore should be discounted in the final calculation or removed prior to analysis. The manner of preliminary treatment of the sample and instrument settings defines the types of carbon which are measured. Instrument manufacturer's instructions should be followed.

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4. Sample Handling and Preservation

4.1 Sampling and storage of samples in glass bottles is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples.
NOTE 1: A brief study performed in the EPA Laboratory indicated that distilled water stored in new, one quart cubitainers did not show any increase in organic carbon after two weeks exposure.

4.2 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the lapse of time between collection of samples and start of analysis should be kept to a minimum. Also, samples should be kept cool (4°C) and protected from sunlight and atmospheric oxygen.

4.3 In instances where analysis cannot be performed within two hours (2 hours) from time of sampling, the sample is acidified ($pH \leq 2$) with HCl or H_2SO_4.

5. Interferences

5.1 Carbonate and bicarbonate carbon represent an interference under the terms of this test and must be removed or accounted for in the final calculation.

5.2 This procedure is applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter type syringe or pipette. The openings of the syringe or pipette limit the maximum size of particles which may be included in the sample.

6. Apparatus

6.1 Apparatus for blending or homogenizing samples: Generally, a Waring-type blender is satisfactory.

6.2 Apparatus for total and dissolved organic carbon:

6.2.1 A number of companies manufacture systems for measuring carbonaceous material in liquid samples. Considerations should be made as to the types of samples to be analyzed, the expected concentration range, and forms of carbon to be measured.

6.2.2 No specific analyzer is recommended as superior.

7. Reagents

7.1 Distilled water used in preparation of standards and for dilution of samples should be ultra pure to reduce the carbon concentration of the blank. Carbon dioxide-free, double distilled water is recommended. Ion exchanged waters are not recommended because of the possibilities of contamination with organic materials from the resins.

7.2 Potassium hydrogen phthalate, stock solution, 1000 mg carbon/liter: Dissolve 0.2128 g of potassium hydrogen phthalate (Primary Standard Grade) in distilled water and dilute to 100.0 ml.
NOTE 2: Sodium oxalate and acetic acid are not recommended as stock solutions.

7.3 Potassium hydrogen phthalate, standard solutions: Prepare standard solutions from the stock solution by dilution with distilled water.

7.4 Carbonate-bicarbonate, stock solution, 1000 mg carbon/liter: Weigh 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate and transfer both to the same 100 ml volumetric flask. Dissolve with distilled water.

7.5 Carbonate-bicarbonate, standard solution: Prepare a series of standards similar to step 7.3.

NOTE 3: This standard is not required by some instruments.

7.6 Blank solution: Use the same distilled water (or similar quality water) used for the preparation of the standard solutions.

8. Procedure

8.1 Follow instrument manufacturer's instructions for calibration, procedure, and calculations.

8.2 For calibration of the instrument, it is recommended that a series of standards encompassing the expected concentration range of the samples be used.

9. Precision and Accuracy

9.1 Twenty-eight analysts in twenty-one laboratories analyzed distilled water solutions containing exact increments of oxidizable organic compounds, with the following results:

Increment as TOC mg/liter	Precision as Standard Deviation TOC, mg/liter	Accuracy as Bias, %	Accuracy as Bias, mg/liter
4.9	3.93	+15.27	+0.75
107	8.32	+ 1.01	+1.08

(FWPCA Method Study 3, Demand Analyses)

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D 2574–79, p 469 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 532, Method 505, (1975).

Analytical Methods

Volatile Organics

5030B/5035/8260B

METHOD 5030B

PURGE-AND-TRAP FOR AQUEOUS SAMPLES

1.0 SCOPE AND APPLICATION

1.1 This method describes a purge-and-trap procedure for the analysis of volatile organic compounds (VOCs) in aqueous samples and water miscible liquid samples. It also describes the analysis of high concentration soil and waste sample extracts prepared in Method 5035. The gas chromatographic determinative steps are found in Methods 8015 and 8021. The method is also applicable to GC/MS Method 8260.

1.2 Method 5030 can be used for most volatile organic compounds that have boiling points below 200°C and are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique; however, quantitation limits (by GC or GC/MS) are approximately ten times higher because of poor purging efficiency. The method is also limited to compounds that elute as sharp peaks from a GC column packed with graphitized carbon lightly coated with a carbowax or a coated capillary column. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides.

1.3 Method 5030, in conjunction with Method 8015 (GC/FID), may be used for the analysis of the aliphatic hydrocarbon fraction in the light ends of total petroleum hydrocarbons, e.g., gasoline. For the aromatic fraction (BTEX), use Method 5030 and Method 8021 (GC/PID). A total determinative analysis of gasoline fractions may be obtained using Methods 8021 GC/PID) in series with Method 8015.

1.4 Water samples can be analyzed directly for volatile organic compounds by purge-and-trap extraction and gas chromatography. Higher concentrations of these analytes in water can be determined by direct injection of the sample into the chromatographic system or by dilution of the sample prior to the purge-and-trap process.

1.5 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Aqueous Samples: An inert gas is bubbled through a portion of the aqueous sample at ambient temperature, and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are adsorbed. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column.

2.2 High Concentration Extracts from Method 5035: An aliquot of the extract prepared in Method 5035 is combined with organic free reagent water in the purging chamber. It is then analyzed by purge-and-trap GC or GC/MS following the normal aqueous method.

3.0 INTERFERENCES

3.1 Impurities in the purge gas, and from organic compounds out-gassing from the plumbing ahead of the trap, account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-polytetrafluoroethylene (non-PTFE) plastic coating, non-PTFE thread sealants, or flow controllers with rubber components in the purging device must be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. These compounds will result in interferences or false positives in the determinative step.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and handling protocols serves as a check on such contamination.

3.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by an analysis of organic-free reagent water to check for cross-contamination. The trap and other parts of the system are subject to contamination. Therefore, frequent bake-out and purging of the entire system may be required.

3.4 The laboratory where volatiles analysis is performed should be completely free of solvents. Special precautions must be taken to determine methylene chloride. The analytical and sample storage areas should be isolated from all atmospheric sources of methylene chloride. Otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed will also lead to random background levels and the same precautions must be taken.

4.0 APPARATUS AND MATERIALS

4.1 Microsyringes - 10-µL, 25-µL, 100-µL, 250-µL, 500-µL, and 1,000-µL. These syringes should be equipped with a 20-gauge (0.006 in ID) needle having a length sufficient to extend from the sample inlet to within 1 cm of the glass frit in the purging device. The needle length will depend upon the dimensions of the purging device employed.

4.2 Syringe valve - Two-way, with Luer ends (three each), if applicable to the purging device.

4.3 Two 5-mL glass hypodermic syringes with Luer-Lok tip (other sizes are acceptable depending on sample volume used).

4.4 Volumetric flasks, Class A - 10-mL and 100-mL, with ground-glass stoppers.

4.5 Vials - 2-mL, for GC autosampler.

4.6 Purge-and-trap device

The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber. Several complete devices are commercially available.

4.6.1 The recommended purging chamber is designed to accept 5-mL samples with a water column at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The sample purger, illustrated in Figure 1, meets these design criteria. Alternate sample purge devices may be used, provided equivalent or improved performance is demonstrated.

4.6.2 The trap used to develop this method was 25 cm long with an inside diameter of 0.105 in. Starting from the inlet, the trap contains the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. It is recommended that 1.0 cm of methyl silicone-coated packing be inserted at the inlet to extend the life of the trap (see Figures 2 and 3). If it is not necessary to analyze for dichlorodifluoromethane or other fluorocarbons of similar volatility, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

4.6.3 The desorber must be capable of rapidly heating the trap to 180°C for desorption. The polymer section of the trap should not be heated higher than 180°C, and the remaining sections should not exceed 220°C during bake-out mode. The desorber design illustrated in Figures 2 and 3 meet these criteria.

4.6.4 The purge-and-trap device may be assembled as a separate unit or may be coupled to a gas chromatograph, as shown in Figures 4 and 5.

4.6.5 Trap Packing Materials

4.6.5.1 2,6-Diphenylene oxide polymer - 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

4.6.5.2 Methyl silicone packing - OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

4.6.5.3 Silica gel - 35/60 mesh, Davison, grade 15 or equivalent.

4.6.5.4 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26, or equivalent, by crushing through 26 mesh screen.

4.6.5.5 Alternate Trap Materials

A number of hydrophobic carbon molecular sieve and graphitized carbon black materials have been developed. Various combinations of these materials have been shown to provide retention properties similar to the Tenax\Silica gel\Carbon trap. Alternate trap construction with such materials is allowed, provided that the adsorption and desorption characteristics obtained achieve equivalent or better method sensitivity and precision in comparison to the performance documented in the Determinative Method.

4.6.5.5.1 The following alternatives have been shown to be viable for most analytes of concern:

7.6-cm Carbopack™ B/1.3-cm Carboseive™ S-III
VOCARB 3000 - 10.0-cm Carbopack™ B/6.0-cm Carboxin ™ 1000/1.0-cm Carboxin™ 1001
VOCARB 4000 - 8.5-cm Carbopack™ C/10.0-cm Carbopack™ B/6.0-cm Carboxin™ 1000/1.0-cm Carboxin™ 1001

These combinations require rapid heating to desorption temperatures of 245°C to 270°C (follow manufacturer's instructions). At these increased temperatures, catalytic and thermal decomposition of analytes has been reported. The VOCARB 4000 combination has also been demonstrated to catalytically break down 2-chloroethyl vinyl ether, and to partially decompose 2,2-dichloropropane. Bromoform and bromomethane have shown some thermal decomposition.

4.6.5.5.2 The amount of thermal decomposition products formed must be routinely tracked by daily monitoring of the formation of chloromethane and bromomethane. A daily check standard containing surrogates, internal standards, and 20 µg/L bromoform must be analyzed prior to the analysis of the daily check standard. If levels of chloromethane or bromomethane exceed 0.5 µg/L, then the trap may be too contaminated with salts or tightly bound contamination for analysis to continue. The trap must be replaced and the system recalibrated.

NOTE: Even newly constructed traps may have become contaminated prior to their first use from airborne vapors. These highly adsorptive materials must be kept tightly sealed in an area of minimum organic vapor contamination.

4.7 Heater or heated oil bath - capable of maintaining the purging chamber to within 1°C, over a temperature range from ambient to 100°C.

4.8 Capillary GC Columns - Any GC column that meets the performance specifications of the determinative method may be used. See the specific determinative method for recommended columns, conditions and retention times.

4.8.1 The wide-bore columns have the capacity to accept the standard gas flows from the trap during thermal desorption, and chromatography can begin with the onset of thermal desorption. Depending on the pumping capacity of the MS, an additional interface between the end of the column and the MS may be required. An open split interface , an all-glass jet separator, or a cryogenic (Sec. 4.8.2) device are acceptable interfaces. The type of interface and its adjustments can have a significant impact on the method detection limits. Other interfaces can be used if the performance specifications described in this method can be achieved.

4.8.2 A system using a narrow-bore column will require lower gas flows of approximately 2 - 4 mL/minute. Because of these low desorption flows, early eluting analytes need to be refocussed to elute in a narrow band. This refocussing may be carried out by using a cryogenic interface. This type of interface usually uses liquid nitrogen to condense the desorbed sample components in a narrow band on an uncoated fused silica precolumn. When all components have been desorbed form the trap, the interface is rapidly heated under a stream of carrier gas to transfer the analytes to the analytical column. The end of the analytical column should be placed within a few mm of the MS ion source. A potential problem with this interface is blockage of the interface by ice caused by desorbing water from the trap. This condition will result in a major loss in sensitivity and chromatographic resolution. Low surrogate compound recoveries can be a sign that this is occurring.

5.0 REAGENTS

5.1 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2 See the determinative method and Method 5000 for guidance on internal and surrogate standards.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to the introductory material to this chapter, Organic Analytes, Sec. 4.1. Samples should be stored in capped bottles, with minimum headspace, at 4°C or less in an area free of solvent fumes. The size of any bubble caused by degassing upon cooling the sample should not exceed 5 - 6 mm. When a bubble is present, also observe the cap and septum to ensure that a proper seal was made at time of sampling. Is there any evidence of leakage? If the sample was improperly sealed, the sample should be discarded.

6.2 All samples should be analyzed within 14 days of collection. Samples not analyzed within this period must be noted and data are considered minimum values.

7.0 PROCEDURE

7.1 The purge-and-trap technique for aqueous samples is found in Sec. 7.2 and guidance for analysis of solvent extracts from the High Concentration Method in Method 5035 is found in Sec. 7.3. The gas chromatographic determinative steps are found in Methods 8015 and 8021. The

method is also applicable to GC/MS Method 8260. For the analysis of gasoline, use Method 8021 with GC/PID for BTEX in series with Method 8015 with the GC/FID detector for hydrocarbons.

7.2 This section provides guidance on the analysis of aqueous samples and samples that are water miscible, by purge-and-trap analysis.

7.2.1 Initial calibration

Prior to using this introduction technique for any GC method, the system must be calibrated. General calibration procedures are discussed in Method 8000, while the specific determinative methods and Method 5000 give details on preparation of standards. The GC/MS methods require instrument tuning prior to proceeding with calibration.

7.2.1.1 Assemble a purge-and-trap device that meets the specification in Sec. 4.6. Condition the Tenax trap overnight at 180°C (condition other traps at the manufacturers recommended temperature) in the purge mode with an inert gas flow of at least 20 mL/min. Prior to use, condition the trap daily for 10 min while backflushing at 180°C with the column at 220°C.

7.2.1.2 Connect the purge-and-trap device to a gas chromatograph or gas chromatograph/mass spectrometer system.

7.2.1.3 Prepare the final solutions containing the required concentrations of calibration standards, including surrogate standards, directly in the purging device. Add 5.0 mL of organic-free reagent water to the purging device. The organic-free reagent water is added to the purging device using a 5-mL glass syringe (a 10-mL or 25-mL syringe may be used if preferred) fitted with a 15-cm 20-gauge needle. The needle is inserted through the sample inlet shown in Figure 1. The internal diameter of the 14-gauge needle that forms the sample inlet will permit insertion of the 20-gauge needle. Next, using a 10-µL or 25-µL micro-syringe equipped with a long needle (Sec. 4.1), take a volume of the secondary dilution solution containing appropriate concentrations of the calibration standards. Add the aliquot of calibration solution directly to the organic-free reagent water in the purging device by inserting the needle through the sample inlet. When discharging the contents of the micro-syringe, be sure that the end of the syringe needle is well beneath the surface of the organic-free reagent water. Similarly, add 10.0 µL of the internal standard solution. Close the 2-way syringe valve at the sample inlet. (The calibration standard, internal standard and surrogate standard may be added directly to the organic free reagent water in the syringe prior to transferring the water to the purging device, see Sec. 7.2.4.7).

7.2.1.4 Follow the purge-and-trap analysis as outlined in Sec. 7.2.4.

7.2.1.5 Calculate response factors (RF) or calibration factors (CF) for each analyte of interest using the procedure described in Method 8000.

7.2.1.6 The average CF (external standards) or RF (internal standards) must be calculated for each compound. For GC/MS analysis, a system performance check must be made before this calibration curve is used (see Method 8260). If the purge-and-trap procedure is used with Method 8021, evaluate the response for the

following four compounds: chloromethane; 1,1-dichloroethane; bromoform; and 1,1,2,2-tetrachloroethane. They are used to check for proper purge flow and to check for degradation caused by contaminated lines or active sites in the system.

7.2.1.6.1 Chloromethane: This compound is the most likely compound to be lost if the purge flow is too fast.

7.2.1.6.2 Bromoform: This compound is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response.

7.2.1.6.3 1,1,2,2-Tetrachloroethane and 1,1-dichloroethane: These compounds are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.2.1.7 The analytes in Method 8021 normally are not as strongly affected by small changes in purge flow or system contamination. When analyzing for very late eluting compounds with Method 8021 (i.e., hexachlorobutadiene, 1,2,3-trichlorobenzene, etc.), cross contamination and memory effects from a high concentration sample or even the standard are a common problem. Extra rinsing of the purge chamber after analysis normally corrects this. The newer purge-and-trap systems often overcome this problem with better bakeout of the system following the purge-and-trap process. Also, the charcoal traps retain less moisture and decrease the problem.

7.2.2 Calibration verification: Refer to Method 8000 for details on calibration verification.

7.2.2.1 To prepare a calibration standard, inject an appropriate volume of a primary dilution standard to an aliquot of organic free reagent water in a volumetric flask, a gas tight syringe, or to a purge device, and inject an appropriate amount of internal standard to the organic free reagent water. Be sure the same amount of internal standard is added to each standard and sample. The volume of organic free reagent water used for calibration must be the same volume used for sample analysis (normally 5 mL). The surrogate and internal standard solutions must be added with a syringe needle long enough to ensure addition below the surface of the water. Assemble the purge-and-trap device as outlined in 4.6. Follow the guidance for the purge-and-trap procedure in Sec. 7.2.4. Ongoing GC or GC/MS calibration criteria must be met as specified in Method 8000 before analyzing samples.

7.2.3 Sample screening

7.2.3.1 Screening of the sample prior to purge-and-trap analysis may provide guidance on whether sample dilution is necessary and may prevent contamination of the purge-and-trap system.

7.2.3.2 SW-846 contains two screening techniques that may be utilized: the automated headspace sampler (Method 5021) connected to a gas chromatograph equipped with a photoionization detector in series with an electrolytic conductivity detector; and extraction of the samples with hexadecane (Method 3820) and analysis of

the extract on a gas chromatograph equipped with a flame ionization detector and/or electron capture detector. In addition, other appropriate screening techniques may be employed at the discretion of the analyst.

7.2.4 Sample introduction and purging

7.2.4.1 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

7.2.4.2 Assemble the purge-and-trap device. The operating conditions for the GC and GC/MS are given in Sec. 7.0 of the specific determinative method to be employed. Whole oven cooling may be needed for certain GC columns and/or certain GC/MS systems to achieve adequate resolution of the gases. Normally a 30 meter wide-bore column will require cooling the GC oven to 25°C or below for resolution of the gases.

7.2.4.3 GC or GC/MS calibration verification criteria must be met (Method 8000) before analyzing samples.

7.2.4.4 Adjust the purge gas flow rate (nitrogen or helium) to 25-40 mL/min (also see Table 1 for guidance on specific analyte groups), on the purge-and-trap device. Optimize the flow rate to provide the best response for chloromethane and bromoform, if these compounds are analytes. Excessive flow rate reduces chloromethane response, whereas insufficient flow reduces bromoform response.

7.2.4.5 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one VOA vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. Alternatively, carefully transfer the remaining sample into a 20-mL VOA vial. Seal the vial with zero headspace. The second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Filling one 10- or 25-mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hrs. Care must be taken to prevent air from leaking into the syringe.

7.2.4.6 The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delays until the diluted sample is in a gas-tight syringe.

7.2.4.6.1 Dilutions may be made in volumetric flasks (10-mL to 100-mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

7.2.4.6.2 Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask selected and add slightly less than this quantity of organic-free reagent water to the flask.

7.2.4.6.3 Inject the proper aliquot of samples from the syringe prepared in Sec. 7.2.4.5 into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with organic-free reagent water. Cap the flask, invert, and shake three times. Repeat the above procedure for additional dilutions.

7.2.4.6.4 Fill a 5-mL syringe with the diluted sample as in Sec. 7.2.4.5.

7.2.4.7 Add 10.0 µL of surrogate spiking solution (found in each determinative method, Sec. 5.0) and, if applicable, 10.0 µL of internal standard spiking solution through the valve bore of the syringe; then close the valve. The surrogate and internal standards may be mixed and added as a single spiking solution. Matrix spiking solutions, if indicated, should be added (10.0 µL) to the sample at this time.

7.2.4.8 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

7.2.4.9 Close both valves and purge the sample for the time and at the temperature specified in Table 1. For GC/MS analysis using Method 8260, purge time is 11 minutes at ambient temperature.

7.2.5 Sample desorption

The procedures employed for sample desorption depend on the type of GC interface used. Procedures for non-cryogenic and cryogenic interfaces are described below. Analysts should also consult the instructions from the manufacturer of the purge-and-trap system and the supplier of the trap packing material.

7.2.5.1 Non-cryogenic interface - After the recommended 11-minute purge (see Table 1 for guidance on purge times for specific analyte groups), place the purge-and-trap system in the desorb mode and preheat the trap to 180°C (or other temperature recommended for the specific trap packing material) without a flow of carrier gas passing through the trap.

NOTE: Some purge-and-trap systems are capable of performing a moisture removal step (e.g., dry purge) which can eliminate excess moisture from the trap and gas lines by purging the trap just prior to the desorption step. However, the utility of a moisture removal step depends on the nature of the trap packing material. In general, when using a carbon-based, hydrophobic trap packing, this step may prevent moisture from entering the GC system and affecting chromatography, but may require that the trap be cooled to keep the temperature at or below 25°C. However, for packings that are less

hydrophobic or hydrophilic (such as silica gel), a moisture removal step may actually create more significant problems, including loss of sensitivity, poor chromatography, and premature failure of the trap packing material, through the release of increasing amounts of water into the GC system during the course of an analytical shift. The problem may be evident as erratic responses for the early-eluting internal standards and surrogates over the course of the day. Optimum results may be achieved through the proper choices of: the moisture control device, the trap packing material, trap temperature during moisture removal, and carrier gas flow. The use of trap back pressure control may also be necessary. Consult instructions from both the manufacturer of the purge-and-trap system and the supplier of the trap packing material before employing a moisture removal step.

Start the flow of the carrier gas, begin the GC temperature program, and start GC data acquisition. The carrier gas flow rate will depend on the trap employed. A flow rate of 15 mL/min is used for the standard silica gel trap (Sec. 4.6.2), while 10 mL/min may be adequate for other traps. Continue the carrier gas flow for about 4 min, or as recommended by the manufacturer. Desorption times as low as 1.5 min may be adequate for analytes in Method 8015.

7.2.5.2 Cryogenic interface - After the 11 minute purge, place the purge-and-trap system in the desorb mode, make sure the cryogenic interface is -150°C or lower, and rapidly heat the trap to 180°C (temperature may vary depending on the trap material) while backflushing with an inert gas at 4 mL/minute for about 5 minutes (1.5 min is normally adequate for analytes in Method 8015). At the end of the 5-minute desorption cycle, rapidly heat the cryogenic trap to 250°C; simultaneously begin the temperature program of the gas chromatograph and start the data acquisition.

7.2.6 Trap Reconditioning

7.2.6.1 After desorbing the sample, recondition the trap by returning the purge-and-trap device to the purge mode. Wait 15 seconds, then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180°C for Methods 8021 and 8260, and 210°C for Method 8015. Trap temperatures up to 220°C may be employed. However, the higher temperatures will shorten the useful life of the trap. (Trap temperatures may vary depending on the trap material). After approximately 7 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

7.2.6.2 While the trap is being desorbed into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5 mL flushes of organic free reagent water (or methanol followed by organic free reagent water) to avoid carryover of volatile organics into subsequent analyses.

7.2.7 Interpretation and calculation of data

7.2.7.1 If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. When a sample is analyzed that has saturated response from a compound, this analysis must be followed by the analysis of organic free reagent water. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can meet the organic-free reagent water criteria specified in Chapter One.

7.2.7.2 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve. Proceed to Method 8000 and the specific determinative method for details on calculating analyte response.

7.2.8 Analysis of water-miscible liquids

7.2.8.1 Water-miscible liquids are analyzed as water samples after first diluting them at least 50-fold with organic-free reagent water.

7.2.8.2 Initial and serial dilutions can be prepared by pipetting 2 mL of the sample into a 100-mL volumetric flask and diluting to volume with organic-free reagent water. Transfer immediately to a 5-mL gas-tight syringe.

7.2.8.3 Alternatively, prepare dilutions directly in a 5-mL syringe filled with organic-free reagent water by adding at least 20.0 µL, but not more than 100.0 µL of liquid sample. The sample is ready for addition of surrogate and, if applicable, internal and matrix spiking standards.

7.3 This section provides guidance on the analysis of solvent extracts from High Concentration Samples prepared by Method 5035.

7.3.1 The GC or GC/MS system should be set up as in Sec. 7.0 of the specific determinative method. This should be done prior to the addition of the solvent extract to organic-free reagent water.

7.3.2 Table 2 can be used to determine the volume of solvent extract to add to the 5 mL of organic-free reagent water for analysis. If a screening procedure was followed, use the estimated concentration to determine the appropriate volume. Otherwise, estimate the concentration range of the sample from the low-concentration analysis to determine the appropriate volume. If the sample was submitted as a high-concentration sample, start with 100.0 µL. All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.3.3 Remove the plunger from a 5.0-mL Luer-lok type syringe equipped with a syringe valve and fill until overflowing with organic-free reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 4.9 mL. Pull the plunger back to 5.0 mL to allow volume for the addition of the sample extract and of standards. Add 10.0 µL of internal standard solution. Also add the volume of solvent extract determined in Sec. 7.3.2 and a volume of the same solvent used in Method 5035 to total 100.0 µL (excluding methanol in standards).

7.3.4 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the water/methanol sample into the purging chamber.

7.3.5 Proceed with the analysis as outlined in the specific determinative method. Analyze all reagent blanks on the same instrument as that used for the samples. The standards and blanks should also contain 100.0 µL of methanol to simulate the sample conditions.

7.4 Sample analysis

The samples prepared by this method may be analyzed by Methods 8015, 8021, and 8260. Refer to these methods for appropriate analysis conditions. For the analysis of gasoline, use Method 8021 with GC/PID for BTEX in series with Method 8015 with the GC/FID detector for hydrocarbons.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 5000 for sample preparation QC procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of an organic-free reagent water method blank that all glassware and reagents are interference free. Each time a set of samples is extracted, or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.3 Standard quality assurance practices should be used with this method. Field duplicates should be collected to validate the precision of the sampling technique. Each analysis batch of 20 or less samples must contain: a reagent blank; either a matrix spike/matrix spike duplicate or a matrix spike and duplicate sample analysis; and a laboratory control sample, unless the determinative method provides other guidance.

8.4 Surrogate standards should be added to all samples when specified in the appropriate determinative method.

9.0 METHOD PERFORMANCE

Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

2. Bellar, T., "Measurement of Volatile Organic Compounds in Soils Using Modified Purge-and-Trap and Capillary Gas Chromatography/Mass Spectrometry", U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, OH, November, 1991.

TABLE 1

PURGE-AND-TRAP OPERATING PARAMETERS

	Analysis Method	
	8015	8021/8260
Purge gas	N_2 or He	N_2 or He
Purge gas flow rate (mL/min)	20	40
Purge time (min)	15.0 ±0.1	11.0 ±0.1
Purge temperature (°C)	85 ±2	Ambient
Desorb temperature (°C)	180	180
Backflush inert gas flow (mL/min)	20-60	20-60[1]
Desorb time (min)	1.5	4

[1] The desorption flow rate for Method 8021 with a wide bore capillary column will optimize at approximately 10 to 15 mL/minute.

TABLE 2

QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS OF HIGH-CONCENTRATION SOILS/SEDIMENTS

Approximate Concentration Range	Volume of Methanol Extract[a]
500-10,000 µg/kg	100 µL
1,000-20,000 µg/kg	50 µL
5,000-100,000 µg/kg	10 µL
25,000-500,000 µg/kg	100 µL of 1/50 dilution[b]

Calculate appropriate dilution factor for concentrations exceeding this table.

[a] The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5 mL syringe whatever volume of methanol is necessary to maintain a volume of 100 µL added to the syringe.

[b] Dilute an aliquot of the methanol extract and then take 100 µL for analysis.

FIGURE 1
EXAMPLE OF PURGING DEVICE

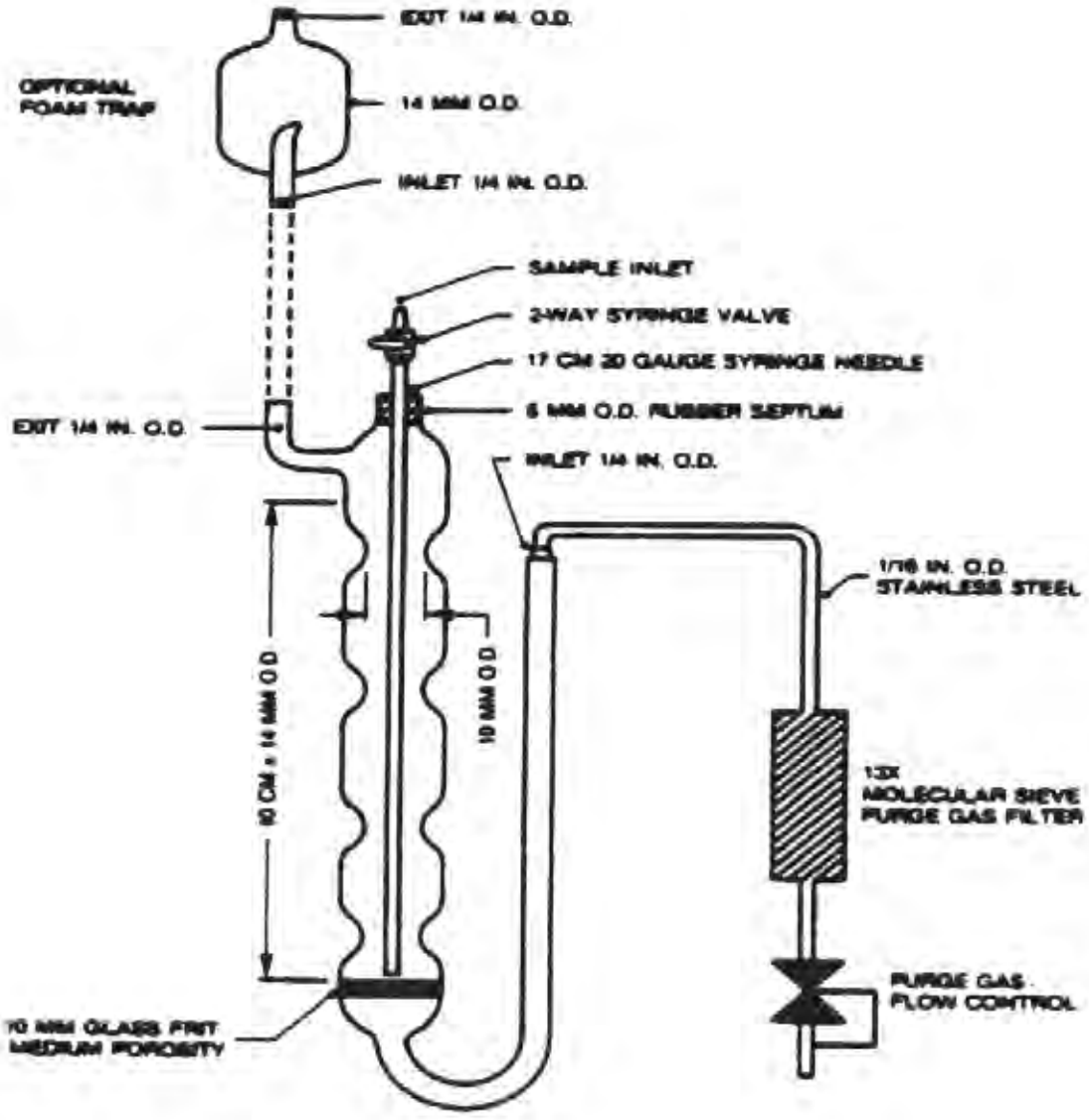


FIGURE 2
EXAMPLE OF TRAP PACKINGS AND CONSTRUCTION
TO INCLUDE DESORB CAPABILITY

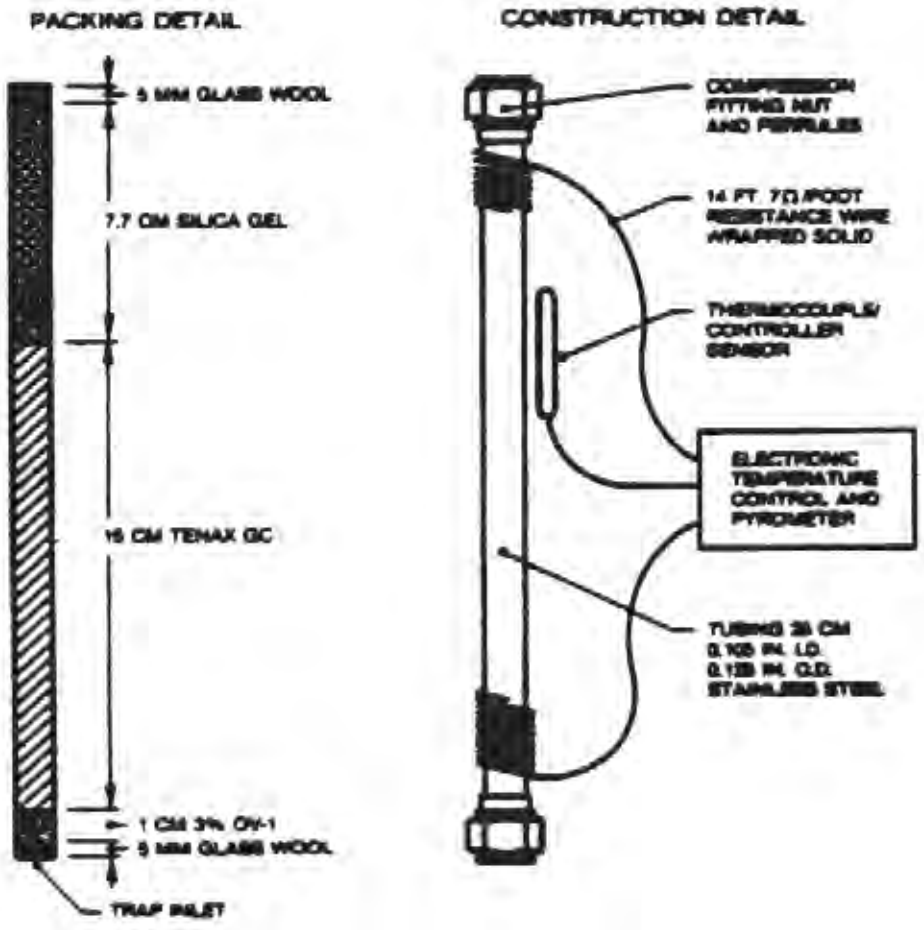


FIGURE 3
SCHEMATIC OF TYPICAL PURGE AND TRAP DEVICE
PURGE MODE

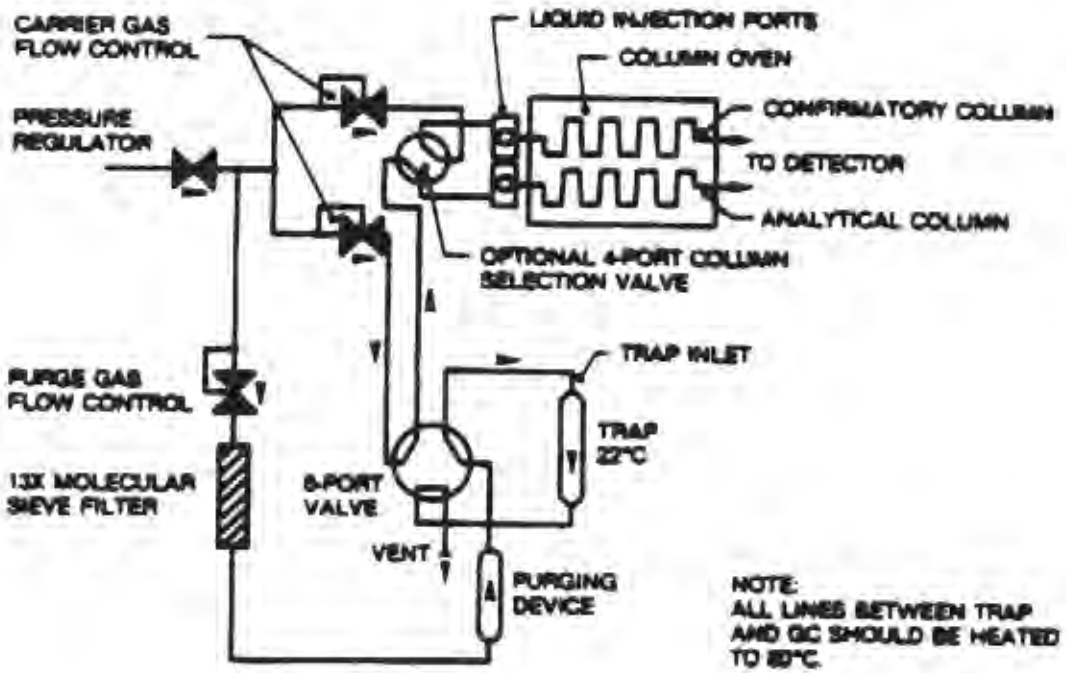
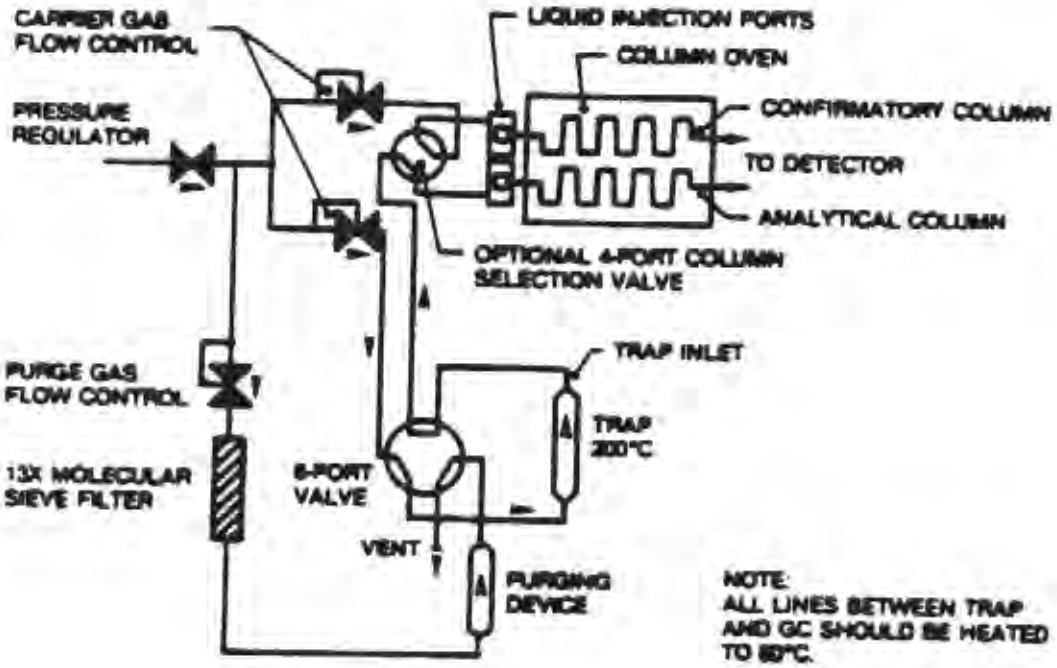
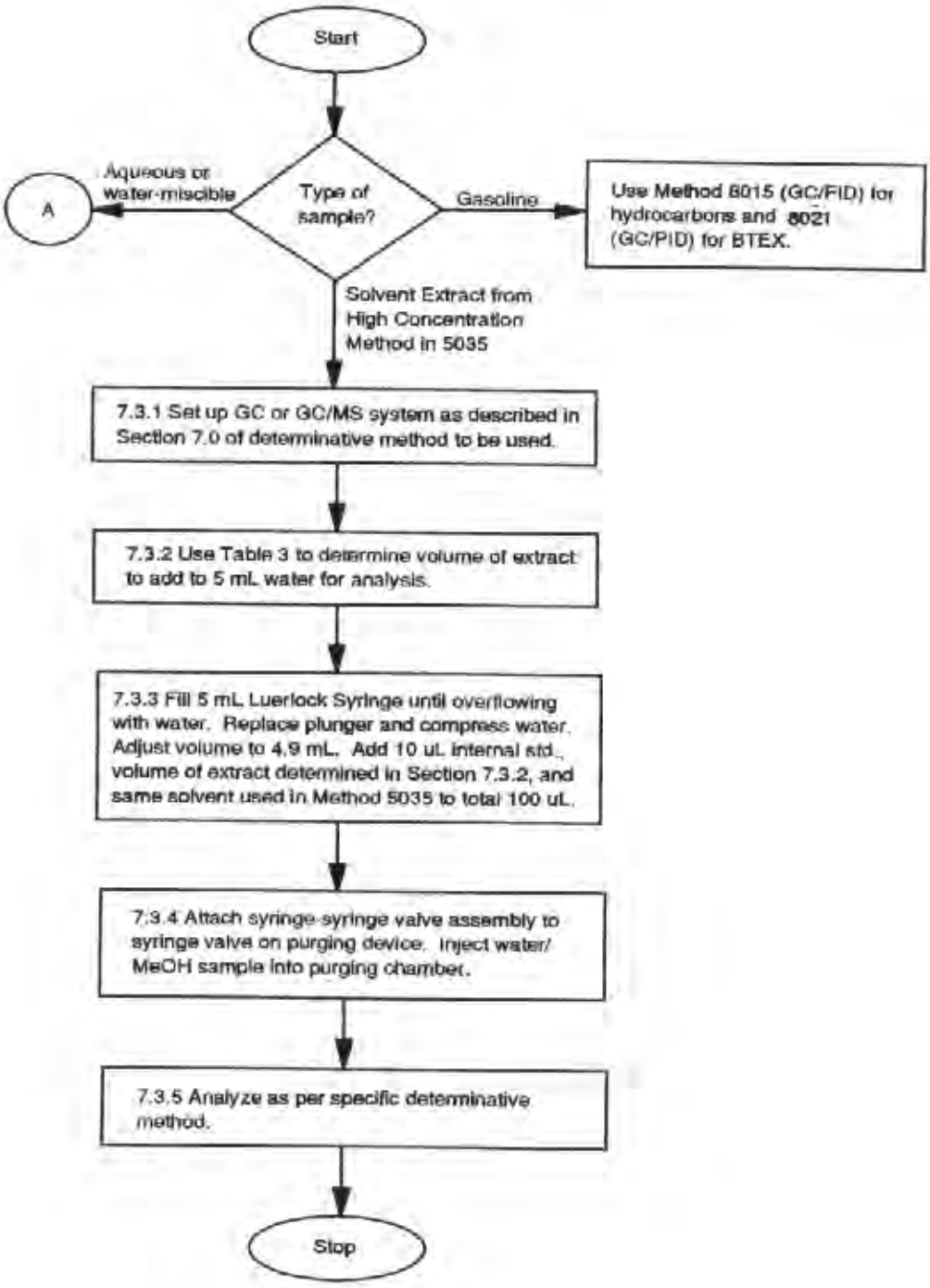
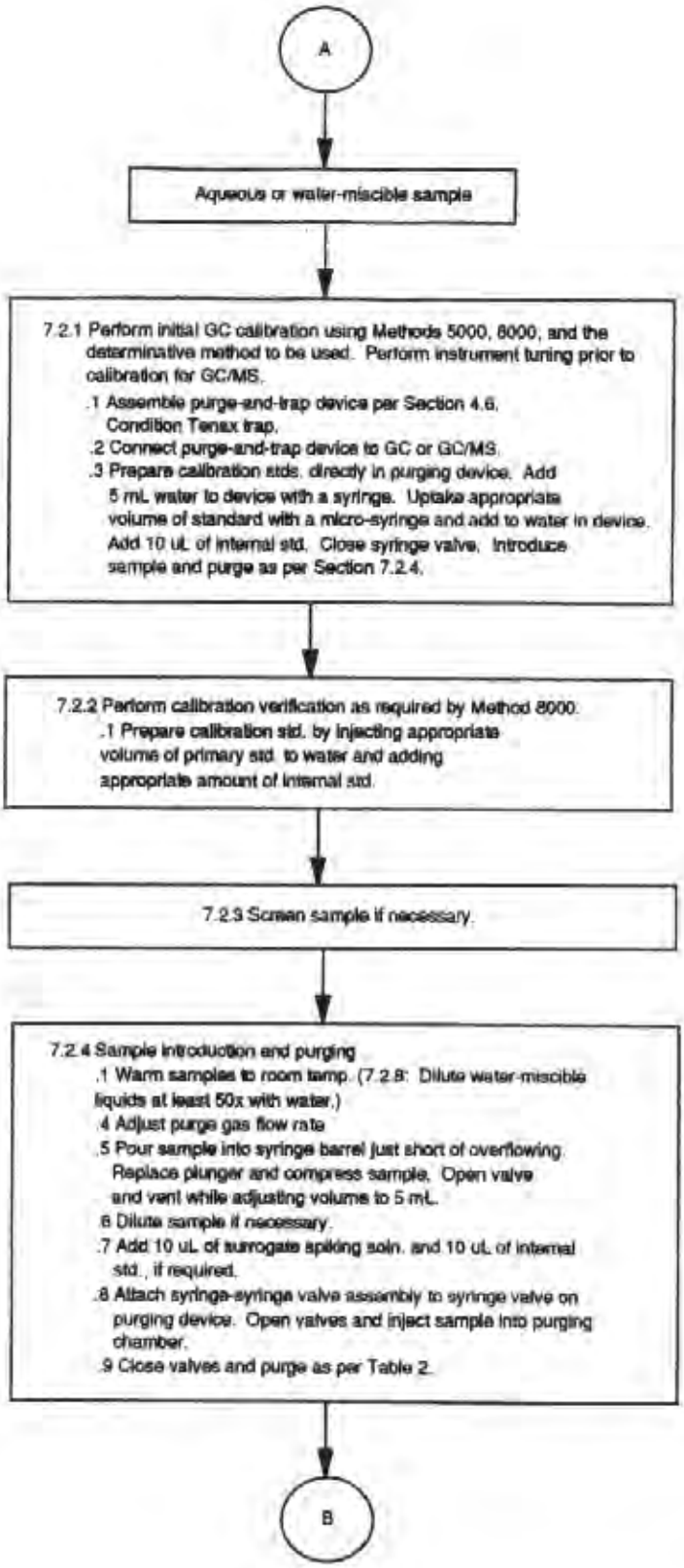
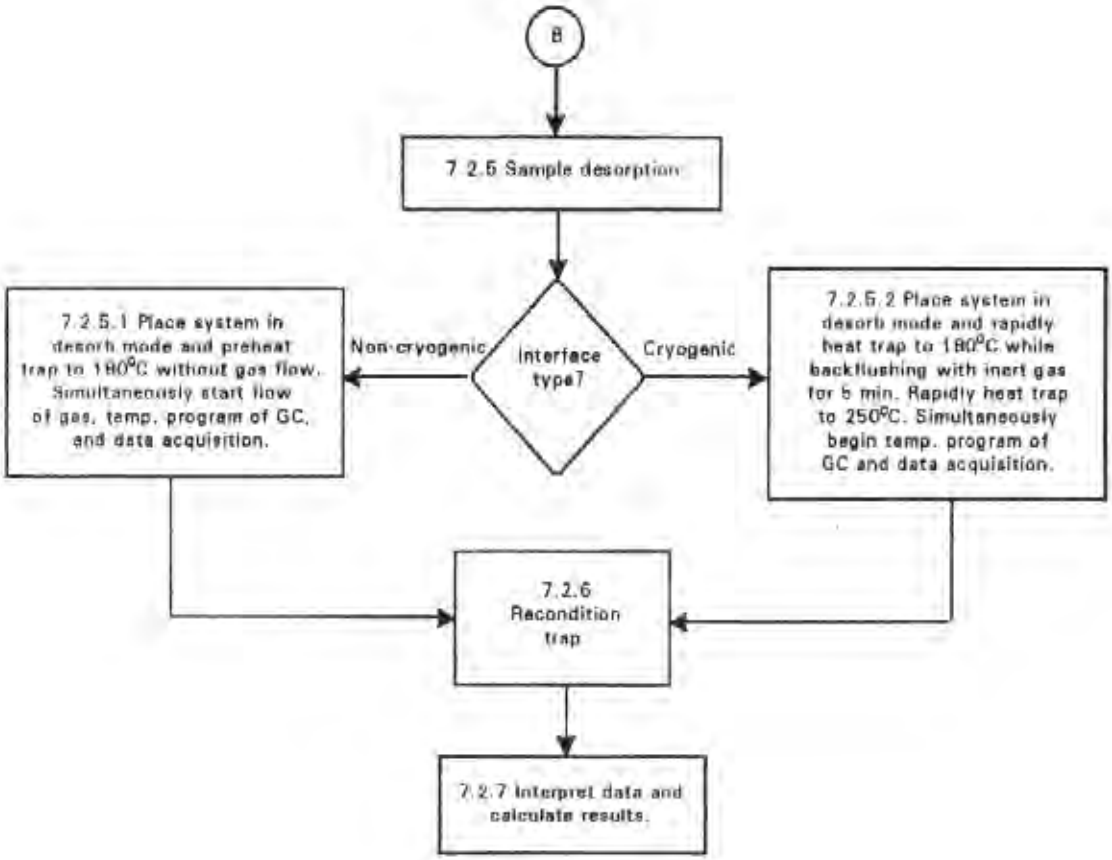


FIGURE 4
SCHEMATIC OF TYPICAL PURGE AND TRAP DEVICE
DESORB MODE




Start
Type of sample?
Aqueous or water-miscible
A
Gasoline
Use Method 8015 (GC/FID) for hydrocarbons and 8021 (GC/PID) for BTEX.
Solvent Extract from High Concentration Method in 5035
7.3.1 Set up GC or GC/MS system as described in Section 7.0 of determinative method to be used.
7.3.2 Use Table 3 to determine volume of extract to add to 5 mL water for analysis.
7.3.3 Fill 5 mL Luerlock Syringe until overflowing with water. Replace plunger and compress water. Adjust volume to 4.9 mL. Add 10 uL internal std., volume of extract determined in Section 7.3.2, and same solvent used in Method 5035 to total 100 uL.
7.3.4 Attach syringe-syringe valve assembly to syringe valve on purging device. Inject water/ MeOH sample into purging chamber.
7.3.5 Analyze as per specific determinative method.
Stop


A
Aqueous or water-miscible sample
7.2.1 Perform initial GC calibration using Methods 5000, 8000, and the determinative method to be used. Perform instrument tuning prior to calibration for GC/MS.
.1 Assemble purge-and-trap device per Section 4.6. Condition Tenax trap.
.2 Connect purge-and-trap device to GC or GC/MS.
.3 Prepare calibration stds. directly in purging device. Add 5 mL water to device with a syringe. Uptake appropriate volume of standard with a micro-syringe and add to water in device. Add 10 uL of internal std. Close syringe valve. Introduce sample and purge as per Section 7.2.4.
7.2.2 Perform calibration verification as required by Method 8000.
.1 Prepare calibration std. by injecting appropriate volume of primary std. to water and adding appropriate amount of internal std.
7.2.3 Screen sample if necessary.
7.2.4 Sample introduction and purging
.1 Warm samples to room temp. (7.2.8: Dilute water-miscible liquids at least 50x with water.)
.4 Adjust purge gas flow rate
.5 Pour sample into syringe barrel just short of overflowing. Replace plunger and compress sample. Open valve and vent while adjusting volume to 5 mL.
.6 Dilute sample if necessary.
.7 Add 10 uL of surrogate spiking soln. and 10 uL of internal std., if required.
.8 Attach syringe-syringe valve assembly to syringe valve on purging device. Open valves and inject sample into purging chamber.
.9 Close valves and purge as per Table 2.
B


B
7.2.5 Sample desorption
Interface type?
Non-cryogenic
Cryogenic
7.2.5.1 Place system in desorb mode and preheat trap to 180°C without gas flow. Simultaneously start flow of gas, temp. program of GC, and data acquisition.
7.2.5.2 Place system in desorb mode and rapidly heat trap to 180°C while backflushing with inert gas for 6 min. Rapidly heat trap to 250°C. Simultaneously begin temp. program of GC and data acquisition.
7.2.6 Recondition trap
7.2.7 Interpret data and calculate results.

METHOD 5035

CLOSED-SYSTEM PURGE-AND-TRAP AND EXTRACTION FOR VOLATILE ORGANICS IN SOIL AND WASTE SAMPLES

1.0 SCOPE AND APPLICATION

1.1 This method describes a closed-system purge-and-trap process for the analysis of volatile organic compounds (VOCs) in solid materials (e.g., soils, sediments, and solid waste). While the method is designed for use on samples containing low levels of VOCs, procedures are also provided for collecting and preparing solid samples containing high concentrations of VOCs and for oily wastes. For these high concentration and oily materials, sample collection and preparation are performed using the procedures described here, and sample introduction is performed using the aqueous purge-and-trap procedure in Method 5030. These procedures may be used in conjunction with any appropriate determinative gas chromatographic procedure, including, but not limited to, Methods 8015, 8021, and 8260.

1.2 The low soil method utilizes a hermetically-sealed sample vial, the seal of which is never broken from the time of sampling to the time of analysis. Since the sample is never exposed to the atmosphere after sampling, the losses of VOCs during sample transport, handling, and analysis are negligible. The applicable concentration range of the low soil method is dependent on the determinative method, matrix, and compound. However, it will generally fall in the 0.5 to 200 µg/kg range.

1.3 Procedures are included for preparing high concentration samples for purging by Method 5030. High concentration samples are those containing VOC levels of >200 µg/kg.

1.4 Procedures are also included for addressing oily wastes that are soluble in a water-miscible solvent. These samples are also purged using Method 5030.

1.5 Method 5035 can be used for most volatile organic compounds that have boiling points below 200°C and that are insoluble or slightly soluble in water. Volatile, water-soluble compounds can be included in this analytical technique. However, quantitation limits (by GC or GC/MS) are approximately ten times higher because of poor purging efficiency.

1.6 Method 5035, in conjunction with Method 8015 (GC/FID), may be used for the analysis of the aliphatic hydrocarbon fraction in the light ends of total petroleum hydrocarbons, e.g., gasoline. For the aromatic fraction (BTEX), use Method 5035 and Method 8021 (GC/PID). A total determinative analysis of gasoline fractions may be obtained using Method 8021 in series with Method 8015.

1.7 As with any preparative method for volatiles, samples should be screened to avoid contamination of the purge-and-trap system by samples that contain very high concentrations of purgeable material above the calibration range of the low concentration method. In addition, because the sealed sample container cannot be opened to remove a sample aliquot without compromising the integrity of the sample, multiple sample aliquots should be collected to allow for screening and reanalysis.

1.8 The closed-system purge-and-trap equipment employed for low concentration samples is not appropriate for soil samples preserved in the field with methanol. Such samples should be analyzed using Method 5030 (see the note in Sec. 6.2.2).

1.9 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Low concentration soil method - generally applicable to and soils and other solid samples with VOC concentrations in the range of 0.5 to 200 µg/kg.

Volatile organic compounds (VOCs) are determined by collecting an approximately 5-g sample, weighed in the field at the time of collection, and placing it in a pre-weighed vial with a septum-sealed screw-cap (see Sec. 4) that already contains a stirring bar and a sodium bisulfate preservative solution. The vial is sealed and shipped to a laboratory or appropriate analysis site. The entire vial is then placed, unopened, into the instrument carousel. Immediately before analysis, organic-free reagent water, surrogates, and internal standards (if applicable) are automatically added without opening the sample vial. The vial containing the sample is heated to 40° C and the volatiles purged into an appropriate trap using an inert gas combined with agitation of the sample. Purged components travel via a transfer line to a trap. When purging is complete, the trap is heated and backflushed with helium to desorb the trapped sample components into a gas chromatograph for analysis by an appropriate determinative method.

2.2 High concentration soil method - generally applicable to soils and other solid samples with VOC concentrations greater than 200 µg/kg.

The sample introduction technique in Sec. 2.1 is not applicable to all samples, particularly those containing high concentrations (generally greater than 200 µg/kg) of VOCs which may overload either the volatile trapping material or exceed the working range of the determinative instrument system (e.g., GC/MS, GC/FID, GC/EC, etc.). In such instances, this method describes two sample collection options and the corresponding sample purging procedures.

2.2.1 The first option is to collect a bulk sample in a vial or other suitable container without the use of the preservative solution described in Sec. 2.1. A portion of that sample is removed from the container in the laboratory and is dispersed in a water-miscible solvent to dissolve the volatile organic constituents. An aliquot of the solution is added to 5 mL of reagent water in a purge tube. Surrogates and internal standards (if applicable) are added to the solution, then purged using Method 5030, and analyzed by an appropriate determinative method. Because the procedure involves opening the vial and removing a portion of the soil, some volatile constituents may be lost during handling.

2.2.2 The second option is to collect an approximately 5-g sample in a pre-weighed vial with a septum-sealed screw-cap (see Sec 4) that contains 5 mL of a water-miscible organic solvent (e.g., methanol). At the time of analysis, surrogates are added to the vial, then an aliquot of the solvent is removed from the vial, purged using Method 5030 and analyzed by an appropriate determinative method.

2.3 High concentration oily waste method - generally applicable to oily samples with VOC concentrations greater than 200 µg/kg that can be diluted in a water-miscible solvent.

Samples that are comprised of oils or samples that contain significant amounts of oil present additional analytical challenges. This procedure is generally appropriate for such samples when they are soluble in a water-miscible solvent.

2.3.1 After demonstrating that a test aliquot of the sample is soluble in methanol or polyethylene glycol (PEG), a separate aliquot of the sample is spiked with surrogates and diluted in the appropriate solvent. An aliquot of the solution is added to 5 mL of reagent water in a purge tube, taking care to ensure that a floating layer of oil is not present in the purge tube. Internal standards (if applicable) are added to the solution which is then purged using Method 5030 and analyzed by an appropriate determinative method.

2.3.2 Samples that contain oily materials that are not soluble in water-miscible solvents must be prepared according to Method 3585.

3.0 INTERFERENCES

3.1 Impurities in the purge gas and from organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running method blanks. The use of non-polytetrafluoroethylene (non-PTFE) plastic coating, non-PTFE thread sealants, or flow controllers with rubber components in the purging device must be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. These compounds will result in interferences or false positives in the determinative step.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and handling protocols serves as a check on such contamination.

3.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed in sequence. Where practical, samples with unusually high concentrations of analytes should be followed by an analysis of organic-free reagent water to check for cross-contamination. If the target compounds present in an unusually concentrated sample are also found to be present in the subsequent samples, the analyst must demonstrate that the compounds are not due to carryover. Conversely, if those target compounds are not present in the subsequent sample, then the analysis of organic-free reagent water is not necessary.

3.4 The laboratory where volatile analysis is performed should be completely free of solvents. Special precautions must be taken to determine methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed will also lead to random background levels and the same precautions must be taken.

4.0 APPARATUS AND MATERIALS

4.1 Sample Containers

The specific sample containers required will depend on the purge-and-trap system to be employed (see Sec. 4.2). Several systems are commercially available. Some systems employ 40-mL clear vials with a special frit and equipped with two PTFE-faced silicone septa. Other

systems permit the use of any good quality glass vial that is large enough to contain at least 5 g of soil or solid material and at least 10 mL of water and that can be sealed with a screw-cap containing a PTFE-faced silicone septum. Consult the purge-and-trap system manufacturer's instructions regarding the suitable specific vials, septa, caps, and mechanical agitation devices.

4.2 Purge-and-Trap System

The purge-and-trap system consists of a unit that automatically adds water, surrogates, and internal standards (if applicable) to a vial containing the sample, purges the VOCs using an inert gas stream while agitating the contents of the vial, and also traps the released VOCs for subsequent desorption into the gas chromatograph. Such systems are commercially available from several sources and shall meet the following specifications.

4.2.1 The purging device should be capable of accepting a vial sufficiently large to contain a 5-g soil sample plus a magnetic stirring bar and 10 mL of water. The device must be capable of heating a soil vial to 40°C and holding it at that temperature while the inert purge gas is allowed to pass through the sample. The device should also be capable of introducing at least 5 mL of organic-free reagent water into the sample vial while trapping the displaced headspace vapors. It must also be capable of agitating the sealed sample during purging, (e.g., using a magnetic stirring bar added to the vial prior to sample collection, sonication, or other means). The analytes being purged must be quantitatively transferred to an absorber trap. The trap must be capable of transferring the absorbed VOCs to the gas chromatograph (see 4.2.2).

NOTE: The equipment used to develop this method was a Dynatech PTA-30 W/S Autosampler. This device was subsequently sold to Varian, and is now available as the Archon Purge and Trap Autosampler. See the Disclaimer at the front of this manual for guidance on the use of alternative equipment.

4.2.2 A variety of traps and trapping materials may be employed with this method. The choice of trapping material may depend on the analytes of interest. Whichever trap is employed, it must demonstrate sufficient adsorption and desorption characteristics to meet the quantitation limits of all the target analytes for a given project and the QC requirements in Method 8000 and the determinative method. The most difficult analytes are generally the gases, especially dichlorodifluoromethane. The trap must be capable of desorbing the late eluting target analytes.

NOTE: Check the responses of the brominated compounds when using alternative charcoal traps (especially Vocarb 4000), as some degradation has been noted when higher desorption temperatures (especially above 240 - 250°C) are employed. 2-Chloroethyl vinyl ether is degraded on Vocarb 4000 but performs adequately when Vocarb 3000 is used. The primary criterion, as stated above, is that all target analytes meet the sensitivity requirements for a given project.

4.2.2.1 The trap used to develop this method was 25 cm long, with an inside diameter of 0.105 inches, and was packed with Carbopack/Carbosieve (Supelco, Inc.).

4.2.2.2 The standard trap used in other EPA purge-and-trap methods is also acceptable. That trap is 25 cm long and has an inside diameter of at least 0.105 in. Starting from the inlet, the trap contains the equal amounts of the adsorbents listed below. It is recommended that 1.0 cm of methyl silicone-coated packing (35/60 mesh, Davison, grade 15 or equivalent) be inserted at the inlet to extend the life of the trap. If

the analysis of dichlorodifluoromethane or other fluorocarbons of similar volatility is not required, then the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap.

4.2.2.2.1 2,6-Diphenylene oxide polymer - 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

4.2.2.2.2 Methyl silicone packing - OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

4.2.2.2.3 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26, or equivalent, by crushing through 26 mesh screen.

4.2.2.3 Trapping materials other than those listed above also may be employed, provided that they meet the specifications in Sec. 4.2.3, below.

4.2.3 The desorber for the trap must be capable of rapidly heating the trap to the temperature recommended by the trap material manufacturer, prior to the beginning of the flow of desorption gas. Several commercial desorbers (purge-and-trap units) are available.

4.3 Syringe and Syringe Valves.

4.3.1 25-mL glass hypodermic syringes with Luer-Lok (or equivalent) tip (other sizes are acceptable depending on sample volume used).

4.3.2 2-way syringe valves with Luer ends.

4.3.3 25-µL micro syringe with a 2 inch x 0.006 inch ID, 22° bevel needle (Hamilton #702N or equivalent).

4.3.4 Micro syringes - 10-, 100-µL.

4.3.5 Syringes - 0.5-, 1.0-, and 5-mL, gas-tight with shut-off valve.

4.4 Miscellaneous.

4.4.1 Glass vials.

4.4.1.1 60-mL, septum-sealed, to collect samples for screening, dry weight determination.

4.4.1.2 40-mL, screw-cap, PTFE lined, septum-sealed. Examine each vial prior to use to ensure that the vial has a flat, uniform sealing surface.

4.4.2 Top-loading balance - Capable of accurately weighing to 0.01 g.

4.4.3 Glass scintillation vials - 20-mL, with screw-caps and PTFE liners, or glass culture tubes with screw-caps and PTFE liners, for dilution of oily waste samples.

4.4.4 Volumetric flasks - Class A, 10-mL and 100-mL, with ground-glass stoppers.

4.4.5 2-mL glass vials, for GC autosampler - Used for oily waste samples extracted with methanol or PEG.

4.4.6 Spatula, stainless steel - narrow enough to fit into a sample vial.

4.4.7 Disposable Pasteur pipettes.

4.4.8 Magnetic stirring bars - PTFE- or glass-coated, of the appropriate size to fit the sample vials. Consult manufacturer's recommendation for specific stirring bars. Stirring bars may be reused, provided that they are thoroughly cleaned between uses. Consult the manufacturers of the purging device and the stirring bars for suggested cleaning procedures.

4.5 Field Sampling Equipment

4.5.1 Purge-and-Trap Soil Sampler - Model 3780PT (Associated Design and Manufacturing Company, 814 North Henry Street, Alexandria, VA 22314), or equivalent.

4.5.2 EnCore™ sampler - (En Chem, Inc., 1795 Industrial Drive, Green Bay, WI 54302), or equivalent.

4.5.3 Alternatively, disposable plastic syringes with a barrel smaller than the neck of the soil vial may be used to collect the sample. The syringe end of the barrel is cut off prior to sampling. One syringe is needed for each sample aliquot to be collected.

4.5.4 Portable balance - For field use, capable of weighing to 0.01 g.

4.5.5 Balance weights - Balances employed in the field should be checked against an appropriate reference weight at least once daily, prior to weighing any samples, or as described in the sampling plan. The specific weights used will depend on the total weight of the sample container, sample, stirring bar, reagent water added, cap, and septum.

5.0 REAGENTS

5.1 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2 Methanol, CH_3OH - purge-and-trap quality or equivalent. Store away from other solvents.

5.3 Polyethylene glycol (PEG), $H(OCH_2CH_2)_nOH$ - free of interferences at the detection limit of the target analytes.

5.4 Low concentration sample preservative.

5.4.1 Sodium bisulfate, $NaHSO_4$ - ACS reagent grade or equivalent.

5.4.2 The preservative should be added to the vial prior to shipment to the field, and must be present in the vial prior to adding the sample.

5.5 See the determinative method and Method 5000 for guidance on internal standards and surrogates to be employed in this procedure.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Refer to the introductory material in this chapter, Organic Analytes, Sec. 4.1, for general sample collection information. The low concentration portion of this method employs sample vials that are filled and weighed in the field and never opened during the analytical process. As a result, sampling personnel should be equipped with a portable balance capable of weighing to 0.01 g.

6.1 Preparation of sample vials

The specific preparation procedures for sample vials depend on the expected concentration range of the sample, with separate preparation procedures for low concentration soil samples and high concentration soil and solid waste samples. Sample vials should be prepared in a fixed laboratory or other controlled environment, sealed, and shipped to the field location. Gloves should be worn during the preparation steps.

6.1.1 Low concentration soil samples

The following steps apply to the preparation of vials used in the collection of low concentration soil samples to be analyzed by the closed-system purge-and-trap equipment described in Method 5035.

6.1.1.1 Add a clean magnetic stirring bar to each clean vial. If the purge-and-trap device (Sec. 4.2) employs a means of stirring the sample other than a magnetic stirrer (e.g., sonication or other mechanical means), then the stir bar is omitted.

6.1.1.2 Add preservative to each vial. The preservative is added to each vial prior to shipping the vial to the field. Add approximately 1 g of sodium bisulfate to each vial. If samples markedly smaller or larger than 5 g are to be collected, adjust the amount of preservative added to correspond to approximately 0.2 g of preservative for each 1 g of sample. Enough sodium bisulfate should be present to ensure a sample pH of ≤2.

6.1.1.3 Add 5 mL of organic-free reagent water to each vial. The water and the preservative will form an acid solution that will reduce or eliminate the majority of the biological activity in the sample, thereby preventing biodegradation of the volatile target analytes.

6.1.1.4 Seal the vial with the screw-cap and septum seal. If the double-ended, fritted, vials are used, seal both ends as recommended by the manufacturer.

6.1.1.5 Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible).

6.1.1.6 Weigh the prepared vial to the nearest 0.01 g, record the tare weight, and write it on the label.

6.1.1.7 Because volatile organics will partition into the headspace of the vial from the aqueous solution and will be lost when the vial is opened, surrogates, matrix spikes, and internal standards (if applicable) should only be added to the vials after the sample has been added to the vial. These standards should be introduced back in the

laboratory, either manually by puncturing the septum with a small-gauge needle or automatically by the sample introduction system, just prior to analysis.

6.1.2 High concentration soil samples collected without a preservative

When high concentration samples are collected without a preservative, a variety of sample containers may be employed, including 60-mL glass vials with septum seals (see Sec. 4.4).

6.1.3 High concentration soil samples collected and preserved in the field

The following steps apply to the preparation of vials used in the collection of high concentration soil samples to be preserved in the field with methanol and analyzed by the aqueous purge-and-trap equipment described in Method 5030.

6.1.3.1 Add 10 mL of methanol to each vial.

6.1.3.2 Seal the vial with the screw-cap and septum seal.

6.1.3.3 Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible).

6.1.3.4 Weigh the prepared vial to the nearest 0.01 g, record the tare weight, and write it on the label.

NOTE: Vials containing methanol should be weighed a second time on the day that they are to be used. Vials found to have lost methanol (reduction in weight of >0.01 g) should not be used for sample collection.

6.1.3.5 Surrogates, internal standards and matrix spikes (if applicable) should be added to the sample after it is returned to the laboratory and prior to analysis.

6.1.4 Oily waste samples

When oily waste samples are known to be soluble in methanol or PEG, sample vials may be prepared as described in Sec. 6.1.3, using the appropriate solvent. However, when the solubility of the waste is unknown, the sample should be collected without the use of a preservative, in a vial such as that described in Sec. 6.1.2.

6.2 Sample collection

Collect the sample according to the procedures outlined in the sampling plan. As with any sampling procedure for volatiles, care must be taken to minimize the disturbance of the sample in order to minimize the loss of the volatile components. Several techniques may be used to transfer a sample to the relatively narrow opening of the low concentration soil vial. These include devices such as the EnCore™ sampler, the Purge-and-Trap Soil Sampler ™ and a cut plastic syringe. Always wear gloves whenever handling the tared sample vials.

6.2.1 Low concentration soil samples

6.2.1.1 Using an appropriate sample collection device, collect approximately 5 g of sample as soon as possible after the surface of the soil or other solid material has been exposed to the atmosphere: generally within a few minutes at most. Carefully wipe the exterior of the sample collection device with a clean cloth or towel.

6.2.1.2 Using the sample collection device, add about 5 g (2 - 3 cm) of soil to the sample vial containing the preservative solution. Quickly brush any soil off the vial threads and immediately seal the vial with the septum and screw-cap. Store samples on ice at 4°C.

NOTE Soil samples that contain carbonate minerals (either from natural sources or applied as an amendment) may effervesce upon contact with the acidic preservative solution in the low concentration sample vial. If the amount of gas generated is very small (i.e., several mL), any loss of volatiles as a result of such effervescence may be minimal if the vial is sealed quickly. However, if larger amounts of gas are generated, not only may the sample lose a significant amount of analyte, but the gas pressure may shatter the vial if the sample vial is sealed. Therefore, when samples are known or suspected to contain high levels of carbonates, a test sample should be collected, added to a vial, and checked for effervescence. If a rapid or vigorous reaction occurs, discard the sample and collect low concentration samples in vials that do not contain the preservative solution.

6.2.1.3 When practical, use a portable balance to weigh the sealed vial containing the sample to ensure that 5.0 ± 0.5 g of sample were added. The balance should be calibrated in the field using an appropriate weight for the sample containers employed (Sec. 4.5.5). Record the weight of the sealed vial containing the sample to the nearest 0.01 g.

6.2.1.4 Alternatively, collect several trial samples with plastic syringes. Weigh each trial sample and note the length of the soil column in the syringe. Use these data to determine the length of soil in the syringe that corresponds to 5.0 ± 0.5 g. Discard each trial sample.

6.2.1.5 As with the collection of aqueous samples for volatiles, collect <u>at least</u> two replicate samples. This will allow the laboratory an additional sample for reanalysis. The second sample should be taken from the same soil stratum or the same section of the solid waste being sampled, and within close proximity to the location from which the original sample was collected.

6.2.1.6 In addition, since the soil vial cannot be opened without compromising the integrity of the sample, at least one additional aliquot of sample must be collected for screening, dry weight determination, and high concentration analysis (if necessary). This third aliquot may be collected in a 60-mL glass vial or a third 40-mL soil sample vial. However, this third vial must *not* contain the sample preservative solution, as an aliquot will be used to determine dry weight. If high concentration samples are collected in vials containing methanol, then two additional aliquots should be collected: one for high concentration analysis collected in a vial containing methanol, and another for the dry weight determination in a vial without either methanol or the low concentration aqueous preservative solution.

6.2.1.7 If samples are known or expected to contain target analytes over a wide range of concentrations, thereby requiring the analyses of multiple sample aliquots, it may be advisable and practical to take an additional sample aliquot in a low concentration soil vial containing the preservative, but collecting only 1-2 g instead of the 5 g collected in Sec. 6.2.1.1. This aliquot may be used for those analytes that exceed the instrument calibration range in the 5-g analysis.

6.2.1.8 The EnCore™ sampler has not been thoroughly evaluated by EPA as a sample storage device. While preliminary results indicate that storage in the EnCore™ device may be appropriate for up to 48 hours, samples collected in this device should be transferred to the soil sample vials as soon as possible, or analyzed within 48 hours.

6.2.1.9 The collection of low concentration soil samples in vials that contain methanol is not appropriate for samples analyzed with the closed-system purge-and-trap equipment described in this method (see Sec. 6.2.2).

6.2.2 High concentration soil samples preserved in the field

The collection of soil samples in vials that contain methanol has been suggested by some as a combined preservation and extraction procedure. However, this procedure is <u>not</u> appropriate for use with the low concentration soil procedure described in this method.

<u>NOTE</u>: The use of methanol preservation has not been formally evaluated by EPA and analysts must be aware of two potential problems. First, the use of methanol as a preservative and extraction solvent introduces a significant dilution factor that will raise the method quantitation limit beyond the operating range of the low concentration direct purge-and-trap procedure (0.5-200 µg/kg). The exact dilution factor will depend on the masses of solvent and sample, but generally exceeds 1000, and may make it difficult to demonstrate compliance with regulatory limits or action levels for some analytes. Because the analytes of interest are volatile, the methanol extract cannot be concentrated to overcome the dilution problem. Thus, for samples of unknown composition, it may still be necessary to collect an aliquot for analysis by this closed-system procedure and another aliquot preserved in methanol and analyzed by other procedures. The second problem is that the addition of methanol to the sample is likely to cause the sample to fail the ignitability characteristic, thereby making the unused sample volume a hazardous waste.

6.2.2.1 When samples are <u>known</u> to contain volatiles at concentrations high enough that the dilution factor will not preclude obtaining results within the calibration range of the appropriate determinative method, a sample may be collected and immediately placed in a sample vial containing purge-and-trap grade methanol.

6.2.2.2 Using an appropriate sample collection device, collect approximately 5 g of sample as soon as possible after the surface of the soil or other solid material has been exposed to the atmosphere: generally within a few minutes at most. Carefully wipe the exterior of the sample collection device with a clean cloth or towel.

6.2.2.3 Using the sample collection device, add about 5 g (2 - 3 cm) of soil to the vial containing 10 mL of methanol. Quickly brush any soil off the vial threads and immediately seal the vial with the septum and screw-cap. Store samples on ice at 4 °C.

6.2.2.4 When practical, use a portable balance to weigh the sealed vial containing the sample to ensure that 5.0 ± 0.5 g of sample were added. The balance should be calibrated in the field using an appropriate weight for the sample containers employed (Sec. 4.5.5). Record the weight of the sealed vial containing the sample to the nearest 0.01 g.

6.2.2.5 Alternatively, collect several trial samples with plastic syringes. Weigh each trial sample and note the length of the soil column in the syringe. Use these data to determine the length of soil in the syringe that corresponds to 5.0 ± 0.5 g. Discard each trial sample.

6.2.2.6 Other sample weights and volumes of methanol may be employed, provided that the analyst can demonstrate that the sensitivity of the overall analytical procedure is appropriate for the intended application.

6.2.2.7 The collection of at least one additional sample aliquot is required for the determination of the dry weight, as described in Sec. 6.2.1.6. Samples collected in methanol should be shipped as described in Sec. 6.3, and must be clearly labeled as containing methanol, so that the samples are not analyzed using the closed-system purge-and-trap equipment described in this procedure.

6.2.3 High concentration soil sample <u>not</u> preserved in the field

The collection of high concentration soil samples that are not preserved in the field generally follows similar procedures as for the other types of samples described in Secs. 6.2.1 and 6.2.2, with the obvious exception that the sample vials contain neither the aqueous preservative solution nor methanol. However, when field preservation is not employed, it is better to collect a larger volume sample, filling the sample container as full as practical in order to minimize the headspace. Such collection procedures generally do not require the collection of a separate aliquot for dry weight determination, but it may be advisable to collect a second sample aliquot for screening purposes, in order to minimize the loss of volatiles in either aliquot.

6.2.4 Oily waste samples

The collection procedures for oily samples depend on knowledge of the waste and its solubility in methanol or other solvents.

6.2.4.1 When an oily waste is <u>known</u> to be soluble in methanol or PEG, the sample may be collected in a vial containing such a solvent (see Sec. 6.1.4), using procedures similar to those described in Sec. 6.2.2.

6.2.4.2 When the solubility of the oily waste is <u>not</u> known, the sample should either be collected in a vial without a preservative, as described in Sec. 6.2.3, or the solubility of a trial sample should be tested in the field, using a vial containing solvent. If the trial sample is soluble in the solvent, then collect the oily waste sample as described in Sec. 6.2.2. Otherwise, collect an unpreserved sample as described in Sec. 6.2.3.

6.3 Sample handling and shipment

All samples for volatiles analysis should be cooled to approximately 4 °C, packed in appropriate containers, and shipped to the laboratory on ice, as described in the sampling plan.

6.4 Sample storage

6.4.1 Once in the laboratory, store samples at 4 °C until analysis. The sample storage area should be free of organic solvent vapors.

6.4.2 All samples should be analyzed as soon as practical, and within the designated holding time from collection. Samples not analyzed within the designated holding time must be noted and the data are considered minimum values.

6.4.3 When the low concentration samples are strongly alkaline or highly calcareous in nature, the sodium bisulfate preservative solution may not be strong enough to reduce the pH of the soil/water solution to below 2. Therefore, when low concentration soils to be sampled are known or suspected to be strongly alkaline or highly calcareous, additional steps may be required to preserve the samples. Such steps include: addition of larger amounts of the sodium bisulfate preservative to non-calcareous samples, storage of low concentration samples at -10°C (taking care not to fill the vials so full that the expansion of the water in the vial breaks the vial), or significantly reducing the maximum holding time for low concentration soil samples. Whichever steps are employed, they should be clearly described in the sampling and QA project plans and distributed to both the field and laboratory personnel. See Sec. 6.2.1.2 for additional information.

7.0 PROCEDURE

This section describes procedures for sample screening, the low concentration soil method, the high concentration soil method, and the procedure for oily waste samples. High concentration samples are to be introduced into the GC system using Method 5030. Oily waste samples are to be introduced into the GC system using Method 5030 if they are soluble in a water-miscible solvent, or using Method 3585 if they are not.

7.1 Sample screening

7.1.1 It is highly recommended that all samples be screened prior to the purge-and-trap GC or GC/MS analysis. Samples may contain higher than expected quantities of purgeable organics that will contaminate the purge-and-trap system, thereby requiring extensive cleanup and instrument maintenance. The screening data are used to determine which is the appropriate sample preparation procedure for the particular sample, the low concentration closed-system direct purge-and-trap method (Sec. 7.2), the high concentration (methanol extraction) method (Sec. 7.3), or the nonaqueous liquid (oily waste) methanol or PEG dilution procedure (Sec. 7.4).

7.1.2 The analyst may employ any appropriate screening technique. Two suggested screening techniques employing SW-846 methods are:

7.1.2.1 Automated headspace (Method 5021) using a gas chromatograph (GC) equipped with a photoionization detector (PID) and an electrolytic conductivity detector (HECD) in series, or,

7.1.2.2 Extraction of the sample with hexadecane (Method 3820) and analysis of the extract on a GC equipped with a FID and/or an ECD.

7.1.3 The analyst may inject a calibration standard containing the analytes of interest at a concentration equivalent to the upper limit of the calibration range of the low concentration soil method. The results from this standard may be used to determine when the screening results approach the upper limit of the low concentration soil method. There are no linearity or other performance criteria associated with the injection of such a standard, and other approaches may be employed to estimate sample concentrations.

7.1.4 Use the low concentration closed-system purge-and-trap method (Sec. 7.2) if the estimated concentration from the screening procedure falls within the calibration range of the selected determinative method. If the concentration exceeds the calibration range of the low concentration soil method, then use either the high concentration soil method (Sec. 7.3), or the oily waste method (Sec. 7.4).

7.2 Low concentration soil method (Approximate concentration range of 0.5 to 200 µg/kg - the concentration range is dependent upon the determinative method and the sensitivity of each analyte.)

7.2.1 Initial calibration

Prior to using this introduction technique for any GC or GC/MS method, the system must be calibrated. General calibration procedures are discussed in Method 8000, while the determinative methods and Method 5000 provide specific information on calibration and preparation of standards. Normally, external standard calibration is preferred for the GC methods (non-MS detection) because of possible interference problems with internal standards. If interferences are not a problem, or when a GC/MS method is used, internal standard calibration may be employed.

7.2.1.1 Assemble a purge-and-trap device that meets the specification in Sec. 4.2 and that is connected to a gas chromatograph or a gas chromatograph/mass spectrometer system.

7.2.1.2 Before initial use, a Carbopack/Carbosieve trap should be conditioned overnight at 245°C by backflushing with an inert gas flow of at least 20 mL/minute. If other trapping materials are substituted for the Carbopack/Carbosieve, follow the manufacturers recommendations for conditioning. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 minutes at 245°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

7.2.1.3 If the standard trap in Sec. 4.2.2.2 is employed, prior to initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min, or according to the manufacturer's recommendations. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

7.2.1.4 Establish the purge-and-trap instrument operating conditions. Adjust the instrument to inject 5 mL of water, to heat the sample to 40°C, and to hold the sample at 40°C for 1.5 minutes before commencing the purge process, or as recommended by the instrument manufacturer.

7.2.1.5 Prepare a minimum of five initial calibration standards containing all the analytes of interest and surrogates, as described in Method 8000, and following the instrument manufacturer's instructions. The calibration standards are prepared in organic-free reagent water. The volume of organic-free reagent water used for calibration must be the same volume used for sample analysis (normally 5 mL added to the vial before shipping it to the field plus the organic-free reagent water added by the instrument). The calibration standards should also contain approximately the same amount of the sodium bisulfate preservative as the sample (e.g., ~1 g), as the presence of the preservative will affect the purging efficiencies of the analytes. The internal standard solution must be added automatically, by the instrument, in the same fashion as used for the samples. Place the soil vial containing the solution in the instrument carousel. In order to calibrate the surrogates using standards at five concentrations, it may be necessary to disable the automatic addition of surrogates to each vial containing a calibration standard (consult the manufacturer's instructions). Prior to purging, heat the sample vial to 40°C for 1.5 minutes, or as recommended by the manufacturer.

7.2.1.6 Carry out the purge-and-trap procedure as outlined in Secs. 7.2.3. to 7.2.5.

7.2.1.7 Calculate calibration factors (CF) or response factors (RF) for each analyte of interest using the procedures described in Method 8000. Calculate the average CF (external standards) or RF (internal standards) for each compound, as described in Method 8000. Evaluate the linearity of the calibration data, or choose another calibration model, as described in Method 8000 and the specific determinative method.

7.2.1.8 For GC/MS analysis, a system performance check must be made before this calibration curve is used (see Method 8260). If the purge-and-trap procedure is used with Method 8021, evaluate the response for the following four compounds: chloromethane; 1,1-dichloroethane; bromoform; and 1,1,2,2-tetrachloroethane. They are used to check for proper purge flow and to check for degradation caused by contaminated lines or active sites in the system.

7.2.1.8.1 Chloromethane is the most likely compound to be lost if the purge flow is too fast.

7.2.1.8.2 Bromoform is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response.

7.2.1.8.3 Tetrachloroethane and 1,1-dichloroethane are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.2.1.9 When analyzing for very late eluting compounds with Method 8021 (i.e., hexachlorobutadiene, 1,2,3-trichlorobenzene, etc.), cross-contamination and memory effects from a high concentration sample or even the standard are a common problem.

Extra rinsing of the purge chamber after analysis normally corrects this. The newer purge-and-trap systems often overcome this problem with better bakeout of the system following the purge-and-trap process. Also, the charcoal traps retain less moisture and decrease the problem.

7.2.2 Calibration verification

Refer to Method 8000 for details on calibration verification. A single standard near the mid-point of calibration range is used for verification. This standard should also contain approximately 1 g of sodium bisulfate.

7.2.3 Sample purge-and-trap

This method is designed for a 5-g sample size, but smaller sample sizes may be used. Consult the instrument manufacturer's instructions regarding larger sample sizes, in order to avoid clogging of the purging apparatus. The soil vial is hermetically sealed at the sampling site, and MUST remain so in order to guarantee the integrity of the sample. Gloves must be worn when handling the sample vial since the vial has been tared. If any soil is noted on the exterior of the vial or cap, it must be carefully removed prior to weighing. Weigh the vial and contents to the nearest 0.01 g, even if the sample weight was determined in the field, and record this weight. This second weighing provides a check on the field sampling procedures and provides additional assurance that the reported sample weight is accurate. Data users should be advised on significant discrepancies between the field and laboratory weights.

7.2.3.1 Remove the sample vial from storage and allow it to warm to room temperature. Shake the vial gently, to ensure that the contents move freely and that stirring will be effective. Place the sample vial in the instrument carousel according to the manufacturer's instructions.

7.2.3.2 Without disturbing the hermetic seal on the sample vial, add 5 mL of organic-free reagent water, the internal standards, and the surrogate compounds. This is carried out using the automated sampler. Other volumes of organic-free reagent water may be used, however, it is imperative that all samples, blanks, and calibration standards have exactly the same final volume of organic-free reagent water. Prior to purging, heat the sample vial to 40°C for 1.5 minutes, or as described by the manufacturer.

7.2.3.3 For the sample selected for matrix spiking, add the matrix spiking solution described in Sec. 5.0 of Method 5000, either manually, or automatically, following the manufacturer's instructions. The concentration of the spiking solution and the amount added should be established as described in Sec. 8.0 of Method 8000.

7.2.3.4 Purge the sample with helium or another inert gas at a flow rate of up to 40 mL/minute (the flow rate may vary from 20 to 40 mL/min, depending on the target analyte group) for 11 minutes while the sample is being agitated with the magnetic stirring bar or other mechanical means. The purged analytes are allowed to flow out of the vial through a glass-lined transfer line to a trap packed with suitable sorbent materials.

7.2.4 Sample Desorption

7.2.4.1 Non-cryogenic interface - After the 11 minute purge, place the purge-and-trap system in the desorb mode and preheat the trap to 245°C without a flow

of desorption gas. Start the flow of desorption gas at 10 mL/minute for about four minutes (1.5 min is normally adequate for analytes in Method 8015). Begin the temperature program of the gas chromatograph and start data acquisition.

7.2.4.2 Cryogenic interface - After the 11 minute purge, place the purge-and-trap system in the desorb mode, make sure that the cryogenic interface is at -150°C or lower, and rapidly heat the trap to 245°C while backflushing with an inert gas at 4 mL/minute for about 5 minutes (1.5 min is normally adequate for analytes in Methods 8015). At the end of the 5-minute desorption cycle, rapidly heat the cryogenic trap to 250°C. Begin the temperature program of the gas chromatograph and start the data acquisition.

7.2.5 Trap Reconditioning

After desorbing the sample for 4 minutes, recondition the trap by returning the purge-and-trap system to the purge mode. Maintain the trap temperature at 245°C (or other temperature recommended by the manufacturer of the trap packing materials). After approximately 10 minutes, turn off the trap heater and halt the purge flow through the trap. When the trap is cool, the next sample can be analyzed.

7.2.6 Data Interpretation

Perform qualitative and quantitative analysis following the guidance given in the determinative method and Method 8000. If the concentration of any target analyte exceeds the calibration range of the instrument, it will be necessary to reanalyze the sample by the high concentration method. Such reanalyses need only address those analytes for which the concentration exceeded the calibration range of the low concentration method. Alternatively, if a sample aliquot of 1-2 g was also collected (see Sec. 6.2.1.7), it may be practical to analyze that aliquot for the analytes that exceeded the instrument calibration range in the 5-g analysis. If results are to be reported on a dry weight basis, proceed to Sec. 7.5.

7.3 High concentration method for soil samples with concentrations generally greater than 200 µg/kg.

The high concentration method for soil is based on a solvent extraction. A solid sample is either extracted or diluted, depending on sample solubility in a water-miscible solvent. An aliquot of the extract is added to organic-free reagent water containing surrogates and, if applicable, internal and matrix spiking standards, purged according to Method 5030, and analyzed by an appropriate determinative method. Wastes that are insoluble in methanol (i.e., petroleum and coke wastes) are diluted with hexadecane (see Sec. 7.3.8).

The specific sample preparation steps depend on whether or not the sample was preserved in the field. Samples that were <u>not</u> preserved in the field are prepared using the steps below beginning at Sec. 7.3.1. If solvent preservation was employed in the field, then the preparation begins with Sec. 7.3.4.

7.3.1 When the high concentration sample is <u>not</u> preserved in the field, the sample consists of the entire contents of the sample container. Do not discard any supernatant liquids. Whenever practical, mix the contents of the sample container by shaking or other mechanical means without opening the vial. When shaking is not practical, quickly mix the contents of the vial with a narrow metal spatula and immediately reseal the vial.

7.3.2 If the sample is from an unknown source, perform a solubility test before proceeding. Remove several grams of material from the sample container. Quickly reseal the container to minimize the loss of volatiles. Weigh 1-g aliquots of the sample into several test tubes or other suitable containers. Add 10 mL of methanol to the first tube, 10 mL of PEG to the second, and 10 mL of hexadecane to the third. Swirl the sample and determine if it is soluble in the solvent. Once the solubility has been evaluated, discard these test solutions. If the sample is soluble in either methanol or PEG, proceed with Sec. 7.3.3. If the sample is only soluble in hexadecane, proceed with Sec. 7.3.8.

7.3.3 For soil and solid waste samples that are soluble in methanol, add 9.0 mL of methanol and 1.0 mL of the surrogate spiking solution to a tared 20-mL vial. Using a top-loading balance, weigh 5 g (wet weight) of sample into the vial. Quickly cap the vial and reweigh the vial. Record the weight to 0.1 g. Shake the vial for 2 min. If the sample was not soluble in methanol, but was soluble in PEG, employ the same procedure described above, but use 9.0 mL of PEG in place of the methanol. Proceed with Sec. 7.3.5.

NOTE: The steps in Secs. 7.3.1, 7.3.2, and 7.3.3 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free from solvent fumes.

7.3.4 For soil and solid waste samples that were collected in methanol or PEG (see Sec. 6.2.2), weigh the vial to 0.1 g as a check on the weight recorded in the field, add the surrogate spiking solution to the vial by injecting it through the septum, shake for 2 min, as described above, and proceed with Sec. 7.3.5.

7.3.5 Pipet approximately 1 mL of the extract from either Sec. 7.3.3 or 7.3.4 into a GC vial for storage, using a disposable pipet, and seal the vial. The remainder of the extract may be discarded. Add approximately 1 mL of methanol or PEG to a separate GC vial for use as the method blank for each set of samples extracted with the same solvent.

7.3.6 The extracts must be stored at 4 °C in the dark, prior to analysis. Add an appropriate aliquot of the extract (see Table 2) to 5.0 mL of organic-free reagent water and analyze by Method 5030 in conjunction with the appropriate determinative method. Proceed to Sec. 7.0 in Method 5030 and follow the procedure for purging high concentration samples.

7.3.7 If results are to be reported on a dry weight basis, determine the dry weight of a separate aliquot of the sample, using the procedure in Sec. 7.5, after the sample extract has been transferred to a GC vial and the vial sealed.

7.3.8 For solids that are not soluble in methanol or PEG (including those samples consisting primarily of petroleum or coking waste) dilute or extract the sample with hexadecane using the procedures in Sec. 7.0 of Method 3585.

7.4 High concentration method for oily waste samples

This procedure for the analysis of oily waste samples involves the dilution of the sample in methanol or PEG. However, care must be taken to avoid introducing any of the floating oil layer into the instrument. A portion of the diluted sample is then added to 5.0 mL of organic-free reagent water, purged according to Method 5030, and analyzed using an appropriate determinative method.

For oily samples that are not soluble in methanol or PEG (including those samples consisting primarily of petroleum or coking waste), dilute or extract with hexadecane using the procedures in Sec. 7.0 of Method 3585.

The specific sample preparation steps depend on whether or not the sample was preserved in the field. Samples that were not preserved in the field are prepared using the steps below, beginning at Sec. 7.4.1. If methanol preservation was employed in the field, then the preparation begins with Sec. 7.4.3.

7.4.1 If the waste was <u>not</u> preserved in the field and it is soluble in methanol or PEG, weigh 1 g (wet weight) of the sample into a tared 10-mL volumetric flask, a tared scintillation vial, or a tared culture tube. If a vial or tube is used instead of a volumetric flask, it must be calibrated prior to use. This operation <u>must</u> be performed prior to opening the sample vial and weighing out the aliquot for analysis.

7.4.1.1 To calibrate the vessel, pipet 10.0 mL of methanol or PEG into the vial or tube and mark the bottom of the meniscus.

7.4.1.2 Discard this solvent, and proceed with weighing out the 1-g sample aliquot.

7.4.2 Quickly add 1.0 mL of surrogate spiking solution to the flask, vial, or tube, and dilute to 10.0 mL with the appropriate solvent (methanol or PEG). Swirl the vial to mix the contents and then shake vigorously for 2 minutes.

7.4.3 If the sample was collected in the field in a vial containing methanol or PEG, weigh the vial to 0.1 g as a check on the weight recorded in the field, add the surrogate spiking solution to the vial by injecting it through the septum. Swirl the vial to mix the contents and then shake vigorously for 2 minutes and proceed with Sec. 7.4.4.

7.4.4 Regardless of how the sample was collected, the target analytes are extracted into the solvent along with the majority of the oily waste (i.e., some of the oil may still be floating on the surface). If oil is floating on the surface, transfer 1 to 2 mL of the extract to a clean GC vial using a Pasteur pipet. Ensure that no oil is transferred to the vial.

7.4.5 Add 10 - 50 µL of the methanol extract to 5 mL of organic-free reagent water for purge-and-trap analysis, using Method 5030.

7.4.6 Prepare a matrix spike sample by adding 10 - 50 µL of the matrix spike standard dissolved in methanol to a 1-g aliquot of the oily waste. Shake the vial to disperse the matrix spike solution throughout the oil. Then add 10 mL of extraction solvent and proceed with the extraction and analysis, as described in Secs. 7.4.2 - 7.4.5. Calculate the recovery of the spiked analytes as described in Method 8000. If the recovery is not within the acceptance limits for the application, use the hexadecane dilution technique in Sec. 7.0 of Method 3585.

7.5 Determination of % Dry Weight

If results are to be reported on a dry weight basis, it is necessary to determine the dry weight of the sample.

<u>NOTE</u> It is highly recommended that the dry weight determination only be made after the analyst has determined that no sample aliquots will be taken from the 60-mL vial for high

concentration analysis. This is to minimize loss of volatiles and to avoid sample contamination from the laboratory atmosphere. There is no holding time associated with the dry weight determination. Thus, this determination can be made any time prior to reporting the sample results, as long as the vial containing the additional sample has remained sealed and properly stored.

7.5.1 Weigh 5-10 g of the sample from the 60-mL VOA vial into a tared crucible.

7.5.2 Dry this aliquot overnight at 105°C. Allow to cool in a desiccator before weighing. Calculate the % dry weight as follows:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 5000 for sample preparation QC procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of an organic-free reagent water method blank that all glassware and reagents are interference free. Each time a set of samples is extracted, or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat this demonstration whenever new staff are trained or significant changes in instrumentation are made. See Sec. 8.0 of Methods 5000 and 8000 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - See Sec. 8.0 in Method 5000 and Method 8000 for procedures to follow to demonstrate acceptable continuing performance on each set of samples to be analyzed. These include the method blank, either a matrix spike/matrix spike duplicate or a matrix spike and duplicate sample analysis, a laboratory control sample (LCS), and the addition of surrogates to each sample and QC sample.

8.5 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 Single laboratory accuracy and precision data were obtained for the method analytes in three soil matrices, sand, a soil collected 10 feet below the surface of a hazardous landfill, called the

C-Horizon, and a surface garden soil. Each sample was fortified with the analytes at a concentration of 20 ng/5 g, which is equivalent to 4 µg/kg. These data are listed in tables found in Method 8260.

9.2 Single laboratory accuracy and precision data were obtained for certain method analytes when extracting oily liquid using methanol as the extraction solvent. The data are presented in a table in Method 8260. The compounds were spiked into three portions of an oily liquid (taken from a waste site) following the procedure for matrix spiking described in Sec. 7.4. This represents a worst case set of data based on recovery data from many sources of oily liquid.

10.0 REFERENCES

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TABLE 1

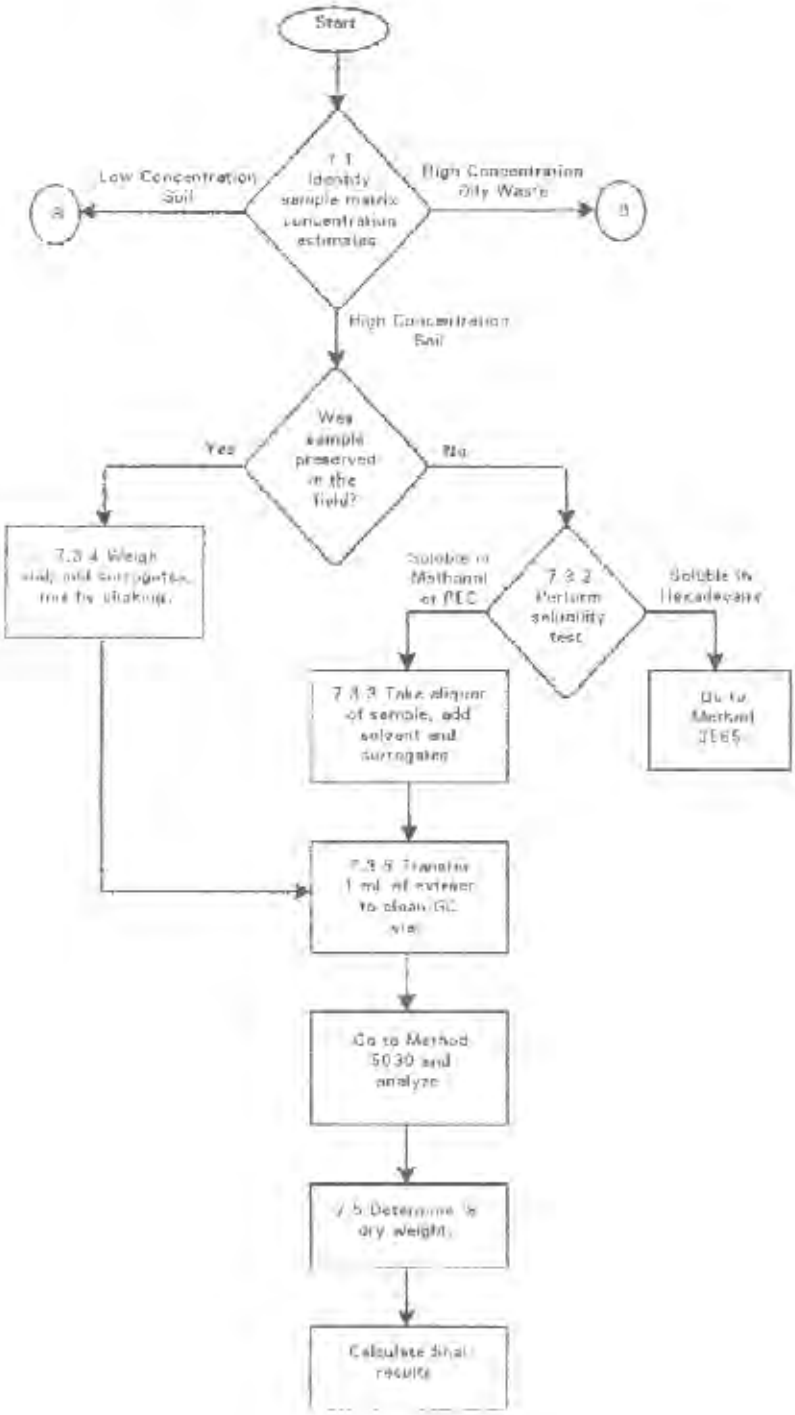
QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS OF HIGH CONCENTRATION SOILS/SEDIMENTS

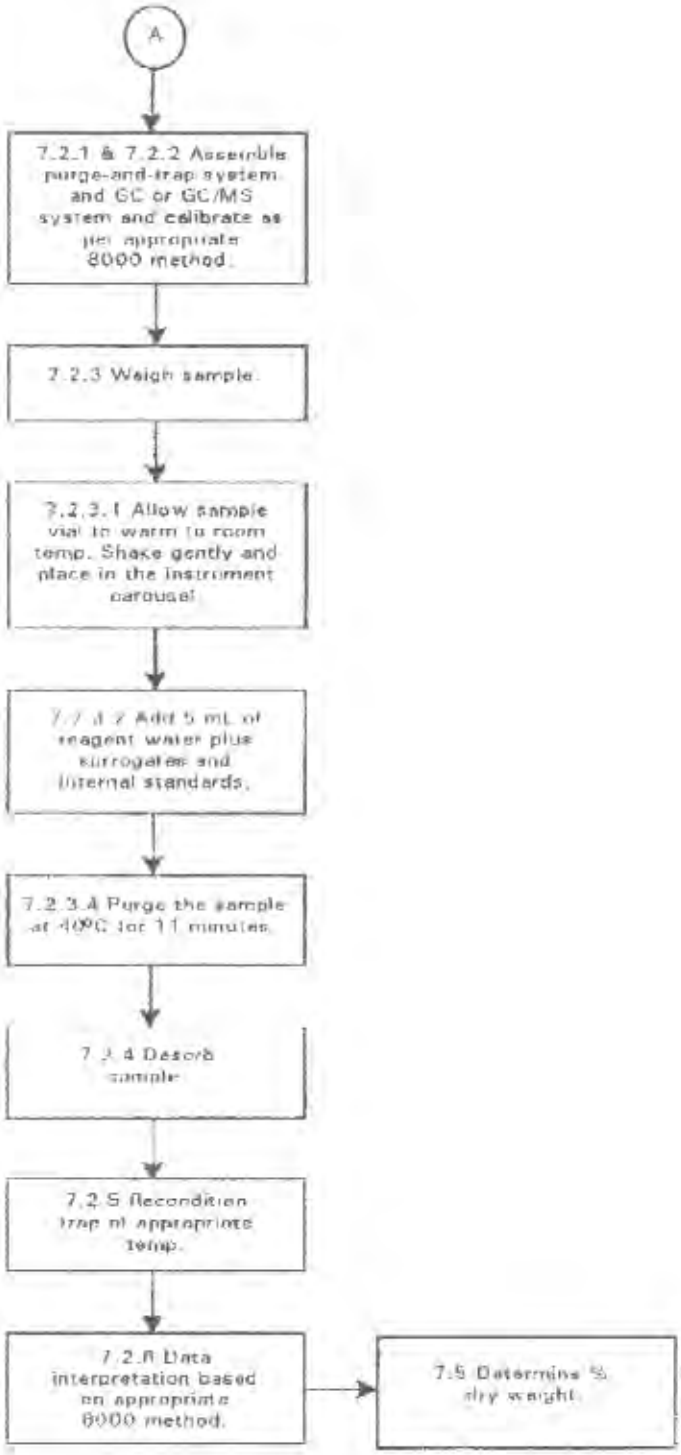
Approximate Concentration Range	Volume of Methanol Extract[a]
500 - 10,000 µg/kg	100 µL
1,000 - 20,000 µg/kg	50 µL
5,000 - 100,000 µg/kg	10 µL
25,000 - 500,000 µg/kg	100 µL of 1/50 dilution[b]

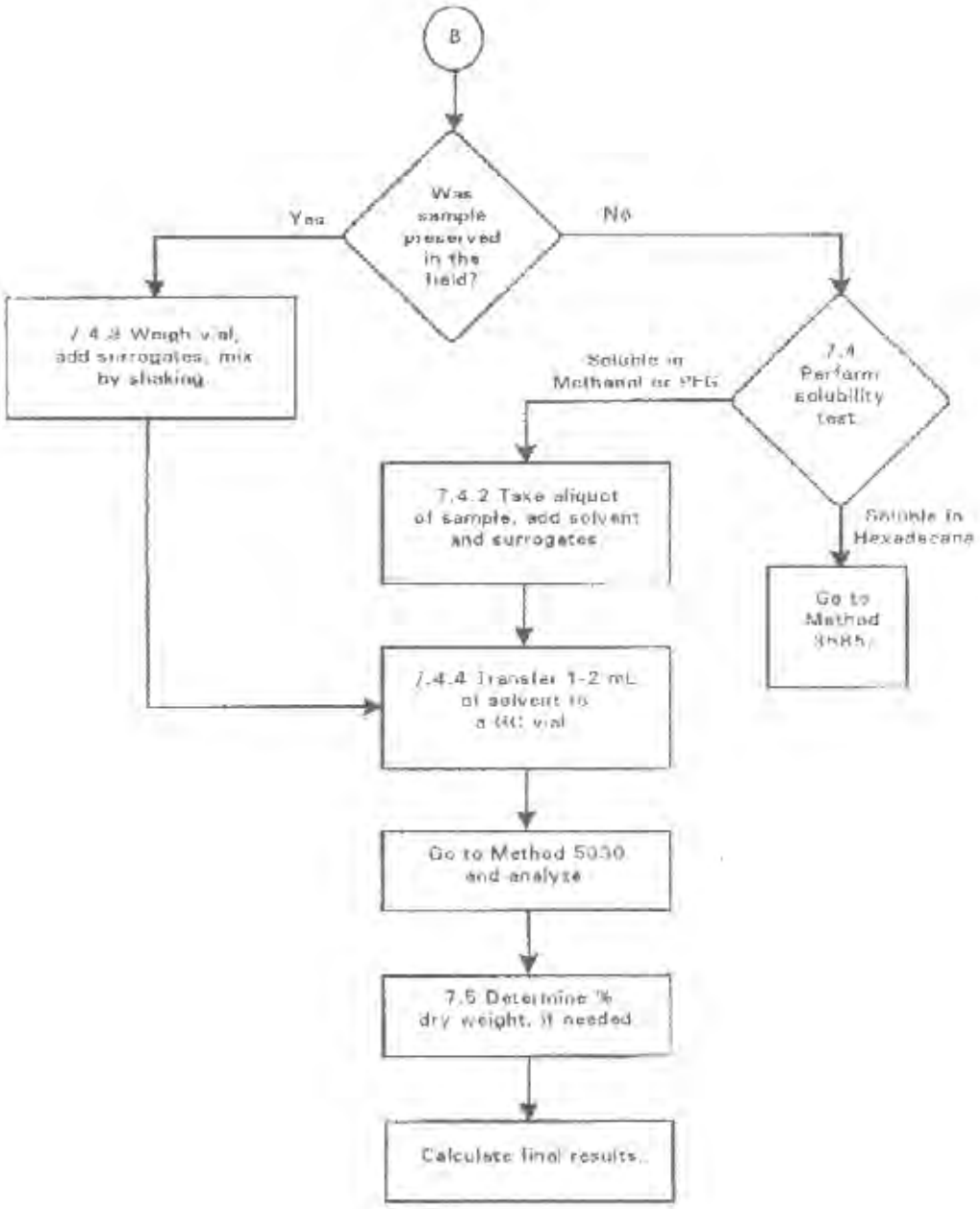
Calculate appropriate dilution factor for concentrations exceeding those in this table.

[a] The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of methanol is necessary to maintain a total volume of 100 µL of methanol

[b] Dilute an aliquot of the methanol extract and then take 100 µL for analysis.


Start
7.1 Identify sample matrix concentration estimates
Low Concentration Soil
High Concentration Oily Waste
A
B
High Concentration Soil
Was sample preserved in the field?
Yes
No
7.3.4 Weigh vial, add surrogates, mix by shaking.
Soluble in Methanol or PEG
7.3.2 Perform solubility test
Soluble in Hexadecane
7.3.3 Take aliquot of sample, add solvent and surrogates
Go to Method 3585
7.3.5 Transfer 1 ml of extract to clean GC vial
Go to Method 5030 and analyze
7.5 Determine % dry weight
Calculate final results


A
7.2.1 & 7.2.2 Assemble purge-and-trap system and GC or GC/MS system and calibrate as per appropriate 8000 method.
7.2.3 Weigh sample.
7.2.3.1 Allow sample vial to warm to room temp. Shake gently and place in the instrument carousel.
7.2.3.2 Add 5 mL of reagent water plus surrogates and internal standards.
7.2.3.4 Purge the sample at 40°C for 11 minutes.
7.2.4 Desorb sample.
7.2.5 Recondition trap at appropriate temp.
7.2.6 Data interpretation based on appropriate 8000 method.
7.5 Determine % dry weight.


B
Was sample preserved in the field?
Yes
No
7.4.3 Weigh vial, add surrogates, mix by shaking
7.4 Perform solubility test
Soluble in Methanol or PEG
Soluble in Hexadecane
7.4.2 Take aliquot of sample, add solvent and surrogates
Go to Method 3580
7.4.4 Transfer 1-2 mL of solvent to a GC vial
Go to Method 5030 and analyze
7.5 Determine % dry weight, if needed
Calculate final results.

METHOD 8260B
VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/
MASS SPECTROMETRY (GC/MS)

1.0 SCOPE AND APPLICATION

1.1 Method 8260 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including various air sampling trapping media, ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. The following compounds can be determined by this method:

		Appropriate Preparation Technique[a]					
Compound	CAS No.[b]	5030/ 5035	5031	5032	5021	5041	Direct Inject.
Acetone	67-64-1	pp	c	c	nd	c	c
Acetonitrile	75-05-8	pp	c	nd	nd	nd	c
Acrolein (Propenal)	107-02-8	pp	c	c	nd	nd	c
Acrylonitrile	107-13-1	pp	c	c	nd	c	c
Allyl alcohol	107-18-6	ht	c	nd	nd	nd	c
Allyl chloride	107-05-1	c	nd	nd	nd	nd	c
Benzene	71-43-2	c	nd	c	c	c	c
Benzyl chloride	100-44-7	c	nd	nd	nd	nd	c
Bis(2-chloroethyl)sulfide	505-60-2	pp	nd	nd	nd	nd	c
Bromoacetone	598-31-2	pp	nd	nd	nd	nd	c
Bromochloromethane	74-97-5	c	nd	c	c	c	c
Bromodichloromethane	75-27-4	c	nd	c	c	c	c
4-Bromofluorobenzene (surr)	460-00-4	c	nd	c	c	c	c
Bromoform	75-25-2	c	nd	c	c	c	c
Bromomethane	74-83-9	c	nd	c	c	c	c
n-Butanol	71-36-3	ht	c	nd	nd	nd	c
2-Butanone (MEK)	78-93-3	pp	c	c	nd	nd	c
t-Butyl alcohol	75-65-0	pp	c	nd	nd	nd	c
Carbon disulfide	75-15-0	pp	nd	c	nd	c	c
Carbon tetrachloride	56-23-5	c	nd	c	c	c	c
Chloral hydrate	302-17-0	pp	nd	nd	nd	nd	c
Chlorobenzene	108-90-7	c	nd	c	c	c	c
Chlorobenzene-d_5 (IS)		c	nd	c	c	c	c
Chlorodibromomethane	124-48-1	c	nd	c	nd	c	c
Chloroethane	75-00-3	c	nd	c	c	c	c
2-Chloroethanol	107-07-3	pp	nd	nd	nd	nd	c
2-Chloroethyl vinyl ether	110-75-8	c	nd	c	nd	nd	c
Chloroform	67-66-3	c	nd	c	c	c	c
Chloromethane	74-87-3	c	nd	c	c	c	c
Chloroprene	126-99-8	c	nd	nd	nd	nd	c
3-Chloropropionitrile	542-76-7	l	nd	nd	nd	nd	pc

(continued)

Compound	CAS No.[b]	Appropriate Preparation Technique[a] 5030/ 5035	5031	5032	5021	5041	Direct Inject.
Crotonaldehyde	4170-30-3	pp	c	nd	nd	nd	c
1,2-Dibromo-3-chloropropane	96-12-8	pp	nd	nd	c	nd	c
1,2-Dibromoethane	106-93-4	c	nd	nd	c	nd	c
Dibromomethane	74-95-3	c	nd	c	c	c	c
1,2-Dichlorobenzene	95-50-1	c	nd	nd	c	nd	c
1,3-Dichlorobenzene	541-73-1	c	nd	nd	c	nd	c
1,4-Dichlorobenzene	106-46-7	c	nd	nd	c	nd	c
1,4-Dichlorobenzene-d_4 (IS)		c	nd	nd	c	nd	c
cis-1,4-Dichloro-2-butene	1476-11-5	c	nd	c	nd	nd	c
trans-1,4-Dichloro-2-butene	110-57-6	pp	nd	c	nd	nd	c
Dichlorodifluoromethane	75-71-8	c	nd	c	c	nd	c
1,1-Dichloroethane	75-34-3	c	nd	c	c	c	c
1,2-Dichloroethane	107-06-2	c	nd	c	c	c	c
1,2-Dichloroethane-d_4 (surr)		c	nd	c	c	c	c
1,1-Dichloroethene	75-35-4	c	nd	c	c	c	c
trans-1,2-Dichloroethene	156-60-5	c	nd	c	c	c	c
1,2-Dichloropropane	78-87-5	c	nd	c	c	c	c
1,3-Dichloro-2-propanol	96-23-1	pp	nd	nd	nd	nd	c
cis-1,3-Dichloropropene	10061-01-5	c	nd	c	nd	c	c
trans-1,3-Dichloropropene	10061-02-6	c	nd	c	nd	c	c
1,2,3,4-Diepoxybutane	1464-53-5	c	nd	nd	nd	nd	c
Diethyl ether	60-29-7	c	nd	nd	nd	nd	c
1,4-Difluorobenzene (IS)	540-36-3	nd	nd	nd	nd	c	nd
1,4-Dioxane	123-91-1	pp	c	c	nd	nd	c
Epichlorohydrin	106-89-8	l	nd	nd	nd	nd	c
Ethanol	64-17-5	l	c	c	nd	nd	c
Ethyl acetate	141-78-6	l	c	nd	nd	nd	c
Ethylbenzene	100-41-4	c	nd	c	c	c	c
Ethylene oxide	75-21-8	pp	c	nd	nd	nd	c
Ethyl methacrylate	97-63-2	c	nd	c	nd	nd	c
Fluorobenzene (IS)	462-06-6	c	nd	nd	nd	nd	nd
Hexachlorobutadiene	87-68-3	c	nd	nd	c	nd	c
Hexachloroethane	67-72-1	l	nd	nd	nd	nd	c
2-Hexanone	591-78-6	pp	nd	c	nd	nd	c
2-Hydroxypropionitrile	78-97-7	l	nd	nd	nd	nd	pc
Iodomethane	74-88-4	c	nd	c	nd	c	c
Isobutyl alcohol	78-83-1	pp	c	nd	nd	nd	c
Isopropylbenzene	98-82-8	c	nd	nd	c	nd	c
Malononitrile	109-77-3	pp	nd	nd	nd	nd	c
Methacrylonitrile	126-98-7	pp	l	nd	nd	nd	c
Methanol	67-56-1	l	c	nd	nd	nd	c
Methylene chloride	75-09-2	c	nd	c	c	c	c
Methyl methacrylate	80-62-6	c	nd	nd	nd	nd	c
4-Methyl-2-pentanone (MIBK)	108-10-1	pp	c	c	nd	nd	c
Naphthalene	91-20-3	c	nd	nd	c	nd	c

(continued)

Compound	CAS No.[b]	Appropriate Preparation Technique[a] 5030/ 5035	5031	5032	5021	5041	Direct Inject.
Nitrobenzene	98-95-3	c	nd	nd	nd	nd	c
2-Nitropropane	79-46-9	c	nd	nd	nd	nd	c
N-Nitroso-di-n-butylamine	924-16-3	pp	c	nd	nd	nd	c
Paraldehyde	123-63-7	pp	c	nd	nd	nd	c
Pentachloroethane	76-01-7	I	nd	nd	nd	nd	c
2-Pentanone	107-87-9	pp	c	nd	nd	nd	c
2-Picoline	109-06-8	pp	c	nd	nd	nd	c
1-Propanol	71-23-8	pp	c	nd	nd	nd	c
2-Propanol	67-63-0	pp	c	nd	nd	nd	c
Propargyl alcohol	107-19-7	pp	I	nd	nd	nd	c
β-Propiolactone	57-57-8	pp	nd	nd	nd	nd	c
Propionitrile (ethyl cyanide)	107-12-0	ht	c	nd	nd	nd	pc
n-Propylamine	107-10-8	c	nd	nd	nd	nd	c
Pyridine	110-86-1	I	c	nd	nd	nd	c
Styrene	100-42-5	c	nd	c	c	c	c
1,1,1,2-Tetrachloroethane	630-20-6	c	nd	nd	c	c	c
1,1,2,2-Tetrachloroethane	79-34-5	c	nd	c	c	c	c
Tetrachloroethene	127-18-4	c	nd	c	c	c	c
Toluene	108-88-3	c	nd	c	c	c	c
Toluene-d_8 (surr)	2037-26-5	c	nd	c	c	c	c
o-Toluidine	95-53-4	pp	c	nd	nd	nd	c
1,2,4-Trichlorobenzene	120-82-1	c	nd	nd	c	nd	c
1,1,1-Trichloroethane	71-55-6	c	nd	c	c	c	c
1,1,2-Trichloroethane	79-00-5	c	nd	c	c	c	c
Trichloroethene	79-01-6	c	nd	c	c	c	c
Trichlorofluoromethane	75-69-4	c	nd	c	c	c	c
1,2,3-Trichloropropane	96-18-4	c	nd	c	c	c	c
Vinyl acetate	108-05-4	c	nd	c	nd	nd	c
Vinyl chloride	75-01-4	c	nd	c	c	c	c
o-Xylene	95-47-6	c	nd	c	c	c	c
m-Xylene	108-38-3	c	nd	c	c	c	c
p-Xylene	106-42-3	c	nd	c	c	c	c

[a] See Sec. 1.2 for other appropriate sample preparation techniques
[b] Chemical Abstract Service Registry Number

c = Adequate response by this technique
ht = Method analyte only when purged at 80 °C
nd = Not determined
I = Inappropriate technique for this analyte
pc = Poor chromatographic behavior
pp = Poor purging efficiency resulting in high Estimated Quantitation Limits
surr = Surrogate
IS = Internal Standard

1.2 There are various techniques by which these compounds may be introduced into the GC/MS system. The more common techniques are listed in the table above. Purge-and-trap, by Methods 5030 (aqueous samples) and 5035 (solid and waste oil samples), is the most commonly used technique for volatile organic analytes. However, other techniques are also appropriate and necessary for some analytes. These include direct injection following dilution with hexadecane (Method 3585) for waste oil samples; automated static headspace by Method 5021 for solid samples; direct injection of an aqueous sample (concentration permitting) or injection of a sample concentrated by azeotropic distillation (Method 5031); and closed system vacuum distillation (Method 5032) for aqueous, solid, oil and tissue samples. For air samples, Method 5041 provides methodology for desorbing volatile organics from trapping media (Methods 0010, 0030, and 0031). In addition, direct analysis utilizing a sample loop is used for sub-sampling from Tedlar® bags (Method 0040). Method 5000 provides more general information on the selection of the appropriate introduction method.

1.3 Method 8260 can be used to quantitate most volatile organic compounds that have boiling points below 200°C. Volatile, water soluble compounds can be included in this analytical technique by the use of azeotropic distillation or closed-system vacuum distillation. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. See Tables 1 and 2 for analytes and retention times that have been evaluated on a purge-and-trap GC/MS system. Also, the method detection limits for 25-mL sample volumes are presented. The following compounds are also amenable to analysis by Method 8260:

Bromobenzene
n-Butylbenzene
sec-Butylbenzene
tert-Butylbenzene
Chloroacetonitrile
1-Chlorobutane
1-Chlorohexane
2-Chlorotoluene
4-Chlorotoluene
Dibromofluoromethane
cis-1,2-Dichloroethene
1,3-Dichloropropane
2,2-Dichloropropane
1,1-Dichloropropene
p-Isopropyltoluene
Methyl acrylate
Methyl-t-butyl ether
Pentafluorobenzene
n-Propylbenzene
1,2,3-Trichlorobenzene
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene

1.4 The estimated quantitation limit (EQL) of Method 8260 for an individual compound is somewhat instrument dependent and also dependent on the choice of sample preparation/introduction method. Using standard quadrapole instrumentation and the purge-and-trap technique, limits should be approximately 5 µg/kg (wet weight) for soil/sediment samples, 0.5 mg/kg (wet weight) for wastes, and 5 µg/L for ground water (see Table 3). Somewhat lower limits may be achieved using an ion trap mass spectrometer or other instrumentation of improved design. No matter which instrument is used, EQLs will be proportionately higher for sample extracts and samples that require dilution or when a reduced sample size is used to avoid saturation of the detector.

1.5 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

2.0 SUMMARY OF METHOD

2.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by other methods (see Sec. 1.2). The analytes are introduced directly to a wide-bore capillary column or cryofocussed on a capillary pre-column before being flash evaporated to a narrow-bore capillary for analysis. The column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph (GC).

2.2 Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. (Wide-bore capillary columns normally require a jet separator, whereas narrow-bore capillary columns may be directly interfaced to the ion source). Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration curve.

2.3 The method includes specific calibration and quality control steps that supersede the general requirements provided in Method 8000.

3.0 INTERFERENCES

3.1 Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of calibration and reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter. Subtracting blank values from sample results is not permitted. If reporting values without correcting for the blank results in what the laboratory feels is a false positive result for a sample, the laboratory should fully explained this in text accompanying the uncorrected data.

3.2 Contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. A technique to prevent this problem is to rinse the purging apparatus and sample syringes with two portions of organic-free reagent water between samples. After the analysis of a sample containing high concentrations of volatile organic compounds, one or more blanks should be analyzed to check for cross-contamination. Alternatively, if the sample immediately following the high concentration sample does not contain the volatile organic compounds present in the high level sample, freedom from contamination has been established.

3.3 For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high concentrations of compounds being determined, it may be necessary to wash the purging device with a soap solution, rinse it with organic-free reagent water, and then dry the purging device in an oven at 105°C. In extreme situations, the entire purge-and-trap device may require dismantling and cleaning. Screening of the samples prior to purge-and-trap GC/MS analysis is highly recommended to prevent contamination of the system. This is especially true for soil and waste samples. Screening may be accomplished with an automated headspace technique (Method 5021) or by Method 3820 (Hexadecane Extraction and Screening of Purgeable Organics).

3.4 Many analytes exhibit low purging efficiencies from a 25-mL sample. This often results in significant amounts of these analytes remaining in the sample purge vessel after analysis. After removal of the sample aliquot that was purged, and rinsing the purge vessel three times with organic-free water, the empty vessel should be subjected to a heated purge cycle prior to the analysis of another sample in the same purge vessel. This will reduce sample-to-sample carryover.

3.5 Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride. Otherwise, random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed from stainless steel or copper tubing. Laboratory clothing worn by the analyst should be clean, since clothing previously exposed to methylene chloride fumes during liquid/liquid extraction procedures can contribute to sample contamination.

3.6 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample container into the sample during shipment and storage. A trip blank prepared from organic-free reagent water and carried through the sampling, handling, and storage protocols can serve as a check on such contamination.

3.7 Use of sensitive mass spectrometers to achieve lower detection level will increase the potential to detect laboratory contaminants as interferences.

3.8 Direct injection - Some contamination may be eliminated by baking out the column between analyses. Changing the injector liner will reduce the potential for cross-contamination. A portion of the analytical column may need to be removed in the case of extreme contamination. The use of direct injection will result in the need for more frequent instrument maintenance.

3.9 If hexadecane is added to waste samples or petroleum samples that are analyzed, some chromatographic peaks will elute after the target analytes. The oven temperature program must include a post-analysis bake out period to ensure that semivolatile hydrocarbons are volatilized.

4.0 APPARATUS AND MATERIALS

4.1 Purge-and-trap device for aqueous samples - Described in Method 5030.

4.2 Purge-and-trap device for solid samples - Described in Method 5035.

4.3 Automated static headspace device for solid samples - Described in Method 5021.

4.4 Azeotropic distillation apparatus for aqueous and solid samples - Described in Method 5031.

4.5 Vacuum distillation apparatus for aqueous, solid and tissue samples - Described in Method 5032.

4.6 Desorption device for air trapping media for air samples - Described in Method 5041.

4.7 Air sampling loop for sampling from Tedlar® bags for air samples - Described in Method 0040.

4.8 Injection port liners (HP Catalog #18740-80200, or equivalent) - modified for direct injection analysis by placing a 1-cm plug of glass wool approximately 50-60 mm down the length of the injection port towards the oven (see illustration below). A 0.53-mm ID column is mounted 1 cm into the liner from the oven side of the injection port, according to manufacturer's specifications.

4.9 Gas chromatography/mass spectrometer/data system

4.9.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection with appropriate interface for sample introduction device. The system includes all required accessories, including syringes, analytical columns, and gases.

4.9.1.1 The GC should be equipped with variable constant differential flow controllers so that the column flow rate will remain constant throughout desorption and temperature program operation.

4.9.1.2 For some column configurations, the column oven must be cooled to less than 30°C, therefore, a subambient oven controller may be necessary.

4.9.1.3 The capillary column is either directly coupled to the source or interfaced through a jet separator, depending on the size of the capillary and the requirements of the GC/MS system.

4.9.1.4 Capillary pre-column interface - This device is the interface between the sample introduction device and the capillary gas chromatograph, and is necessary when using cryogenic cooling. The interface condenses the desorbed sample components and focuses them into a narrow band on an uncoated fused-silica capillary pre-column. When the interface is flash heated, the sample is transferred to the analytical capillary column.

4.9.1.5 During the cryofocussing step, the temperature of the fused-silica in the interface is maintained at -150°C under a stream of liquid nitrogen. After the desorption period, the interface must be capable of rapid heating to 250°C in 15 seconds or less to complete the transfer of analytes.

4.9.2 Gas chromatographic columns

4.9.2.1 Column 1 - 60 m x 0.75 mm ID capillary column coated with VOCOL (Supelco), 1.5-µm film thickness, or equivalent.

4.9.2.2 Column 2 - 30 - 75 m x 0.53 mm ID capillary column coated with DB-624 (J&W Scientific), Rt$_x$-502.2 (RESTEK), or VOCOL (Supelco), 3-µm film thickness, or equivalent.

4.9.2.3 Column 3 - 30 m x 0.25 - 0.32 mm ID capillary column coated with 95% dimethyl - 5% diphenyl polysiloxane (DB-5, Rt$_x$-5, SPB-5, or equivalent), 1-µm film thickness.

4.9.2.4 Column 4 - 60 m x 0.32 mm ID capillary column coated with DB-624 (J&W Scientific), 1.8-µm film thickness, or equivalent.

4.9.3 Mass spectrometer - Capable of scanning from 35 to 300 amu every 2 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for 4-Bromofluorobenzene (BFB) which meets all of the criteria in Table 4 when 5-50 ng of the GC/MS tuning standard (BFB) are injected through the GC. To ensure sufficient precision of mass spectral data, the desirable MS scan rate allows acquisition of at least five spectra while a sample component elutes from the GC.

An ion trap mass spectrometer may be used if it is capable of axial modulation to reduce ion-molecule reactions and can produce electron impact-like spectra that match those in the EPA/NIST Library. Because ion-molecule reactions with water and methanol in an ion trap mass spectrometer may produce interferences that coelute with chloromethane and chloroethane, the base peak for both of these analytes will be at m/z 49. This ion should be used as the quantitation ion in this case. The mass spectrometer must be capable of producing a mass spectrum for BFB which meets all of the criteria in Table 3 when 5 or 50 ng are introduced.

4.9.4 GC/MS interface - Two alternatives may be used to interface the GC to the mass spectrometer.

4.9.4.1 Direct coupling, by inserting the column into the mass spectrometer, is generally used for 0.25 - 0.32 mm ID columns.

4.9.4.2 A jet separator, including an all-glass transfer line and glass enrichment device or split interface, is used with a 0.53 mm column.

4.9.4.3 Any enrichment device or transfer line may be used, if all of the performance specifications described in Sec. 8.0 (including acceptable calibration at 50 ng or less) can be achieved. GC/MS interfaces constructed entirely of glass or of glass-lined materials are recommended. Glass may be deactivated by silanizing with dichlorodimethylsilane.

4.9.5 Data system - A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

4.10 Microsyringes - 10-, 25-, 100-, 250-, 500-, and 1,000-µL.

4.11 Syringe valve - Two-way, with Luer ends (three each), if applicable to the purging device.

4.12 Syringes - 5-, 10-, or 25-mL, gas-tight with shutoff valve.

4.13 Balance - Analytical, capable of weighing 0.0001 g, and top-loading, capable of weighing 0.1 g.

4.14 Glass scintillation vials - 20-mL, with PTFE-lined screw-caps or glass culture tubes with PTFE-lined screw-caps.

4.15 Vials - 2-mL, for GC autosampler.

4.16 Disposable pipets - Pasteur.

4.17 Volumetric flasks, Class A - 10-mL and 100-mL, with ground-glass stoppers.

4.18 Spatula - Stainless steel.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Methanol, CH_3OH - Pesticide quality or equivalent, demonstrated to be free of analytes. Store apart from other solvents.

5.4 Reagent Hexadecane - Reagent hexadecane is defined as hexadecane in which interference is not observed at the method detection limit of compounds of interest. Hexadecane quality is demonstrated through the analysis of a solvent blank injected directly into the GC/MS. The results of such a blank analysis must demonstrate that all interfering volatiles have been removed from the hexadecane.

5.5 Polyethylene glycol, $H(OCH_2CH_2)_nOH$ - Free of interferences at the detection limit of the target analytes.

5.6 Hydrochloric acid (1:1 v/v), HCl - Carefully add a measured volume of concentrated HCl to an equal volume of organic-free reagent water.

5.7 Stock solutions - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol, using assayed liquids or gases, as appropriate.

5.7.1 Place about 9.8 mL of methanol in a 10-mL tared ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.7.2 Add the assayed reference material, as described below.

5.7.2.1 Liquids - Using a 100-µL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.7.2.2 Gases - To prepare standards for any compounds that boil below 30°C (e.g., bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5-mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to

5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared by using a lecture bottle equipped with a septum. Attach PTFE tubing to the side arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.7.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially-prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.7.4 Transfer the stock standard solution into a bottle with a PTFE-lined screw-cap. Store, with minimal headspace and protected from light, at -10°C or less or as recommended by the standard manufacturer. Standards should be returned to the freezer as soon as the analyst has completed mixing or diluting the standards to prevent the evaporation of volatile target compounds.

5.7.5 Frequency of Standard Preparation

5.7.5.1 Standards for the permanent gases should be monitored frequently by comparison to the initial calibration curve. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for gases usually need to be replaced after one week or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Dichlorodifluoromethane and dichloromethane will usually be the first compounds to evaporate from the standard and should, therefore, be monitored very closely when standards are held beyond one week.

5.7.5.2 Standards for the non-gases should be monitored frequently by comparison to the initial calibration. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for non-gases usually need to be replaced after six months or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Standards of reactive compounds such as 2-chloroethyl vinyl ether and styrene may need to be prepared more frequently.

5.7.6 Preparation of Calibration Standards From a Gas Mixture

An optional calibration procedure involves using a certified gaseous mixture daily, utilizing a commercially-available gaseous analyte mixture of bromomethane, chloromethane, chloroethane, vinyl chloride, dichloro-difluoromethane and trichlorofluoromethane in nitrogen. Mixtures of documented quality are stable for as long as six months without refrigeration. (VOA-CYL III, RESTEK Corporation, Cat. #20194 or equivalent).

5.7.6.1 Before removing the cylinder shipping cap, be sure the valve is completely closed (turn clockwise). The contents are under pressure and should be used in a well-ventilated area.

5.7.6.2 Wrap the pipe thread end of the Luer fitting with PTFE tape. Remove the shipping cap from the cylinder and replace it with the Luer fitting.

5.7.6.3 Transfer half the working standard containing other analytes, internal standards, and surrogates to the purge apparatus.

5.7.6.4 Purge the Luer fitting and stem on the gas cylinder prior to sample removal using the following sequence:

a) Connect either the 100-µL or 500-µL Luer syringe to the inlet fitting of the cylinder.

b) Make sure the on/off valve on the syringe is in the open position.

c) Slowly open the valve on the cylinder and withdraw a full syringe volume.

d) Be sure to close the valve on the cylinder before you withdraw the syringe from the Luer fitting.

e) Expel the gas from the syringe into a well-ventilated area.

f) Repeat steps a through e one more time to fully purge the fitting.

5.7.6.5 Once the fitting and stem have been purged, quickly withdraw the volume of gas you require using steps 5.6.6.1.4(a) through (d). Be sure to close the valve on the cylinder and syringe before you withdraw the syringe from the Luer fitting.

5.7.6.6 Open the syringe on/off valve for 5 seconds to reduce the syringe pressure to atmospheric pressure. The pressure in the cylinder is ~30 psi.

5.7.6.7 The gas mixture should be quickly transferred into the reagent water through the female Luer fitting located above the purging vessel.

NOTE: Make sure the arrow on the 4-way valve is pointing toward the female Luer fitting when transferring the sample from the syringe. Be sure to switch the 4-way valve back to the closed position before removing the syringe from the Luer fitting.

5.7.6.8 Transfer the remaining half of the working standard into the purging vessel. This procedure insures that the total volume of gas mix is flushed into the purging vessel, with none remaining in the valve or lines.

5.7.6.9 The concentration of each compound in the cylinder is typically 0.0025 µg/µL.

5.7.6.10 The following are the recommended gas volumes spiked into 5 mL of water to produce a typical 5-point calibration:

Gas Volume	Calibration Concentration
40 µL	20 µg/L
100 µL	50 µg/L
200 µL	100 µg/L
300 µL	150 µg/L
400 µL	200 µg/L

5.7.6.11 The following are the recommended gas volumes spiked into 25 mL of water to produce a typical 5-point calibration:

Gas Volume	Calibration Concentration
10 µL	1 µg/L
20 µL	2 µg/L
50 µL	5 µg/L
100 µL	10 µg/L
250 µL	25 µg/L

5.8 Secondary dilution standards - Using stock standard solutions, prepare secondary dilution standards in methanol containing the compounds of interest, either singly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Store in a vial with no headspace. Replace after one week. Secondary standards for gases should be replaced after one week unless the acceptability of the standard can be documented. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations. The analyst should also handle and store standards as stated in Sec. 5.7.4 and return them to the freezer as soon as standard mixing or diluting is completed to prevent the evaporation of volatile target compounds.

5.9 Surrogate standards - The recommended surrogates are toluene-d_8, 4-bromofluorobenzene, 1,2-dichloroethane-d_4, and dibromofluoromethane. Other compounds may be used as surrogates, depending upon the analysis requirements. A stock surrogate solution in methanol should be prepared as described above, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 50-250 µg/10 mL, in methanol. Each sample undergoing GC/MS analysis must be spiked with 10 µL of the surrogate spiking solution prior to analysis. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then more dilute surrogate solutions may be required.

5.10 Internal standards - The recommended internal standards are fluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected by GC/MS. Prepare internal standard stock and secondary dilution standards in methanol using the procedures described in Secs. 5.7 and 5.8. It is recommended that the secondary dilution standard be prepared at a concentration of 25 mg/L of each internal standard compound. Addition of 10 µL of this standard to 5.0 mL of sample or calibration standard would be the equivalent of 50 µg/L. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then more dilute internal standard solutions may be required. Area counts of the internal standard peaks should be between 50-200% of the areas of the target analytes in the mid-point calibration analysis.

5.11 4-Bromofluorobenzene (BFB) standard - A standard solution containing 25 ng/µL of BFB in methanol should be prepared. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then a more dilute BFB standard solution may be required.

5.12 Calibration standards -There are two types of calibration standards used for this method: initial calibration standards and calibration verification standards. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

5.12.1 Initial calibration standards should be prepared at a minimum of five different concentrations from the secondary dilution of stock standards (see Secs. 5.7 and 5.8) or from a premixed certified solution. Prepare these solutions in organic-free reagent water. At least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining standards should correspond to the range of concentrations found in typical samples but should not exceed the working range of the GC/MS system. Initial calibration standards should be mixed from fresh stock standards and dilution standards when generating an initial calibration curve.

5.12.2 Calibration verification standards should be prepared at a concentration near the mid-point of the initial calibration range from the secondary dilution of stock standards (see Secs. 5.7 and 5.8) or from a premixed certified solution. Prepare these solutions in organic-free reagent water. See Sec. 7.4 for guidance on calibration verification.

5.12.3 It is the intent of EPA that all target analytes for a particular analysis be included in the initial calibration and calibration verification standard(s). These target analytes may not include the entire list of analytes (Sec. 1.1) for which the method has been demonstrated. However, the laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s).

5.12.4 The calibration standards must also contain the internal standards chosen for the analysis.

5.13 Matrix spiking and laboratory control sample (LCS) standards - Matrix spiking standards should be prepared from volatile organic compounds which are representative of the compounds being investigated. At a minimum, the matrix spike should include 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. The matrix spiking solution should contain compounds that are expected to be found in the types of samples to be analyzed.

5.13.1 Some permits may require the spiking of specific compounds of interest, especially if polar compounds are a concern, since the spiking compounds listed above would not be representative of such compounds. The standard should be prepared in methanol, with each compound present at a concentration of 250 µg/10.0 mL.

5.13.2 The spiking solutions should not be prepared from the same standards as the calibration standards. However, the same spiking standard prepared for the matrix spike may be used for the LCS.

5.13.3 If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute matrix spiking solutions may be required.

5.14 Great care must be taken to maintain the integrity of all standard solutions. It is recommended all standards in methanol be stored at -10°C or less, in amber bottles with PTFE-lined screw-caps.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Various alternative methods are provided for sample introduction. All internal standards, surrogates, and matrix spiking compounds (when applicable) must be added to the samples before introduction into the GC/MS system. Consult the sample introduction method for the procedures by which to add such standards.

7.1.1 Direct injection - This includes: injection of an aqueous sample containing a very high concentration of analytes; injection of aqueous concentrates from Method 5031 (azeotropic distillation); and injection of a waste oil diluted 1:1 with hexadecane (Method 3585). Direct injection of aqueous samples (non-concentrated) has very limited applications. It is only used for the determination of volatiles at the toxicity characteristic (TC) regulatory limits or at concentrations in excess of 10,000 µg/L. It may also be used in conjunction with the test for ignitability in aqueous samples (along with Methods 1010 and 1020), to determine if alcohol is present at greater than 24%.

7.1.2 Purge-and-trap - This includes purge-and-trap for aqueous samples (Method 5030) and purge-and-trap for solid samples (Method 5035). Method 5035 also provides techniques for extraction of high concentration solid and oily waste samples by methanol (and other water-miscible solvents) with subsequent purge-and-trap from an aqueous matrix using Method 5030.

7.1.2.1 Traditionally, the purge-and-trap of aqueous samples is performed at ambient temperature, while purging of soil/solid samples is performed at 40°C, to improve purging efficiency.

7.1.2.2 Aqueous and soil/solid samples may also be purged at temperatures above those being recommended as long as all calibration standards, samples, and QC samples are purged at the same temperature, appropriate trapping material is used to handle the excess water, and the laboratory demonstrates acceptable method performance for the project. Purging of aqueous samples at elevated temperatures (e.g., 40°C) may improve the purging performance of many of the water soluble compounds which have poor purging efficiencies at ambient temperatures.

7.1.3 Vacuum distillation - this technique may be used for the introduction of volatile organics from aqueous, solid, or tissue samples (Method 5032) into the GC/MS system.

7.1.4 Automated static headspace - this technique may be used for the introduction of volatile organics from solid samples (Method 5021) into the GC/MS system.

7.1.5 Cartridge desorption - this technique may be for the introduction of volatile organics from sorbent cartridges (Method 5041) used in the sampling of air. The sorbent cartridges are from the volatile organics sampling train (VOST) or SMVOC (Method 0031).

7.2 Recommended chromatographic conditions

7.2.1 General conditions

Injector temperature:	200 - 225°C
Transfer line temperature:	250 - 300°C

7.2.2 Column 1 and Column 2 with cryogenic cooling (example chromatograms are presented in Figures 1 and 2)

Carrier gas (He) flow rate:	15 mL/min
Initial temperature:	10°C, hold for 5 minutes
Temperature program:	6°C/min to 70°C, then 15°C/min to 145°C
Final temperature:	145°C, hold until all expected compounds have eluted.

7.2.5 Direct injection - Column 2

Carrier gas (He) flow rate:	4 mL/min
Column:	J&W DB-624, 70m x 0.53 mm
Initial temperature:	40°C, hold for 3 minutes
Temperature program:	8°C/min
Final temperature:	260°C, hold until all expected compounds have eluted.
Column Bake out:	75 minutes
Injector temperature:	200-225°C
Transfer line temperature:	250-300°C

7.2.6 Direct split interface - Column 4

Carrier gas (He) flow rate:	1.5 mL/min
Initial temperature:	35°C, hold for 2 minutes
Temperature program:	4°C/min to 50°C 10°C/min to 220°C
Final temperature:	220°C, hold until all expected compounds have eluted
Split ratio:	100:1
Injector temperature:	125°C

7.3 Initial calibration

Establish the GC/MS operating conditions, using the following as guidance:

Mass range:	35 - 260 amu
Scan time:	0.6 - 2 sec/scan
Source temperature:	According to manufacturer's specifications
Ion trap only:	Set axial modulation, manifold temperature, and emission current to manufacturer's recommendations

7.3.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 4 for a 5-50 ng injection or purging of 4-bromofluorobenzene (2-µL injection of the BFB standard). Analyses must not begin until these criteria are met.

7.3.1.1 In the absence of specific recommendations on how to acquire the mass spectrum of BFB from the instrument manufacturer, the following approach has been shown to be useful: The mass spectrum of BFB may be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of

BFB. Do not background subtract part of the BFB peak. Alternatively, the analyst may use other documented approaches suggested by the instrument manufacturer.

7.3.1.2 Use the BFB mass intensity criteria in Table 4 as tuning acceptance criteria. Alternatively, other documented tuning criteria may be used (e.g., CLP, Method 524.2, or manufacturer's instructions), provided that method performance is not adversely affected.

NOTE: All subsequent standards, samples, MS/MSDs, LCSs, and blanks associated with a BFB analysis must use identical mass spectrometer instrument conditions.

7.3.2 Set up the sample introduction system as outlined in the method of choice (see Sec. 7.1). A different calibration curve is necessary for each method because of the differences in conditions and equipment. A set of at least five different calibration standards is necessary (see Sec. 5.12 and Method 8000). Calibration must be performed using the sample introduction technique that will be used for samples. For Method 5030, the purging efficiency for 5 mL of water is greater than for 25 mL. Therefore, develop the standard curve with whichever volume of sample that will be analyzed.

7.3.2.1 To prepare a calibration standard, add an appropriate volume of a secondary dilution standard solution to an aliquot of organic-free reagent water in a volumetric flask. Use a microsyringe and rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask. Aqueous standards are not stable and should be prepared daily. Transfer 5.0 mL (or 25 mL if lower detection limits are required) of each standard to a gas tight syringe along with 10 µL of internal standard. Then transfer the contents to the appropriate device or syringe. Some of the introduction methods may have specific guidance on the volume of calibration standard and the way the standards are transferred to the device.

7.3.2.2 The internal standards selected in Sec. 5.10 should permit most of the components of interest in a chromatogram to have retention times of 0.80 - 1.20, relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 1). If interferences are noted, use the next most intense ion as the quantitation ion.

7.3.2.3 To prepare a calibration standard for direct injection analysis of waste oil, dilute standards in hexadecane.

7.3.3 Proceed with the analysis of the calibration standards following the procedure in the introduction method of choice. For direct injection, inject 1 - 2 µL into the GC/MS system. The injection volume will depend upon the chromatographic column chosen and the tolerance of the specific GC/MS system to water.

7.3.4 Tabulate the area response of the characteristic ions (see Table 5) against the concentration for each target analyte and each internal standard. Calculate response factors (RF) for each target analyte relative to one of the internal standards. The internal standard selected for the calculation of the RF for a target analyte should be the internal standard that has a retention time closest to the analyte being measured (Sec. 7.6.2).

The RF is calculated as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Peak area (or height) of the analyte or surrogate.
A_{is} = Peak area (or height) of the internal standard.
C_s = Concentration of the analyte or surrogate.
C_{is} = Concentration of the internal standard.

7.3.5 System performance check compounds (SPCCs) - Calculate the mean RF for each target analyte using the five RF values calculated from the initial (5-point) calibration curve. A system performance check should be made before this calibration curve is used. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum average response factor. These compounds are chloromethane; 1,1-dichloroethane; bromoform; chlorobenzene; and 1,1,2,2-tetrachloroethane. These compounds are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system. Example problems include:

7.3.5.1 Chloromethane is the most likely compound to be lost if the purge flow is too fast.

7.3.5.2 Bromoform is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio relative to m/z 95 may improve bromoform response.

7.3.5.3 Tetrachloroethane and 1,1-dichloroethane are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.3.5.4 The minimum mean response factors for the volatile SPCCs are as follows:

Chloromethane	0.10
1,1-Dichloroethane	0.10
Bromoform	0.10
Chlorobenzene	0.30
1,1,2,2-Tetrachloroethane	0.30

7.3.6 Calibration check compounds (CCCs)

7.3.6.1 The purpose of the CCCs are to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. Meeting the CCC criteria is not a substitute for successful calibration of the target analytes using one of the approaches described in Sec. 7.0 of Method 8000.

7.3.6.2 Calculate the standard deviation (SD) and relative standard deviation (RSD) of the response factors for all target analytes from the initial calibration, as follows:

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (RF_i - \overline{RF})^2}{n-1}} \qquad RSD = \frac{SD}{\overline{RF}} \times 100$$

where:

RF_i = RF for each of the calibration standards
$\overline{RF}$ = mean RF for each compound from the initial calibration
n = Number of calibration standards, e.g., 5

7.3.6.3 The RSD should be less than or equal to 15% for each target analyte. However, the RSD for each individual Calibration Check Compound (CCC) must be equal or less than 30%. If the CCCs are not included in the list of analytes for a project, and therefore not included in the calibration standards, refer to Sec. 7.0 of Method 8000. The CCCs are:

1,1-Dichloroethene	Toluene
Chloroform	Ethylbenzene
1,2-Dichloropropane	Vinyl chloride

7.3.6.4 If an RSD of greater than 30% is measured for any CCC, then corrective action to eliminate a system leak and/or column reactive sites is necessary before reattempting calibration.

7.3.7 Evaluation of retention times - The relative retention times of each target analyte in each calibration standard should agree within 0.06 relative retention time units. Late-eluting compounds usually have much better agreement.

7.3.8 Linearity of target analytes

7.3.8.1 If the RSD of any target analyte is 15% or less, then the response factor is assumed to be constant over the calibration range, and the average response factor may be used for quantitation (Sec. 7.7.2).

7.3.8.2 If the RSD of any target analyte is greater than 15%, refer to Sec. 7.0 of Method 8000 for additional calibration options. One of the options must be applied to GC/MS calibration in this situation, or a new initial calibration must be performed.

NOTE: Method 8000 specifies a linearity criterion of 20% RSD. That criterion pertains to GC and HPLC methods other than GC/MS. Method 8260 requires 15% RSD as evidence of sufficient linearity to employ an average response factor.

7.3.8.3 When the RSD exceeds 15%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc.

NOTE: The 20% RSD criteria in Method 8000 pertains to GC and HPLC methods other than GC/MS. Method 8260 requires 15% RSD.

7.4 GC/MS calibration verification - Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

7.4.1 Prior to the analysis of samples or calibration standards, inject or introduce 5-50 ng of the 4-bromofluorobenzene standard into the GC/MS system. The resultant mass spectra for the BFB must meet the criteria given in Table 4 before sample analysis begins. These criteria must be demonstrated each 12-hour shift during which samples are analyzed.

7.4.2 The initial calibration curve (Sec. 7.3) for each compound of interest should be verified once every 12 hours prior to sample analysis, using the introduction technique used for samples. This is accomplished by analyzing a calibration standard at a concentration near the midpoint concentration for the calibrating range of the GC/MS. The results from the calibration standard analysis should meet the verification acceptance criteria provided in Secs. 7.4.4 through 7.4.7.

NOTE: The BFB and calibration verification standard may be combined into a single standard as long as both tuning and calibration verification acceptance criteria for the project can be met without interferences.

7.4.3 A method blank should be analyzed after the calibration standard, or at any other time during the analytical shift, to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples. See Sec. 8.0 of Method 8000 for method blank performance criteria.

7.4.4 System Performance Check Compounds (SPCCs)

7.4.4.1 A system performance check must be made during every 12-hour analytical shift. Each SPCC compound in the calibration verification standard must meet its minimum response factor (see Sec. 7.3.5.4). This is the same check that is applied during the initial calibration.

7.4.4.2 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

7.4.5 Calibration Check Compounds (CCCs)

7.4.5.1 After the system performance check is met, the CCCs listed in Sec. 7.3.6 are used to check the validity of the initial calibration. Use percent difference when performing the average response factor model calibration. Use percent drift when calibrating using a regression fit model. Refer to Sec. 7.0 of Method 8000 for guidance on calculating percent difference and drift.

7.4.5.2 If the percent difference or drift for each CCC is less than or equal to 20%, the initial calibration is assumed to be valid. If the criterion is not met (i.e., greater

than 20% difference or drift), for any one CCC, then corrective action must be taken prior to the analysis of samples. If the CCC's are not included in the list of analytes for a project, and therefore not included in the calibration standards, then all analytes must meet the 20% difference or drift criterion.

7.4.5.3 Problems similar to those listed under SPCCs could affect the CCCs. If the problem cannot be corrected by other measures, a new five-point initial calibration must be generated. The CCC criteria must be met before sample analysis begins.

7.4.6 Internal standard retention time - The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.4.7 Internal standard response - If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to + 100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.5 GC/MS analysis of samples

7.5.1 It is highly recommended that the sample be screened to minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds. Some of the screening options available utilizing SW-846 methods are automated headspace-GC/FID (Methods 5021/8015), automated headspace-GC/PID/ELCD (Methods 5021/8021), or waste dilution-GC/PID/ELCD (Methods 3585/8021) using the same type of capillary column. When used only for screening purposes, the quality control requirements in the methods above may be reduced as appropriate. Sample screening is particularly important when Method 8260 is used to achieve low detection levels.

7.5.2 BFB tuning criteria and GC/MS calibration verification criteria must be met before analyzing samples.

7.5.3 All samples and standard solutions must be allowed to warm to ambient temperature before analysis. Set up the introduction device as outlined in the method of choice.

7.5.4 The process of taking an aliquot destroys the validity of remaining volume of an aqueous sample for future analysis. Therefore, if only one VOA vial is provided to the laboratory, the analyst should prepare two aliquots for analysis at this time, to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. For aqueous samples, one 20-mL syringe could be used to hold two 5-mL aliquots. If the second aliquot is to be taken from the syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

7.5.5 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. If lower detection limits are required, use a 25-mL syringe, and adjust the final volume to 25.0 mL.

7.5.6 The following procedure may be used to dilute aqueous samples for analysis of volatiles. All steps must be performed without delays, until the diluted sample is in a gas-tight syringe.

7.5.6.1 Dilutions may be made in volumetric flasks (10- to 100-mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilution steps may be necessary for extremely large dilutions.

7.5.6.2 Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask, and add slightly less than this quantity of organic-free reagent water to the flask.

7.5.6.3 Inject the appropriate volume of the original sample from the syringe into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with organic-free reagent water. Cap the flask, invert, and shake three times. Repeat above procedure for additional dilutions.

7.5.6.4 Fill a 5-mL syringe with the diluted sample, as described in Sec. 7.5.5.

7.5.7 Compositing aqueous samples prior to GC/MS analysis

7.5.7.1 Add 5 mL of each sample (up to 5 samples are allowed) to a 25-mL glass syringe. Special precautions must be made to maintain zero headspace in the syringe. Larger volumes of a smaller number of samples may be used, provided that equal volumes of each sample are composited.

7.5.7.2 The samples must be cooled to 4°C or less during this step to minimize volatilization losses. Sample vials may be placed in a tray of ice during the processing.

7.5.7.3 Mix each vial well and draw out a 5-mL aliquot with the 25-mL syringe.

7.5.7.4 Once all the aliquots have been combined on the syringe, invert the syringe several times to mix the aliquots. Introduce the composited sample into the instrument, using the method of choice (see Sec. 7.1).

7.5.7.5 If less than five samples are used for compositing, a proportionately smaller syringe may be used, unless a 25-mL sample is to be purged.

7.5.8 Add 10 µL of the surrogate spiking solution and 10 µL of the internal standard spiking solution to each sample either manually or by autosampler. The surrogate and internal standards may be mixed and added as a single spiking solution. The addition of 10 µL of the surrogate spiking solution to 5 mL of aqueous sample will yield a concentration of 50 µg/L of each surrogate standard. The addition of 10 µL of the surrogate spiking solution to 5 g of a non-aqueous sample will yield a concentration of 50 µg/kg of each standard.

If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute surrogate and internal standard solutions may be required.

7.5.9 Add 10 µL of the matrix spike solution (Sec. 5.13) to a 5-mL aliquot of the sample chosen for spiking. Disregarding any dilutions, this is equivalent to a concentration of 50 µg/L of each matrix spike standard.

7.5.9.1 Follow the same procedure in preparing the laboratory control sample (LCS), except the spike is added to a clean matrix. See Sec. 8.4 and Method 5000 for more guidance on the selection and preparation of the matrix spike and the LCS.

7.5.9.2 If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute matrix spiking and LCS solutions may be required.

7.5.10 Analyze the sample following the procedure in the introduction method of choice.

7.5.10.1 For direct injection, inject 1 to 2 µL into the GC/MS system. The volume limitation will depend upon the chromatographic column chosen and the tolerance of the specific GC/MS system to water (if an aqueous sample is being analyzed).

7.5.10.2 The concentration of the internal standards, surrogates, and matrix spiking standards (if any) added to the injection aliquot must be adjusted to provide the same concentration in the 1-2 µL injection as would be introduced into the GC/MS by purging a 5-mL aliquot.

NOTE: It may be a useful diagnostic tool to monitor internal standard retention times and responses (area counts) in all samples, spikes, blanks, and standards to effectively check drifting method performance, poor injection execution, and anticipate the need for system inspection and/or maintenance.

7.5.11 If the initial analysis of the sample or a dilution of the sample has a concentration of any analyte that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion.

7.5.11.1 When ions from a compound in the sample saturate the detector, this analysis must be followed by the analysis of an organic-free reagent water blank. If the blank analysis is not free of interferences, then the system must be decontaminated. Sample analysis may not resume until the blank analysis is demonstrated to be free of interferences.

7.5.11.2 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.5.12 The use of selected ion monitoring (SIM) is acceptable in situations requiring detection limits below the normal range of full EI spectra. However, SIM may provide a lesser degree of confidence in the compound identification unless multiple ions are monitored for each compound.

7.6 Qualitative analysis

7.6.1 The qualitative identification of each compound determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met.

7.6.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.6.1.2 The relative retention time (RRT) of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

7.6.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.6.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.6.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

7.6.1.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.6.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library

searches may the analyst assign a tentative identification. Use the following guidelines for making tentative identifications:

(1) Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

7.7 Quantitative analysis

7.7.1 Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. The internal standard used shall be the one nearest the retention time of that of a given analyte.

7.7.2 If the RSD of a compound's response factors is 15% or less, then the concentration in the extract may be determined using the average response factor ($\overline{RF}$) from initial calibration data (7.3.6). See Method 8000, Sec. 7.0, for the equations describing internal standard calibration and either linear or non-linear calibrations.

7.7.3 Where applicable, the concentration of any non-target analytes identified in the sample (Sec. 7.6.2) should be estimated. The same formulae should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1.

7.7.4 The resulting concentration should be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation and/or sample introduction techniques can be found in Methods 3500 and 5000. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000, Sec. 7.0 and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples. In addition, instrument QC requirements may be found in the following sections of Method 8260:

8.2.1 The GC/MS system must be tuned to meet the BFB specifications in Secs. 7.3.1 and 7.4.1.

8.2.2 There must be an initial calibration of the GC/MS system as described in Sec. 7.3.

8.2.3 The GC/MS system must meet the SPCC criteria described in Sec. 7.4.4 and the CCC criteria in Sec. 7.4.5, each 12 hours.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

8.4.1 Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a method blank should be analyzed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

8.4.2 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

8.4.3 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.4.4 See Method 8000, Sec. 8.0 for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0 for information on evaluating surrogate data and developing and updating surrogate limits.

8.6 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the calibration verification standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g., the column changed), recalibration of the system must take place.

8.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

9.2 This method has been tested using purge-and-trap (Method 5030) in a single laboratory using spiked water. Using a wide-bore capillary column, water was spiked at concentrations between 0.5 and 10 µg/L. Single laboratory accuracy and precision data are presented for the method analytes in Table 6. Calculated MDLs are presented in Table 1.

9.3 The method was tested using purge-and-trap (Method 5030) with water spiked at 0.1 to 0.5 µg/L and analyzed on a cryofocussed narrow-bore column. The accuracy and precision data for these compounds are presented in Table 7. MDL values were also calculated from these data and are presented in Table 2.

9.4 Direct injection (Method 3585) has been used for the analysis of waste motor oil samples using a wide-bore column. Single laboratory precision and accuracy data are presented in Tables 10 and 11 for TCLP volatiles in oil. The performance data were developed by spiking and analyzing seven replicates each of new and used oil. The oils were spiked at the TCLP regulatory concentrations for most analytes, except for the alcohols, ketones, ethyl acetate and chlorobenzene which are spiked at 5 ppm, well below the regulatory concentrations. Prior to spiking, the new oil (an SAE 30-weight motor oil) was heated at 80°C overnight to remove volatiles. The used oil (a mixture of used oil drained from passenger automobiles) was not heated and was contaminated with 20 - 300 ppm of BTEX compounds and isobutanol. These contaminants contributed to the extremely high recoveries of the BTEX compounds in the used oil. Therefore, the data from the deuterated analogs of these analytes represent more typical recovery values.

9.5 Single laboratory accuracy and precision data were obtained for the Method 5035 analytes in three soil matrices: sand; a soil collected 10 feet below the surface of a hazardous landfill, called C-Horizon; and a surface garden soil. Sample preparation was by Method 5035. Each

sample was fortified with the analytes at a concentration of 4 µg/kg. These data are listed in Tables 17, 18, and 19. All data were calculated using fluorobenzene as the internal standard added to the soil sample prior to extraction. This causes some of the results to be greater than 100% recovery because the precision of results is sometimes as great as 28%.

9.5.1 In general, the recoveries of the analytes from the sand matrix are the highest, the C-Horizon soil results are somewhat less, and the surface garden soil recoveries are the lowest. This is due to the greater adsorptive capacity of the garden soil. This illustrates the necessity of analyzing matrix spike samples to assess the degree of matrix effects.

9.5.2 The recoveries of some of the gases, or very volatile compounds, such as vinyl chloride, trichlorofluoromethane, and 1,1-dichloroethene, are somewhat greater than 100%. This is due to the difficulty encountered in fortifying the soil with these compounds, allowing an equilibration period, then extracting them with a high degree of precision. Also, the garden soil results in Table 19 include some extraordinarily high recoveries for some aromatic compounds, such as toluene, xylenes, and trimethylbenzenes. This is due to contamination of the soil prior to sample collection, and to the fact that no background was subtracted.

9.6 Performance data for nonpurgeable volatiles using azeotropic distillation (Method 5031) are included in Tables 12 to 16.

9.7 Performance data for volatiles prepared using vacuum distillation (Method 5032) in soil, water, oil and fish tissue matrices are included in Tables 20 to 27.

9.8 Single laboratory accuracy and precision data were obtained for the Method 5021 analytes in two soil matrices: sand and a surface garden soil. Replicate samples were fortified with the analytes at concentrations of 10 µg/kg. These data are listed in Table 30. All data were calculated using the internal standards listed for each analyte in Table 28. The recommended internal standards were selected because they generated the best accuracy and precision data for the analyte in both types of soil.

9.8.1 If a detector other than an MS is used for analysis, consideration must be given to the choice of internal standards and surrogates. They must not coelute with any other analyte and must have similar properties to the analytes. The recoveries of the analytes are 50% or higher for each matrix studied. The recoveries of the gases or very volatile compounds are greater than 100% in some cases. Also, results include high recoveries of some aromatic compounds, such as toluene, xylenes, and trimethylbenzenes. This is due to contamination of the soil prior to sample collection.

9.8.2 The method detection limits using Method 5021 listed in Table 29 were calculated from results of seven replicate analyses of the sand matrix. Sand was chosen because it demonstrated the least degree of matrix effect of the soils studied. These MDLs were calculated utilizing the procedure described in Chapter One and are intended to be a general indication of the capabilities of the method.

9.9 The MDL concentrations listed in Table 31 were determined using Method 5041 in conjunction with Method 8260. They were obtained using cleaned blank VOST tubes and reagent water. Similar results have been achieved with field samples. The MDL actually achieved in a given analysis will vary depending upon instrument sensitivity and the effects of the matrix. Preliminary spiking studies indicate that under the test conditions, the MDLs for spiked compounds in extremely complex matrices may be larger by a factor of 500 - 1000.

9.10 The EQL of sample taken by Method 0040 and analyzed by Method 8260 is estimated to be in the range of 0.03 to 0.9 ppm (See Table 33). Matrix effects may cause the individual compound detection limits to be higher.

10.0 REFERENCES

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TABLE 1

CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC COMPOUNDS ON WIDE-BORE CAPILLARY COLUMNS

Compound	Retention Time (minutes)			MDL[a]
	Column 1[a]	Column 2[b]	Column 2[c]	(µg/L)
Dichlorodifluoromethane	1.35	0.70	3.13	0.10
Chloromethane	1.49	0.73	3.40	0.13
Vinyl Chloride	1.56	0.79	3.93	0.17
Bromomethane	2.19	0.96	4.80	0.11
Chloroethane	2.21	1.02	--	0.10
Trichlorofluoromethane	2.42	1.19	6.20	0.08
Acrolein	3.19			
Iodomethane	3.56			
Acetonitrile	4.11			
Carbon disulfide	4.11			
Allyl chloride	4.11			
Methylene chloride	4.40	2.06	9.27	0.03
1,1-Dichloroethene	4.57	1.57	7.83	0.12
Acetone	4.57			
trans-1,2-Dichloroethene	4.57	2.36	9.90	0.06
Acrylonitrile	5.00			
1,1-Dichloroethane	6.14	2.93	10.80	0.04
Vinyl acetate	6.43			
2,2-Dichloropropane	8.10	3.80	11.87	0.35
2-Butanone	--			
cis-1,2-Dichloroethene	8.25	3.90	11.93	0.12
Propionitrile	8.51			
Chloroform	9.01	4.80	12.60	0.03
Bromochloromethane	--	4.38	12.37	0.04
Methacrylonitrile	9.19			
1,1,1-Trichloroethane	10.18	4.84	12.83	0.08
Carbon tetrachloride	11.02	5.26	13.17	0.21
1,1-Dichloropropene	--	5.29	13.10	0.10
Benzene	11.50	5.67	13.50	0.04
1,2-Dichloroethane	12.09	5.83	13.63	0.06
Trichloroethene	14.03	7.27	14.80	0.19
1,2-Dichloropropane	14.51	7.66	15.20	0.04
Bromodichloromethane	15.39	8.49	15.80	0.08
Dibromomethane	15.43	7.93	5.43	0.24
Methyl methacrylate	15.50			
1,4-Dioxane	16.17			
2-Chloroethyl vinyl ether	--			
4-Methyl-2-pentanone	17.32			
trans-1,3-Dichloropropene	17.47	--	16.70	--
Toluene	18.29	10.00	17.40	0.11
cis-1,3-Dichloropropene	19.38	--	17.90	--

TABLE 1 (cont.)

Compound	Retention Time (minutes)			MDL[a]
	Column 1[a]	Column 2[b]	Column 2"[c]	(µg/L)
1,1,2-Trichloroethane	19.59	11.05	18.30	0.10
Ethyl methacrylate	20.01			
2-Hexanone	20.30			
Tetrachloroethene	20.26	11.15	18.60	0.14
1,3-Dichloropropane	20.51	11.31	18.70	0.04
Dibromochloromethane	21.19	11.85	19.20	0.05
1,2-Dibromoethane	21.52	11.83	19.40	0.06
1-Chlorohexane	–	13.29	–	0.05
Chlorobenzene	23.17	13.01	20.67	0.04
1,1,1,2-Tetrachloroethane	23.36	13.33	20.87	0.05
Ethylbenzene	23.38	13.39	21.00	0.06
p-Xylene	23.54	13.69	21.30	0.13
m-Xylene	23.54	13.68	21.37	0.05
o-Xylene	25.16	14.52	22.27	0.11
Styrene	25.30	14.60	22.40	0.04
Bromoform	26.23	14.88	22.77	0.12
Isopropylbenzene (Cumene)	26.37	15.46	23.30	0.15
cis-1,4-Dichloro-2-butene	27.12			
1,1,2,2-Tetrachloroethane	27.29	16.35	24.07	0.04
Bromobenzene	27.46	15.86	24.00	0.03
1,2,3-Trichloropropane	27.55	16.23	24.13	0.32
n-Propylbenzene	27.58	16.41	24.33	0.04
2-Chlorotoluene	28.19	16.42	24.53	0.04
trans-1,4-Dichloro-2-butene	28.26			
1,3,5-Trimethylbenzene	28.31	16.90	24.83	0.05
4-Chlorotoluene	28.33	16.72	24.77	0.06
Pentachloroethane	29.41			
1,2,4-Trimethylbenzene	29.47	17.70	31.50	0.13
sec-Butylbenzene	30.25	18.09	26.13	0.13
tert-Butylbenzene	30.59	17.57	26.60	0.14
p-Isopropyltoluene	30.59	18.52	26.50	0.12
1,3-Dichlorobenzene	30.56	18.14	26.37	0.12
1,4-Dichlorobenzene	31.22	18.39	26.60	0.03
Benzyl chloride	32.00			
n-Butylbenzene	32.23	19.49	27.32	0.11
1,2-Dichlorobenzene	32.31	19.17	27.43	0.03
1,2-Dibromo-3-chloropropane	35.30	21.08	–	0.26
1,2,4-Trichlorobenzene	38.19	23.08	31.50	0.04
Hexachlorobutadiene	38.57	23.68	32.07	0.11
Naphthalene	39.05	23.52	32.20	0.04
1,2,3-Trichlorobenzene	40.01	24.18	32.97	0.03

TABLE 1 (cont.)

Compound	Retention Time (minutes) Column 1[a]	Column 2[b]	Column 2"[c]	MDL[d] (µg/L)
INTERNAL STANDARDS/SURROGATES				
1,4-Difluorobenzene	13.26			
Chlorobenzene-d_5	23.10			
1,4-Dichlorobenzene-d_4	31.16			
4-Bromofluorobenzene	27.83	15.71	23.63	
1,2-Dichlorobenzene-d_4	32.30	19.08	27.25	
Dichloroethane-d_4	12.08			
Dibromofluoromethane	--			
Toluene-d_8	18.27			
Pentafluorobenzene	--			
Fluorobenzene	13.00	6.27	14.06	

[a] Column 1 - 60 meter x 0.75 mm ID VOCOL capillary. Hold at 10°C for 8 minutes, then program to 180°C at 4°C/min.

[b] Column 2 - 30 meter x 0.53 mm ID DB-624 wide-bore capillary using cryogenic oven. Hold at 10°C for 5 minutes, then program to 160°C at 6°C/min.

[c] Column 2" - 30 meter x 0.53 mm ID DB-624 wide-bore capillary, cooling GC oven to ambient temperatures. Hold at 10°C for 6 minutes, program to 70°C at 10 °C/min, program to 120°C at 5°C/min, then program to 180°C at 8°C/min.

[d] MDL based on a 25-mL sample volume.

TABLE 2

CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC COMPOUNDS ON NARROW-BORE CAPILLARY COLUMNS

Compound	Retention Time (minutes) Column 3[a]	MDL[b] (µg/L)
Dichlorodifluoromethane	0.88	0.11
Chloromethane	0.97	0.05
Vinyl chloride	1.04	0.04
Bromomethane	1.29	0.03
1,1-Dichloroethane	4.03	0.03
cis-1,2-Dichloroethene	5.07	0.06
2,2-Dichloropropane	5.31	0.08
Chloroform	5.55	0.04
Bromochloromethane	5.63	0.09
1,1,1-Trichloroethane	6.76	0.04
1,2-Dichloroethane	7.00	0.02
1,1-Dichloropropene	7.16	0.12
Carbon tetrachloride	7.41	0.02
Benzene	7.41	0.03
1,2-Dichloropropane	8.94	0.02
Trichloroethene	9.02	0.02
Dibromomethane	9.09	0.01
Bromodichloromethane	9.34	0.03
Toluene	11.51	0.08
1,1,2-Trichloroethane	11.99	0.08
1,3-Dichloropropane	12.48	0.08
Dibromochloromethane	12.80	0.07
Tetrachloroethene	13.20	0.05
1,2-Dibromoethane	13.60	0.10
Chlorobenzene	14.33	0.03
1,1,1,2-Tetrachloroethane	14.73	0.07
Ethylbenzene	14.73	0.03
p-Xylene	15.30	0.06
m-Xylene	15.30	0.03
Bromoform	15.70	0.20
o-Xylene	15.78	0.06
Styrene	15.78	0.27
1,1,2,2-Tetrachloroethane	15.78	0.20
1,2,3-Trichloropropane	16.26	0.09
Isopropylbenzene	16.42	0.10
Bromobenzene	16.42	0.11
2-Chlorotoluene	16.74	0.08
n-Propylbenzene	16.82	0.10
4-Chlorotoluene	16.82	0.06

TABLE 2 (cont.)

Compound	Retention Time (minutes) Column 3[a]	MDL[b] (µg/L)
1,3,5-Trimethylbenzene	16.99	0.06
tert-Butylbenzene	17.31	0.33
1,2,4-Trimethylbenzene	17.31	0.09
sec-Butylbenzene	17.47	0.12
1,3-Dichlorobenzene	17.47	0.05
p-Isopropyltoluene	17.63	0.26
1,4-Dichlorobenzene	17.63	0.04
1,2-Dichlorobenzene	17.79	0.05
n-Butylbenzene	17.95	0.10
1,2-Dibromo-3-chloropropane	18.03	0.50
1,2,4-Trichlorobenzene	18.84	0.20
Naphthalene	19.07	0.10
Hexachlorobutadiene	19.24	0.10
1,2,3-Trichlorobenzene	19.24	0.14

[a] Column 3 - 30 meter x 0.32 mm ID DB-5 capillary with 1 µm film thickness.

[b] MDL based on a 25-mL sample volume.

TABLE 3

ESTIMATED QUANTITATION LIMITS FOR VOLATILE ANALYTES[a]

Estimated Quantitation Limits		
5-mL Ground Water Purge (µg/L)	25-mL Ground water Purge (µg/L)	Low Soil/Sediment[b] µg/kg
5	1	5

[a] Estimated Quantitation Limit (EQL) - The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The EQL is generally 5 to 10 times the MDL. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes the EQL analyte concentration is selected for the lowest non-zero standard in the calibration curve. Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable. See the following footnote for further guidance on matrix-dependent EQLs.

[b] EQLs listed for soil/sediment are based on wet weight. Normally data are reported on a dry weight basis; therefore, EQLs will be higher, based on the percent dry weight in each sample.

Other Matrices	Factor[c]
Water miscible liquid waste	50
High concentration soil and sludge	125
Non-water miscible waste	500

[c] EQL = [EQL for low soil sediment (Table 3)] x [Factor].

For non-aqueous samples, the factor is on a wet-weight basis.

TABLE 4

BFB (4-BROMOFLUOROBENZENE) MASS INTENSITY CRITERIA[a]

m/z	Required Intensity (relative abundance)
50	15 to 40% of m/z 95
75	30 to 60% of m/z 95
95	Base peak, 100% relative abundance
96	5 to 9% of m/z 95
173	Less than 2% of m/z 174
174	Greater than 50% of m/z 95
175	5 to 9% of m/z 174
176	Greater than 95% but less than 101% of m/z 174
177	5 to 9% of m/z 176

[a] Alternate tuning criteria may be used, (e.g. CLP, Method 524.2, or manufacturers' instructions), provided that method performance is not adversely affected.

TABLE 5

CHARACTERISTIC MASSES (m/z) FOR PURGEABLE ORGANIC COMPOUNDS

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Acetone	58	43
Acetonitrile	41	40, 39
Acrolein	56	55, 58
Acrylonitrile	53	52, 51
Allyl alcohol	57	58, 39
Allyl chloride	76	41, 39, 78
Benzene	78	-
Benzyl chloride	91	126, 65, 128
Bromoacetone	136	43, 138, 93, 95
Bromobenzene	156	77, 158
Bromochloromethane	128	49, 130
Bromodichloromethane	83	85, 127
Bromoform	173	175, 254
Bromomethane	94	96
iso-Butanol	74	43
n-Butanol	56	41
2-Butanone	72	43
n-Butylbenzene	91	92, 134
sec-Butylbenzene	105	134
tert-Butylbenzene	119	91, 134
Carbon disulfide	76	78
Carbon tetrachloride	117	119
Chloral hydrate	82	44, 84, 86, 111
Chloroacetonitrile	48	75
Chlorobenzene	112	77, 114
1-Chlorobutane	56	49
Chlorodibromomethane	129	208, 206
Chloroethane	64 (49*)	66 (51*)
2-Chloroethanol	49	44, 43, 51, 80
Bis(2-chloroethyl) sulfide	109	111, 158, 160
2-Chloroethyl vinyl ether	63	65, 106
Chloroform	83	85
Chloromethane	50 (49*)	52 (51*)
Chloroprene	53	88, 90, 51
3-Chloropropionitrile	54	49, 89, 91
2-Chlorotoluene	91	126
4-Chlorotoluene	91	126
1,2-Dibromo-3-chloropropane	75	155, 157
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109, 188
Dibromomethane	93	95, 174

TABLE 5 (cont.)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
1,2-Dichlorobenzene	146	111, 148
1,2-Dichlorobenzene-d_4	152	115, 150
1,3-Dichlorobenzene	146	111, 148
1,4-Dichlorobenzene	146	111, 148
cis-1,4-Dichloro-2-butene	75	53, 77, 124, 89
trans-1,4-Dichloro-2-butene	53	88, 75
Dichlorodifluoromethane	85	87
1,1-Dichloroethane	63	65, 83
1,2-Dichloroethane	62	98
1,1-Dichloroethene	96	61, 63
cis-1,2-Dichloroethene	96	61, 98
trans-1,2-Dichloroethene	96	61, 98
1,2-Dichloropropane	63	112
1,3-Dichloropropane	76	78
2,2-Dichloropropane	77	97
1,3-Dichloro-2-propanol	79	43, 81, 49
1,1-Dichloropropene	75	110, 77
cis-1,3-Dichloropropene	75	77, 39
trans-1,3-Dichloropropene	75	77, 39
1,2,3,4-Diepoxybutane	55	57, 56
Diethyl ether	74	45, 59
1,4-Dioxane	88	58, 43, 57
Epichlorohydrin	57	49, 62, 51
Ethanol	31	45, 27, 46
Ethyl acetate	88	43, 45, 61
Ethylbenzene	91	106
Ethylene oxide	44	43, 42
Ethyl methacrylate	69	41, 99, 86, 114
Hexachlorobutadiene	225	223, 227
Hexachloroethane	201	166, 199, 203
2-Hexanone	43	58, 57, 100
2-Hydroxypropionitrile	44	43, 42, 53
Iodomethane	142	127, 141
Isobutyl alcohol	43	41, 42, 74
Isopropylbenzene	105	120
p-Isopropyltoluene	119	134, 91
Malononitrile	66	39, 65, 38
Methacrylonitrile	41	67, 39, 52, 66
Methyl acrylate	55	85
Methyl-t-butyl ether	73	57
Methylene chloride	84	86, 49
Methyl ethyl ketone	72	43
Methyl iodide	142	127, 141

TABLE 5 (cont.)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Methyl methacrylate	69	41, 100, 39
4-Methyl-2-pentanone	100	43, 58, 85
Naphthalene	128	-
Nitrobenzene	123	51, 77
2-Nitropropane	46	-
2-Picoline	93	66, 92, 78
Pentachloroethane	167	130, 132, 165, 169
Propargyl alcohol	55	39, 38, 53
β-Propiolactone	42	43, 44
Propionitrile (ethyl cyanide)	54	52, 55, 40
n-Propylamine	59	41, 39
n-Propylbenzene	91	120
Pyridine	79	52
Styrene	104	78
1,2,3-Trichlorobenzene	180	182, 145
1,2,4-Trichlorobenzene	180	182, 145
1,1,1,2-Tetrachloroethane	131	133, 119
1,1,2,2-Tetrachloroethane	83	131, 85
Tetrachloroethene	164	129, 131, 166
Toluene	92	91
1,1,1-Trichloroethane	97	99, 61
1,1,2-Trichloroethane	83	97, 85
Trichloroethene	95	97, 130, 132
Trichlorofluoromethane	151	101, 153
1,2,3-Trichloropropane	75	77
1,2,4-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
Vinyl acetate	43	86
Vinyl chloride	62	64
o-Xylene	106	91
m-Xylene	106	91
p-Xylene	106	91
Internal Standards/Surrogates:		
Benzene-d_6	84	83
Bromobenzene-d_5	82	162
Bromochloromethane-d_2	51	131
1,4-Difluorobenzene	114	
Chlorobenzene-d_5	117	
1,4-Dichlorobenzene-d_4	152	115, 150
1,1,2-Trichloroethane-d_3	100	
4-Bromofluorobenzene	95	174, 176
Chloroform-d_1	84	
Dibromofluoromethane	113	

TABLE 5 (cont.)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Internal Standards/Surrogates		
Dichloroethane-d_4	102	
Toluene-d_8	98	
Pentafluorobenzene	168	
Fluorobenzene	96	77

* Characteristic ion for an ion trap mass spectrometer (to be used when ion-molecule reactions are observed).

TABLE 6

SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR PURGEABLE VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED WITH A WIDE-BORE CAPILLARY COLUMN (METHOD 5030)

Compound	Conc. Range (µg/L)	Number of Samples	% Recovery[a]	Standard Deviation of Recovery[b]	RSD
Benzene	0.1 - 10	31	97	6.5	5.7
Bromobenzene	0.1 - 10	30	100	5.5	5.5
Bromochloromethane	0.5 - 10	24	90	5.7	6.4
Bromodichloromethane	0.1 - 10	30	95	5.7	6.1
Bromoform	0.5 - 10	18	101	6.4	6.3
Bromomethane	0.5 - 10	18	95	7.8	8.2
n-Butylbenzene	0.5 - 10	18	100	7.6	7.6
sec-Butylbenzene	0.5 - 10	16	100	7.6	7.6
tert-Butylbenzene	0.5 - 10	18	102	7.4	7.3
Carbon tetrachloride	0.5 - 10	24	84	7.4	8.8
Chlorobenzene	0.1 - 10	31	98	5.8	5.9
Chloroethane	0.5 - 10	24	89	8.0	9.0
Chloroform	0.5 - 10	24	90	5.5	6.1
Chloromethane	0.5 - 10	23	93	8.3	8.9
2-Chlorotoluene	0.1 - 10	31	90	5.6	6.2
4-Chlorotoluene	0.1 - 10	31	99	8.2	8.3
1,2-Dibromo-3-Chloropropane	0.5 - 10	24	83	16.6	19.9
Dibromochloromethane	0.1 - 10	31	92	6.5	7.0
1,2-Dibromoethane	0.5 - 10	24	102	4.0	3.9
Dibromomethane	0.5 - 10	24	100	5.6	5.6
1,2-Dichlorobenzene	0.1 - 10	31	93	5.8	6.2
1,3-Dichlorobenzene	0.5 - 10	24	99	6.8	6.9
1,4-Dichlorobenzene	0.2 - 20	31	103	6.6	6.4
Dichlorodifluoromethane	0.5 - 10	18	90	6.9	7.7
1,1-Dichlorobenzene	0.5 - 10	24	96	5.1	5.3
1,2-Dichlorobenzene	0.1 - 10	31	95	5.1	5.4
1,1-Dichloroethene	0.1 - 10	34	94	6.3	6.7
cis-1,2-Dichloroethene	0.5 - 10	18	101	6.7	6.7
trans-1,2-Dichloroethene	0.1 - 10	30	93	5.2	5.6
1,2-Dichloropropane	0.1 - 10	30	97	5.9	6.1
1,3-Dichloropropane	0.1 - 10	31	96	5.7	6.0
2,2-Dichloropropane	0.5 - 10	12	86	14.6	16.9
1,1-Dichloropropene	0.5 - 10	18	98	8.7	8.9
Ethylbenzene	0.1 - 10	31	99	8.4	8.6
Hexachlorobutadiene	0.5 - 10	18	100	6.8	6.8
Isopropylbenzene	0.5 - 10	16	101	7.7	7.6
p-Isopropyltoluene	0.1 - 10	23	99	6.7	6.7
Methylene chloride	0.1 - 10	30	95	5.0	5.3

TABLE 6 (cont.)

Compound	Conc. Range (µg/L)	Number of Samples	% Recovery[a]	Standard Deviation of Recovery[b]	RSD
Naphthalene	0.1 -100	31	104	8.6	8.2
n-Propylbenzene	0.1 - 10	31	100	5.8	5.8
Styrene	0.1 -100	39	102	7.3	7.2
1,1,1,2-Tetrachloroethane	0.5 - 10	24	90	6.1	6.8
1,1,2,2-Tetrachloroethane	0.1 - 10	30	91	5.7	6.3
Tetrachloroethene	0.5 - 10	24	89	6.0	6.8
Toluene	0.5 - 10	18	102	8.1	8.0
1,2,3-Trichlorobenzene	0.5 - 10	18	109	9.4	8.6
1,2,4-Trichlorobenzene	0.5 - 10	18	108	9.0	8.3
1,1,1-Trichloroethane	0.5 - 10	18	98	7.9	8.1
1,1,2-Trichloroethane	0.5 - 10	18	104	7.6	7.3
Trichloroethene	0.5 - 10	24	90	6.5	7.3
Trichlorofluoromethane	0.5 - 10	24	89	7.2	8.1
1,2,3-Trichloropropane	0.5 - 10	16	108	15.6	14.4
1,2,4-Trimethylbenzene	0.5 - 10	18	99	8.0	8.1
1,3,5-Trimethylbenzene	0.5 - 10	23	92	6.8	7.4
Vinyl chloride	0.5 - 10	18	98	6.5	6.7
o-Xylene	0.1 - 31	18	103	7.4	7.2
m-Xylene	0.1 - 10	31	97	6.3	6.5
p-Xylene	0.5 - 10	18	104	8.0	7.7

[a] Recoveries were calculated using internal standard method. The internal standard was fluorobenzene.

[b] Standard deviation was calculated by pooling data from three concentrations.

TABLE 7

SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR PURGEABLE VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED WITH A NARROW-BORE CAPILLARY COLUMN (METHOD 5030)

Compound	Conc. (µg/L)	Number of Samples	% Recovery[a]	Standard Deviation of Recovery[b]	RSD
Benzene	0.1	7	99	6.2	6.3
Bromobenzene	0.5	7	97	7.4	7.6
Bromochloromethane	0.5	7	97	5.8	6.0
Bromodichloromethane	0.1	7	100	4.6	4.6
Bromoform	0.5	7	101	5.4	5.3
Bromomethane	0.5	7	99	7.1	7.2
n-Butylbenzene	0.5	7	94	6.0	6.4
sec-Butylbenzene	0.5	7	110	7.1	6.5
tert-Butylbenzene	0.5	7	110	2.5	2.3
Carbon tetrachloride	0.1	7	108	6.8	6.3
Chlorobenzene	0.1	7	91	5.8	6.4
Chloroethane	0.1	7	100	5.8	5.8
Chloroform	0.1	7	105	3.2	3.0
Chloromethane	0.5	7	101	4.7	4.7
2-Chlorotoluene	0.5	7	99	4.6	4.6
4-Chlorotoluene	0.5	7	96	7.0	7.3
1,2-Dibromo-3-chloropropane	0.5	7	92	10.0	10.9
Dibromochloromethane	0.1	7	99	5.6	5.7
1,2-Dibromoethane	0.5	7	97	5.6	5.8
Dibromomethane	0.5	7	93	5.6	6.0
1,2-Dichlorobenzene	0.1	7	97	3.5	3.6
1,3-Dichlorobenzene	0.1	7	101	6.0	5.9
1,4-Dichlorobenzene	0.1	7	106	6.5	6.1
Dichlorodifluoromethane	0.1	7	99	8.8	8.9
1,1-Dichloroethane	0.5	7	98	6.2	6.3
1,2-Dichloroethane	0.1	7	100	6.3	6.3
1,1-Dichloroethene	0.1	7	95	9.0	9.5
cis-1,2-Dichloroethene	0.1	7	100	3.5	3.7
trans-1,2-Dichloroethene	0.1	7	98	7.2	7.3
1,2-Dichloropropane	0.5	7	96	6.0	6.3
1,3-Dichloropropane	0.5	7	99	5.8	5.9
2,2-Dichloropropane	0.5	7	99	4.9	4.9
1,1-Dichloropropene	0.5	7	102	7.4	7.3
Ethylbenzene	0.5	7	99	5.2	5.3
Hexachlorobutadiene	0.5	7	100	6.7	6.7
Isopropylbenzene	0.5	7	102	6.4	6.3
p-Isopropyltoluene	0.5	7	113	13.0	11.5
Methylene chloride	0.5	7	97	13.0	13.4
Naphthalene	0.5	7	98	7.2	7.3

TABLE 7 (cont.)

Compound	Conc. (µg/L)	Number of Samples	% Recovery[a]	Standard Deviation of Recovery[b]	RSD
n-Propylbenzene	0.5	7	99	6.6	6.7
Styrene	0.5	7	96	19.0	19.8
1,1,1,2-Tetrachloroethane	0.5	7	100	4.7	4.7
1,1,2,2-Tetrachloroethane	0.5	7	100	12.0	12.0
Tetrachloroethene	0.1	7	96	5.0	5.2
Toluene	0.5	7	100	5.9	5.9
1,2,3-Trichlorobenzene	0.5	7	102	8.9	8.7
1,2,4-Trichlorobenzene	0.5	7	91	16.0	17.6
1,1,1-Trichloroethane	0.5	7	100	4.0	4.0
1,1,2-Trichloroethane	0.5	7	102	4.9	4.8
Trichloroethene	0.1	7	104	2.0	1.9
Trichlorofluoromethane	0.1	7	97	4.6	4.7
1,2,3-Trichloropropane	0.5	7	96	6.5	6.8
1,2,4-Trimethylbenzene	0.5	7	96	6.5	6.8
1,3,5-Trimethylbenzene	0.5	7	101	4.2	4.2
Vinyl chloride	0.1	7	104	0.2	0.2
o-Xylene	0.5	7	106	7.5	7.1
m-Xylene	0.5	7	106	4.6	4.3
p-Xylene	0.5	7	97	6.1	6.3

[a] Recoveries were calculated using internal standard method. Internal standard was fluorobenzene.

TABLE 8

SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Water	Soil/Sediment
4-Bromofluorobenzene[a]	86-115	74-121
Dibromofluoromethane[a]	86-118	80-120
Toluene-d_8[a]	88-110	81-117
Dichloroethane-d_4[a]	80-120	80-120

[a] Single laboratory data, for guidance only.

TABLE 9

QUANTITY OF EXTRACT REQUIRED FOR ANALYSIS OF HIGH CONCENTRATION SAMPLES

Approximate Concentration Range (µg/kg)	Volume of Extract[a]
500 - 10,000	100 µL
1,000 - 20,000	50 µL
5,000 - 100,000	10 µL
25,000 - 500,000	100 µL of 1/50 dilution[b]

Calculate appropriate dilution factor for concentrations exceeding this table.

[a] The volume of solvent added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of solvent is necessary to maintain a volume of 100 µL added to the syringe.

[b] Dilute an aliquot of the solvent extract and then take 100 µL for analysis.

TABLE 10

DIRECT INJECTION ANALYSIS OF NEW OIL AT 5 PPM (METHOD 3585)

Compound	Recovery (%)	%RSD	Blank (ppm)	Spike (ppm)
Acetone	91	14.8	1.9	5.0
Benzene	86	21.3	0.1	0.5
n-Butanol*,**	107	27.8	0.5	5.0
iso-Butanol*,**	95	19.5	0.9	5.0
Carbon tetrachloride	86	44.7	0.0	0.5
Carbon disulfide**	53	22.3	0.0	5.0
Chlorobenzene	81	29.3	0.0	5.0
Chloroform	84	29.3	0.0	6.0
1,4-Dichlorobenzene	98	24.9	0.0	7.5
1,2-Dichloroethane	101	23.1	0.0	0.5
1,1-Dichloroethene	97	45.3	0.0	0.7
Diethyl ether	76	24.3	0.0	5.0
Ethyl acetate	113	27.4	0.0	5.0
Ethylbenzene	83	30.1	0.2	5.0
Hexachloroethane	71	30.3	0.0	3.0
Methylene chloride	98	45.3	0.0	5.0
Methyl ethyl ketone	79	24.6	0.4	5.0
MIBK	93	31.4	0.0	5.0
Nitrobenzene	89	30.3	0.0	2.0
Pyridine	31	35.9	0.0	5.0
Tetrachloroethene	82	27.1	0.0	0.7
Trichlorofluoromethane	76	27.6	0.0	5.0
1,1,2-Trichlorotrifluoroethane	69	29.2	0.0	5.0
Toluene	73	21.9	0.6	5.0
Trichloroethene	66	28.0	0.0	0.5
Vinyl chloride	63	35.2	0.0	0.2
o-Xylene	83	29.5	0.4	5.0
m/p-Xylene	84	29.5	0.6	10.0

* Alternate mass employed
** IS quantitation

Data are taken from Reference 9.

TABLE 11

SINGLE LABORATORY PERFORMANCE
DATA FOR THE DIRECT INJECTION METHOD - USED OIL (METHOD 3585)

Compound	Recovery (%)	%RSD	Blank (ppm)	Spike (ppm)
Acetone**	105	54	2.0	5.0
Benzene	3135	44	14	0.5
Benzene-d_6	56	44	2.9	0.5
n-Butanol**	100	71	12	5.0
iso-Butanol*,**	132	27	0	5.0
Carbon tetrachloride	143	68	0	0.5
Carbon tetrachloride-^{13}C	99	44	5.1	0.5
Carbon disulfide**	95	63	0	5.0
Chlorobenzene	148	71	0	5.0
Chlorobenzene-d_5	60	44	3.6	5.0
Chloroform	149	74	0	6.0
Chloroform-d_1	51	44	2.6	6.0
1,4-Dichlorobenzene	142	72	0	7.5
1,4-Dichlorobenzene-d_4	53	44	3.4	7.5
1,2-Dichloroethane**	191	54	0	0.5
1,1-Dichloroethene*	155	51	0	0.7
1,1-Dichloroethene-d_2	68	44	3.4	0.7
Diethyl ether**	95	66	0	5.0
Ethyl acetate*,**	126	39	0	5.0
Ethylbenzene	1298	44	54	5.0
Ethylbenzene-d_{10}	63	44	3.6	5.0
Hexachloroethane	132	72	0	3.0
Hexachloroethane-^{13}C	54	45	3.5	3.0
Methylene chloride**	86	65	0.3	5.0
Methyl ethyl ketone**	107	64	0	5.0
4-Methyl-2-pentanone (MIBK)**	100	74	0.1	5.0
Nitrobenzene	111	80	0	2.0
Nitrobenzene-d_5	65	53	4.0	2.0
Pyridine**	68	85	0	5.0
Pyridine-d_5	ND	–	0	5.0
Tetrachloroethene**	101	73	0	0.7
Trichlorofluoromethane**	91	70	0	5.0
1,1,2-Cl_3F_3ethane**	81	70	0	5.0
Toluene	2881	44	128	5.0
Toluene-d_8	63	44	3.6	5.0
Trichloroethene	152	57	0	0.5
Trichloroethene-d_1	55	44	2.8	0.5

TABLE 11 (cont.)

Compound	Recovery (%)	%RSD	Blank (ppm)	Spike (ppm)
Vinyl chloride**	100	69	0	0.2
o-Xylene	2292	44	105	5.0
o-Xylene-d_{10}	76	44	4.2	5.0
m-/p-Xylene	2583	44	253	10.0
p-Xylene-d_{10}	67	44	3.7	10.0

* Alternate mass employed
** IS quantitation
ND = Not Detected

Data are based on seven measurements and are taken from Reference 9.

TABLE 12

METHOD DETECTION LIMITS (METHOD 5031)

Compound	MDL (µg/L) Macro[a]	Concentration Factor Macro	Micro
Acetone	31	25-500	-
Acetonitrile	57	25-500	200
Acrolein	-	-	100
Acrylonitrile	16	25-500	100
Allyl Alcohol	7	25-500	-
1-Butanol	-	-	250
Crotonaldehyde	12	25-500	-
1,4-Dioxane	12	25-500	150
Ethyl Acetate	-	-	100
Isobutyl alcohol	7	25-500	-
Methanol	38	25-500	140
Methyl Ethyl Ketone	16	25-500	-
2-Methyl-1-propanol	-	-	250
n-Nitroso-di-n-butylamine	14	25-500	-
Paraldehyde	10	25-500	-
2-Picoline	7	25-500	-
1-Propanol	-	-	240
Propionitrile	11	25-500	200
Pyridine	4	25-500	-
o-Toluidine	13	25-500	-

[a] Produced by analysis of seven aliquots of reagent water spiked at 25 ppb at the listed compounds; calculations based on internal standard technique and use of the following equation:

MDL = 3.134 x Std. Dev. of low concentration spike (ppb).

[b] When a 40-mL sample is used, and the first 100 µL of distillate are collected.

TABLE 13

TARGET COMPOUNDS, SURROGATES, AND INTERNAL STANDARDS (METHOD 5031)

Target Compound	Surrogate	Internal Standard
Acetone	d_6-Acetone	d_8-Isopropyl alcohol
Acetonitrile	d_3-Acetonitrile	d_8-Isopropyl alcohol
Acrylonitrile	d_8-Isopropyl alcohol	
Allyl alcohol	d_7-Dimethyl formamide	
Crotonaldehyde	d_8-Isopropyl alcohol	
1,4-Dioxane	d_8-1,4-Dioxane	d_7-Dimethyl formamide
Isobutyl alcohol	d_7-Dimethyl formamide	
Methanol	d_3-Methanol	d_8-Isopropyl alcohol
Methyl ethyl ketone	d_8-Isopropyl alcohol	
N-Nitroso-di-n-butylamine	d_7-Dimethyl formamide	
Paraldehyde	d_7-Dimethyl formamide	
2-Picoline	d_7-Dimethyl formamide	
Propionitrile	d_8-Isopropyl alcohol	
Pyridine	d_5-Pyridine	d_7-Dimethyl formamide
o-Toluidine	d_7-Dimethyl formamide	

TABLE 14

RECOMMENDED CONCENTRATIONS FOR CALIBRATION SOLUTIONS (METHOD 5031)

Compound	Concentration(s) (ng/µL)
Internal Standards	
d_5-benzyl alcohol	10.0
d_{14}-Diglyme	10.0
d_7-Dimethyl formamide	10.0
d_8-Isopropyl alcohol	10.0
Surrogates	
d_6-Acetone	10.0
d_3-Acetonitrile	10.0
d_8-1,4-Dioxane	10.0
d_3-Methanol	10.0
d_5-Pyridine	10.0
Target Compounds	
Acetone	1.0, 5.0, 10.0, 25.0, 100.0
Acetonitrile	1.0, 5.0, 10.0, 25.0, 100.0
Acrylonitrile	1.0, 5.0, 10.0, 25.0, 100.0
Allyl alcohol	1.0, 5.0, 10.0, 25.0, 100.0
Crotonaldehyde	1.0, 5.0, 10.0, 25.0, 100.0
1,4-Dioxane	1.0, 5.0, 10.0, 25.0, 100.0
Isobutyl alcohol	1.0, 5.0, 10.0, 25.0, 100.0
Methanol	1.0, 5.0, 10.0, 25.0, 100.0
Methyl ethyl ketone	1.0, 5.0, 10.0, 25.0, 100.0
N-Nitroso-di-n-butylamine	1.0, 5.0, 10.0, 25.0, 100.0
Paraldehyde	1.0, 5.0, 10.0, 25.0, 100.0
2-Picoline	1.0, 5.0, 10.0, 25.0, 100.0
Propionitrile	1.0, 5.0, 10.0, 25.0, 100.0
Pyridine	1.0, 5.0, 10.0, 25.0, 100.0
o-Toluidine	1.0, 5.0, 10.0, 25.0, 100.0

TABLE 15

CHARACTERISTIC IONS AND RETENTION TIMES FOR VOCs (METHOD 5031)

Compound	Quantitation Ion[a]	Secondary Ions	Retention Time (min)[b]
Internal Standards			
d_8-Isopropyl alcohol	49		1.75
d_{14}-Diglyme	66	98,64	9.07
d_7-Dimethyl formamide	50	80	9.20
Surrogates			
d_6-Acetone	46	64,42	1.03
d_3-Methanol	33	35,30	1.75
d_3-Acetonitrile	44	42	2.63
d_8-1,4-Dioxane	96	64,34	3.97
d_5-Pyridine	84	56,79	6.73
d_6-Phenol[c]	99	71	15.43
Target Compounds			
Acetone	43	58	1.05
Methanol	31	29	1.52
Methyl ethyl ketone	43	72,57	1.53
Methacrylonitrile[c]	67	41	2.38
Acrylonitrile	53	52,51	2.53
Acetonitrile	41	40,39	2.73
Methyl isobutyl ketone[c]	85	100,58	2.78
Propionitrile	54	52,55	3.13
Crotonaldehyde	41	70	3.43
1,4-Dioxane	58	88,57	4.00
Paraldehyde	45	89	4.75
Isobutyl alcohol	43	33,42	5.05
Allyl alcohol	57	39	5.63
Pyridine	79	50,52	6.70
2-Picoline	93	66	7.27
N-Nitroso-di-n-butylamine	84	116	12.82
Aniline[c]	93	66,92	13.23
o-Toluidine	106	107	13.68
Phenol[c]	94	66,65	15.43

[a] These ions were used for quantitation in selected ion monitoring.
[b] GC column: DB-Wax, 30 meter x 0.53 mm, 1 µm film thickness.
Oven program: 45°C for 4 min, increased to 220°C at 12°C/min.
[c] Compound removed from target analyte list due to poor accuracy and precision.

TABLE 16

METHOD ACCURACY AND PRECISION BY MEAN PERCENT RECOVERY AND PERCENT RELATIVE STANDARD DEVIATION[a] (METHOD 5031 - MACRODISTILLATION TECHNIQUE)
(Single Laboratory and Single Operator)

Compound	25 ppb Spike		100 ppb Spike		500 ppb Spike	
	Mean %R	%RSD	Mean %R	%RSD	Mean %R	%RSD
d_6-Acetone	66	24	69	14	65	16
d_3-Acetonitrile	89	18	80	18	70	10
d_8-1,4-Dioxane	56	34	58	11	61	18
d_3-Methanol	43	29	48	19	56	14
d_5-Pyridine	83	6.3	84	7.8	85	9.0
Acetone	67	45	63	14	60	14
Acetonitrile	44	35	52	15	56	15
Acrylonitrile	49	42	47	27	45	27
Allyl alcohol	69	13	70	9.7	73	10
Crotonaldehyde	68	22	68	13	69	13
1,4-Dioxane	63	25	55	16	54	13
Isobutyl alcohol	66	14	66	5.7	65	7.9
Methanol	50	36	46	22	49	18
Methyl ethyl ketone	55	37	56	20	52	19
N-Nitroso-di-n-butylamine	57	21	61	15	72	18
Paraldehyde	65	20	66	11	60	8.9
Picoline	81	12	81	6.8	84	8.0
Propionitrile	67	22	69	13	68	13
Pyridine	74	7.4	72	6.7	74	7.3
o-Toluidine	52	31	54	15	58	12

[a] Data from analysis of seven aliquots of reagent water spiked at each concentration, using a quadrapole mass spectrometer in the selected ion monitoring mode.

TABLE 17

RECOVERIES IN SAND SAMPLES FORTIFIED AT 4 µg/kg (ANALYSIS BY METHOD 5035)

Compound	Recovery per Replicate (ng) 1	2	3	4	5	Mean	RSD	Mean Rec
Vinyl chloride	8.0	7.5	6.7	5.4	6.6	6.8	13.0	34.2
Trichlorofluoromethane	13.3	16.5	14.9	13.0	10.3	13.6	15.2	68.0
1,1-Dichloroethene	17.1	16.7	15.1	14.8	15.6	15.9	5.7	79.2
Methylene chloride	24.5	22.7	19.7	19.4	20.6	21.4	9.1	107
trans-1,2-Dichloroethene	22.7	23.6	19.4	18.3	20.1	20.8	0.7	104
1,2-Dichloroethane	18.3	18.0	16.7	15.6	15.9	16.9	6.4	84.4
cis-1,2-Dichloroethene	26.1	23.1	22.6	20.3	20.8	22.6	9.0	113
Bromochloromethane	24.5	25.4	20.9	20.1	20.1	22.2	10.2	111
Chloroform	26.5	26.0	22.1	18.9	22.1	23.1	12.2	116
1,1,1-Trichloroethane	21.5	23.0	23.9	16.7	31.2	23.4	21.2	117
Carbon tetrachloride	23.6	24.2	22.6	18.3	23.3	22.4	9.4	112
Benzene	22.4	23.9	20.4	17.4	19.2	20.7	11.2	103
Trichloroethene	21.5	20.5	19.2	14.4	19.1	18.9	12.7	94.6
1,2-Dichloropropane	24.9	26.3	23.1	19.0	23.3	23.3	10.5	117
Dibromomethane	25.4	26.4	21.6	20.4	23.6	23.5	9.6	117
Bromodichloromethane	25.7	26.7	24.1	17.9	23.0	23.5	13.1	117
Toluene	28.3	25.0	24.8	16.3	23.6	23.6	16.9	118
1,1,2-Trichloroethane	25.4	24.5	21.6	17.7	22.1	22.2	12.1	111
1,3-Dichloropropane	25.4	24.2	22.7	17.0	22.2	22.3	12.8	112
Dibromochloromethane	26.3	26.2	23.7	18.2	23.2	23.5	12.5	118
Chlorobenzene	22.9	22.5	19.8	14.6	19.4	19.9	15.0	99.3
1,1,1,2-Tetrachloroethane	22.4	27.7	25.1	19.4	22.6	23.4	12.0	117
Ethylbenzene	25.6	25.0	22.1	14.9	24.0	22.3	17.5	112
p-Xylene	22.5	22.0	19.8	13.9	20.3	19.7	15.7	98.5
o-Xylene	24.2	23.1	21.6	14.0	20.4	20.7	17.3	103
Styrene	23.9	21.5	20.9	14.3	20.5	20.2	15.7	101
Bromoform	26.8	25.6	26.0	20.1	23.5	24.4	9.9	122
iso-Propylbenzene	25.3	25.1	24.2	15.4	24.6	22.9	16.6	114
Bromobenzene	19.9	21.8	20.0	15.5	19.1	19.3	10.7	96.3
1,2,3-Trichloropropane	25.9	23.0	25.6	15.9	21.4	22.2	15.8	111
n-Propylbenzene	26.0	23.8	22.6	13.9	21.9	21.6	19.0	106
2-Chlorotoluene	23.6	23.8	21.3	13.0	21.5	20.6	19.2	103
4-Chlorotoluene	21.0	19.7	18.4	12.1	18.3	17.9	17.1	89.5
1,3,5-Trimethylbenzene	24.0	22.1	22.5	13.8	22.9	21.1	17.6	105
sec-Butylbenzene	25.9	25.3	27.8	16.1	28.6	24.7	18.1	124
1,2,4-Trimethylbenzene	30.6	39.2	22.4	18.0	22.7	26.6	28.2	133
1,3-Dichlorobenzene	20.3	20.6	18.2	13.0	17.6	17.9	15.2	89.7
p-iso-Propyltoluene	21.6	22.1	21.6	16.0	22.8	20.8	11.8	104
1,4-Dichlorobenzene	18.1	21.2	20.0	13.2	17.4	18.0	15.3	90.0
1,2-Dichlorobenzene	18.4	22.5	22.5	15.2	19.9	19.7	13.9	96.6
n-Butylbenzene	13.1	20.3	19.5	10.8	18.7	16.5	23.1	82.4
1,2,4-Trichlorobenzene	14.5	14.9	15.7	8.8	12.3	13.3	18.8	66.2
Hexachlorobutadiene	17.6	22.5	21.6	13.2	21.6	19.3	18.2	96.3
1,2,3-Trichlorobenzene	14.9	15.9	16.5	11.9	13.9	14.6	11.3	73.1

Data in Tables 17, 18, and 19 are from Reference 15.

TABLE 18
RECOVERIES IN C-HORIZON SOILS FORTIFIED AT 4 µg/kg (ANALYSIS BY METHOD 5035)

Compound	Recovery per Replicate (ng) 1	2	3	4	5	Mean	RSD	Mean Rec
Vinyl chloride	33.4	31.0	30.9	29.7	28.6	30.8	5.2	154
Trichlorofluoromethane	37.7	20.8	20.0	21.8	20.5	24.1	28.2	121
1,1-Dichloroethene	21.7	33.5	39.8	30.2	32.5	31.6	18.5	158
Methylene chloride	20.9	19.4	18.7	18.3	18.4	19.1	5.1	95.7
trans-1,2-Dichloroethene	21.8	18.9	20.4	17.9	17.8	19.4	7.9	96.8
1,1-Dichloroethane	23.8	21.9	21.3	21.3	20.5	21.8	5.2	109
cis-1,2-Dichloroethene	21.6	18.8	18.5	18.2	18.2	19.0	6.7	95.2
Bromochloromethane	22.3	19.5	19.3	19.0	19.2	20.0	6.0	100
Chloroform	20.5	17.1	17.3	16.5	15.9	17.5	9.2	87.3
1,1,1-Trichloroethane	16.4	11.9	10.7	9.5	9.4	11.6	22.4	57.8
Carbon tetrachloride	13.1	11.3	13.0	11.8	11.2	12.1	6.7	60.5
Benzene	21.1	19.3	18.7	18.2	16.9	18.8	7.4	94.1
Trichloroethene	19.6	16.4	16.5	16.5	15.5	16.9	8.3	84.5
1,2-Dichloropropane	21.8	19.0	18.3	18.8	16.5	18.9	9.0	94.4
Dibromomethane	20.9	17.9	17.9	17.2	18.3	18.4	6.9	92.1
Bromodichloromethane	20.9	18.0	18.9	18.2	17.3	18.6	6.6	93.2
Toluene	22.2	17.3	18.8	17.0	15.9	18.2	12.0	91.2
1,1,2-Trichloroethane	21.0	16.5	17.2	17.2	16.5	17.7	9.6	88.4
1,3-Dichloropropane	21.4	17.3	18.7	18.6	16.7	18.5	8.8	92.6
Dibromochloromethane	20.9	18.1	19.0	18.8	16.6	18.7	7.5	93.3
Chlorobenzene	20.8	18.4	17.6	16.8	14.8	17.7	11.2	88.4
1,1,1,2-Tetrachloroethane	19.5	19.0	17.8	17.2	16.5	18.0	6.2	90.0
Ethylbenzene	21.1	18.3	18.5	16.9	15.3	18.0	10.6	90.0
p-Xylene	20.0	17.4	18.2	16.3	14.4	17.3	10.9	86.3
o-Xylene	20.7	17.2	16.8	16.2	14.8	17.1	11.4	85.7
Styrene	18.3	15.9	16.2	15.3	13.7	15.9	9.3	79.3
Bromoform	20.1	15.9	17.1	17.5	16.1	17.3	8.6	86.7
iso-Propylbenzene	21.0	18.1	19.2	18.4	15.6	18.4	9.6	92.2
Bromobenzene	20.4	16.2	17.2	16.7	15.4	17.2	10.1	85.9
1,1,2,2-Tetrachloroethane	23.3	17.9	21.2	18.8	16.8	19.6	12.1	96.0
1,2,3-Trichloropropane	18.4	14.6	15.6	16.1	15.6	16.1	8.0	80.3
n-Propylbenzene	20.4	18.9	17.9	17.0	14.3	17.7	11.6	88.4
2-Chlorotoluene	19.1	17.3	16.1	16.0	14.4	16.7	9.2	83.6
4-Chlorotoluene	19.0	15.5	16.8	15.9	13.6	16.4	10.6	81.8
1,3,5-Trimethylbenzene	20.8	18.0	17.4	16.1	14.7	17.4	11.7	86.9
sec-Butylbenzene	21.4	18.3	18.9	17.0	14.9	18.1	11.8	90.5
1,2,4-Trimethylbenzene	20.5	18.6	16.8	15.3	13.7	17.0	14.1	85.0
1,3-Dichlorobenzene	17.6	15.9	15.6	14.2	14.4	15.6	7.9	77.8
p-iso-Propyltoluene	20.5	17.0	17.1	15.6	13.4	16.7	13.9	83.6
1,4-Dichlorobenzene	18.5	13.8	14.8	16.7	14.9	15.7	10.5	78.7
1,2-Dichlorobenzene	18.4	15.0	15.4	15.3	13.5	15.5	10.5	77.6
n-Butylbenzene	19.6	15.9	15.9	14.4	18.9	16.9	11.7	84.6
1,2,4-Trichlorobenzene	15.2	17.2	17.4	13.6	12.1	15.1	13.5	75.4
Hexachlorobutadiene	18.7	16.2	15.5	13.8	16.6	16.1	10.0	80.7
Naphthalene	13.9	11.1	10.2	10.8	11.4	11.5	11.0	57.4
1,2,3-Trichlorobenzene	14.9	15.2	16.8	13.7	12.7	14.7	9.5	73.2

TABLE 19
RECOVERIES IN GARDEN SOIL FORTIFIED AT 4 µg/kg (ANALYSIS BY METHOD 5035)

Compound	Recovery per Replicate (ng) 1	2	3	4	5	Mean	RSD	Mean Rec
Vinyl chloride	12.7	10.9	9.8	8.1	7.2	9.7	20.2	48.7
Trichlorofluoromethane	33.7	6.4	30.3	27.8	22.9	24.2	39.6	121
1,1-Dichloroethene	27.7	20.5	24.1	15.1	13.2	20.1	26.9	101
Methylene chloride	25.4	23.9	24.7	22.2	24.2	24.1	4.4	120
trans-1,2-Dichloroethene	2.8	3.0	3.3	2.2	2.4	2.7	15.0	13.6
1,1-Dichloroethane	24.1	26.3	27.0	20.5	21.2	23.8	11.0	119
cis-1,2-Dichloroethene	8.3	10.2	8.7	5.8	6.4	7.9	20.1	39.4
Bromochloromethane	11.1	11.8	10.2	8.8	9.0	10.2	11.2	50.9
Chloroform	16.7	16.9	17.0	13.8	15.0	15.9	7.9	79.3
1,1,1-Trichloroethane	24.6	22.8	22.1	16.2	20.9	21.3	13.4	107
Carbon tetrachloride	19.4	20.3	22.2	20.0	20.2	20.4	4.6	102
Benzene	21.4	22.0	22.4	19.6	20.4	21.2	4.9	106
Trichloroethene	12.4	16.5	14.9	9.0	9.9	12.5	22.9	62.7
1,2-Dichloropropane	19.0	18.8	19.7	16.0	17.6	18.2	7.1	91.0
Dibromomethane	7.3	8.0	6.9	5.6	6.8	6.9	11.3	34.6
Bromodichloromethane	14.9	15.9	15.9	12.8	13.9	14.7	8.3	73.3
Toluene	42.6	39.3	45.1	39.9	45.3	42.4	5.9	212
1,1,2-Trichloroethane	13.9	15.2	1.4	21.3	14.9	15.9	17.0	79.6
1,3-Dichloropropane	13.3	16.7	11.3	10.9	9.5	12.3	20.3	61.7
Dibromochloromethane	14.5	13.1	14.5	11.9	14.4	13.7	7.6	68.3
Chlorobenzene	8.4	10.0	8.3	6.9	7.8	8.3	12.1	41.3
1,1,1,2-Tetrachloroethane	16.7	16.7	15.6	15.8	15.7	16.1	3.2	80.4
Ethylbenzene	22.1	21.4	23.1	20.1	22.6	21.9	4.8	109
p-Xylene	41.4	38.4	43.8	38.3	44.0	41.2	6.1	206
o-Xylene	31.7	30.8	34.3	30.4	33.2	32.1	4.6	160
Styrene	0	0	0	0	0	0	0	0
Bromoform	8.6	8.9	9.1	7.0	7.7	8.3	9.4	41.4
iso-Propylbenzene	18.1	18.8	9.7	18.3	19.6	18.9	3.5	94.4
Bromobenzene	5.1	5.4	5.3	4.4	4.0	4.8	11.6	24.1
1,1,2,2-Tetrachloroethane	14.0	13.5	14.7	15.3	17.1	14.9	8.5	74.5
1,2,3-Trichloropropane	11.0	12.7	11.7	11.7	11.9	11.8	4.5	59.0
n-Propylbenzene	13.4	13.3	14.7	12.8	13.9	13.6	4.7	68.1
2-Chlorotoluene	8.3	9.0	11.7	8.7	7.9	9.1	14.8	45.6
4-Chlorotoluene	5.1	5.4	5.5	4.8	4.5	5.0	7.9	25.2
1,3,5-Trimethylbenzene	31.3	27.5	33.0	31.1	33.6	31.3	6.8	157
sec-Butylbenzene	13.5	13.4	16.4	13.8	15.4	14.5	8.3	72.5
1,2,4-Trimethylbenzene	38.7	32.4	40.8	34.1	40.3	37.3	9.1	186
1,3-Dichlorobenzene	3.6	3.6	3.7	3.0	3.2	3.4	8.0	17.2
p-iso-Propyltoluene	14.7	14.1	16.1	13.9	15.1	14.8	5.2	73.8
1,4-Dichlorobenzene	3.0	3.5	3.3	2.6	2.8	3.0	10.2	15.0
1,2-Dichlorobenzene	3.6	4.3	4.0	3.5	3.6	3.8	8.3	19.0
n-Butylbenzene	17.4	13.8	14.0	18.9	24.0	17.6	21.2	88.0
1,2,4-Trichlorobenzene	2.8	2.9	3.3	2.6	3.2	3.0	8.5	15.0
Hexachlorobutadiene	4.8	4.0	6.1	5.6	6.0	5.3	15.1	26.4
Naphthalene	5.5	5.1	5.5	4.7	5.6	5.3	6.2	26.5
1,2,3-Trichlorobenzene	2.2	2.3	2.4	2.2	2.3	2.3	3.5	11.4

Data in Table 19 are from Reference 15.

TABLE 20

VOLATILE ORGANIC ANALYTE RECOVERY FROM SOIL USING VACUUM DISTILLATION (METHOD 5032)[a]

Compound	Soil/H_2O[b] Recovery Mean	RSD	Soil/Oil[c] Recovery Mean	RSD	Soil/Oil/H_2O Recovery Mean	RSD
Chloromethane	61	20	40	18	108	68
Bromomethane	58	20	47	13	74	13
Vinyl chloride	54	12	46	11	72	20
Chloroethane	46	10	41	8	52	14
Methylene chloride	60	2	65	8	76	11
Acetone	INT[e]	INT	44	8		
Carbon disulfide	47	13	53	10	47	4
1,1-Dichloroethene	48	9	47	5	58	3
1,1-Dichloroethane	61	6	58	9	61	6
trans-1,2-Trichloroethane	54	7	60	7	56	5
cis-1,2-Dichloroethene	60	4	72	6	63	8
Chloroform	104	11	93	6	114	15
1,2-Dichloroethane	177	50	117	8	151	22
2-Butanone	INT	36	38	INT		
1,1,1-Trichloroethane	124	13	72	16	134	26
Carbon tetrachloride	172	122	INT	INT		
Vinyl acetate	88	11	INT			
Bromodichloromethane	93	4	91	23	104	23
1,1,2,2-Tetrachloroethane	96	13	50	12	104	7
1,2-Dichloropropane	105	8	102	6	111	8
trans-1,3-Dichloropropene	134	10	84	16	107	8
Trichloroethene	98	9	99	10	100	5
Dibromochloromethane	119	8	125	31	142	16
1,1,2-Trichloroethane	126	10	72	16	97	4
Benzene	99	7	CONT[f]	CONT		
cis-1,3-Dichloropropene	123	12	94	13	112	9
Bromoform	131	13	58	18	102	9
2-Hexanone	155	18	164	19	173	29
4-Methyl-2-pentanone	152	20	185	20	169	18
Tetrachloroethene	90	9	123	14	128	7
Toluene	94	3	CONT	CONT		
Chlorobenzene	98	7	93	18	112	5
Ethylbenzene	114	13	CONT	CONT		
Styrene	106	8	93	18	112	5
p-Xylene	97	9	CONT	CONT		
o-Xylene	105	8	112	12	144	13

TABLE 20 (cont.)

Compound	Soil/H_2O[b] Recovery Mean	RSD	Soil/Oil[c] Recovery Mean	RSD	Soil/Oil/H_2O Recovery Mean	RSD
Surrogates						
1,2-Dichloroethane	177	50	117	8	151	22
Toluene-d_8	96	6	79	12	82	6
Bromofluorobenzene	139	13	37	13	62	5

[a] Results are for 10 min. distillations times, and condenser temperature held at -10°C. A 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness was used for chromatography. Standards and samples were replicated and precision value reflects the propagated errors. Each analyte was spiked at 50 ppb. Vacuum distillation efficiencies (Method 5032) are modified by internal standard corrections. Method 8260 internal standards may introduce bias for some analytes. See Method 5032 to identify alternate internal standards with similar efficiencies to minimize bias.

[b] Soil samples spiked with 0.2 mL water containing analytes and then 5 mL water added to make slurry.

[c] Soil sample + 1 g cod liver oil, spiked with 0.2 mL water containing analytes.

[d] Soil samples + 1 g cod liver oil, spiked as above with 5 mL of water added to make slurry.

[e] Interference by co-eluting compounds prevented accurate measurement of analyte.

[f] Contamination of sample matrix by analyte prevented assessment of efficiency.

TABLE 21

VACUUM DISTILLATION EFFICIENCIES FOR VOLATILE ORGANIC ANALYTES IN FISH TISSUE (METHOD 5032)[a]

Compound	Efficiency Mean (%)	RSD (%)
Chloromethane	N/A[b]	
Bromomethane	N/A[b]	
Vinyl chloride	N/A[b]	
Chloroethane	N/A[b]	
Methylene chloride	CONT[c]	
Acetone	CONT[c]	
Carbon disulfide	79	36
1,1-Dichloroethene	122	39
1,1-Dichloroethane	126	35
trans-1,2-Trichloroethene	109	46
cis-1,2-Dichloroethene	106	22
Chloroform	111	32
1,2-Dichloroethane	117	27
2-Butanone	INT[d]	
1,1,1-Trichloroethane	106	30
Carbon tetrachloride	83	34
Vinyl acetate	INT[d]	
Bromodichloromethane	97	22
1,1,2,2-Tetrachloroethane	67	20
1,2-Dichloropropane	117	23
trans-1,3-Dichloropropene	92	22
Trichloroethene	98	31
Dibromochloromethane	71	19
1,1,2-Trichloroethane	92	20
Benzene	129	35
cis-1,3-Dichloropropene	102	24
Bromoform	58	19
2-Hexanone	INT[d]	
4-Methyl-2-pentanone	113	37
Tetrachloroethene	66	20
Toluene	CONT[c]	
Chlorobenzene	65	19
Ethylbenzene	74	19
Styrene	57	14
p-Xylene	46	13
o-Xylene	83	20

TABLE 21 (cont.)

Compound	Efficiency Mean (%)	RSD (%)
Surrogates		
1,2-Dichloroethane	115	27
Toluene-d_8	88	24
Bromofluorobenzene	52	15

[a] Results are for 10 min. distillation times and condenser temperature held at -10°C. Five replicate 10-g aliquots of fish spiked at 25 ppb were analyzed using GC/MS external standard quantitation. A 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness was used for chromatography. Standards were replicated and results reflect 1 sigma propagated standard deviation.

[b] No analyses.

[c] Contamination of sample matrix by analyte prevented accurate assessment of analyte efficiency.

[d] Interfering by co-eluting compounds prevented accurate measurement of analyte.

TABLE 22

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES IN FISH TISSUE (METHOD 5032)[a]

Compound	Method Detection Limit (ppb) External Standard Method	Internal Standard Method
Chloromethane	7.8	7.3
Bromomethane	9.7	9.8
Vinyl chloride	9.5	9.4
Chloroethane	9.2	10.0
Methylene chloride	CONT[b]	CONT[b]
Acetone	CONT[b]	CONT[b]
Carbon disulfide	5.4	4.9
1,1-Dichloroethene	4.0	5.7
1,1-Dichloroethane	4.0	3.5
trans-1,2-Dichloroethene	4.4	4.0
cis-1,2-Dichloroethene	4.7	4.1
Chloroform	5.6	5.0
1,2-Dichloroethane	3.3	3.2
2-Butanone	INT[c]	INT[c]
1,1,1-Trichloroethane	1.1	4.2
Carbon tetrachloride	3.2	3.5
Vinyl acetate	INT[c]	INT[c]
Bromodichloromethane	3.2	2.8
1,1,2,2-Tetrachloroethane	4.4	3.8
1,2-Dichloropropane	3.8	3.7
trans-1,3-Dichloropropene	3.4	3.0
Trichloroethene	3.1	4.0
Dibromochloromethane	3.5	3.2
1,1,2-Trichloroethane	4.4	3.3
Benzene	3.6	3.2
cis-1,3-Dichloropropene	3.5	3.0
Bromoform	4.9	4.0
2-Hexanone	7.7	8.0
4-Methyl-2-pentanone	7.5	8.0
Tetrachloroethene	4.3	4.0
Toluene	3.0	2.5
Chlorobenzene	3.3	2.8
Ethylbenzene	3.6	3.5
Styrene	3.5	3.3
p-Xylene	3.7	3.5
o-Xylene	3.3	4.7

Footnotes are on the following page.

TABLE 22 (cont.)

[a] Values shown are the average MDLs for studies on three non-consecutive days, involving seven replicate analyses of 10 g of fish tissue spiked a 5 ppb. Daily MDLs were calculated as three times the standard deviation. Quantitation was performed by GC/MS Method 8260 and separation with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness.

[b] Contamination of sample by analyte prevented determination.

[c] Interference by co-eluting compounds prevented accurate quantitation.

TABLE 23

VOLATILE ORGANIC ANALYTES RECOVERY FOR WATER
USING VACUUM DISTILLATION (METHOD 5032)[a]

Compound	5 mL H_2O[b] Recovery Mean	RSD	20 mL H_2O[c] Recovery Mean	RSD	20 mL H_2O/Oil Recovery Mean	RSD
Chloromethane	114	27	116	29	176	67
Bromomethane	131	14	121	14	113	21
Vinyl chloride	131	13	120	16	116	23
Chloroethane	110	15	99	8	96	16
Methylene chloride	87	16	105	15	77	6
Acetone	83	22	65	34	119	68
Carbon disulfide	138	17	133	23	99	47
1,1-Dichloroethene	105	11	89	4	96	18
1,1-Dichloroethane	118	10	119	11	103	25
trans-1,2-Dichloroethene	105	11	107	14	96	18
cis-1,2-Dichloroethene	106	7	99	5	104	23
Chloroform	114	6	104	8	107	21
1,2-Dichloroethane	104	6	109	8	144	19
2-Butanone	83	50	106	31	INT[c]	
1,1,1-Trichloroethane	118	9	109	9	113	23
Carbon tetrachloride	102	6	108	12	109	27
Vinyl acetate	90	16	99	7	72	36
Bromodichloromethane	104	3	110	5	99	5
1,1,2,2-Tetrachloroethane	85	17	81	7	111	43
1,2-Dichloropropane	100	6	103	2	104	7
trans-1,3-Dichloropropene	105	8	105	4	92	4
Trichloroethene	98	4	99	2	95	5
Dibromochloroethane	99	8	99	6	90	25
1,1,2-Trichloroethane	98	7	100	4	76	12
Benzene	97	4	100	5	112	10
cis-1,3-Dichloropropene	106	5	105	4	98	3
Bromoform	93	16	94	8	57	21
2-Hexanone	60	17	63	16	78	23
4-Methyl-2-pentanone	79	24	63	14	68	15
Tetrachloroethene	101	3	97	7	77	14
Toluene	100	6	97	8	85	5
Chlorobenzene	98	6	98	4	88	16
Ethylbenzene	100	3	92	8	73	13
Styrene	98	4	97	9	88	16
p-Xylene	96	4	94	8	60	12
o-Xylene	96	7	95	6	72	14

TABLE 23 (cont.)

Compound	5 mL H_2O[b] Recovery Mean	RSD	20 mL H_2O[c] Recovery Mean	RSD	20 mL H_2O/Oil Recovery Mean	RSD
Surrogates						
1,2-Dichloroethane	104	6	109	6	144	19
Toluene-d_8	104	5	102	2	76	7
Bromofluorobenzene	106	6	106	9	40	8

[a] Results are for 10 min. distillation times, and condenser temperature held at -10°C. A 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness was used for chromatography. Standards and samples were replicated and precision values reflect the propagated errors. Concentrations of analytes were 50 ppb for 5-mL samples and 25 ppb for 20-mL samples. Recovery data generated with comparison to analyses of standards without the water matrix.

[b] Sample contained 1 gram cod liver oil and 20 mL water. An emulsion was created by adding 0.2 mL of water saturated with lecithin.

[c] Interference by co-eluting compounds prevented accurate assessment of recovery.

TABLE 24

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES USING VACUUM DISTILLATION (METHOD 5032) (INTERNAL STANDARD METHOD)[a]

Compound	Water[b] (µg/L)	Soil[c] (µg/kg)	Tissue[d] (µg/kg)	Oil[e] (mg/kg)
Chloromethane	3.2	8.0	7.3	N/A[f]
Bromomethane	2.8	4.9	9.8	N/A[f]
Vinyl chloride	3.5	6.0	9.4	N/A[f]
Chloroethane	5.9	6.0	10.0	N/A[f]
Methylene chloride	3.1	4.0	CONT[g]	0.05
Acetone	5.6	CONT[g]	CONT[g]	0.06
Carbon disulfide	2.5	2.0	4.9	0.18
1,1-Dichloroethene	2.9	3.2	5.7	0.18
1,1-Dichloroethane	2.2	2.0	3.5	0.14
trans-1,2-Dichloroethene	2.2	1.4	4.0	0.10
cis-1,2-Dichloroethene	2.0	2.3	4.1	0.07
Chloroform	2.4	1.8	5.0	0.07
1,2-Dichloroethane	1.7	1.5	3.2	0.06
2-Butanone	7.4	INT[h]	INT[h]	INT[h]
1,1,1-Trichloroethane	1.8	1.7	4.2	0.10
Carbon tetrachloride	1.4	1.5	3.5	0.13
Vinyl acetate	11.8	INT[h]	INT[h]	INT[h]
Bromodichloromethane	1.6	1.4	2.8	0.06
1,1,2,2-Tetrachloroethane	2.5	2.1	3.8	0.02
1,2-Dichloropropane	2.2	2.1	3.7	0.15
trans-1,3-Dichloropropene	1.5	1.7	3.0	0.05
Trichloroethene	1.6	1.7	4.0	0.04
Dibromochloromethane	1.7	1.5	3.2	0.07
1,1,2-Trichloroethane	2.1	1.7	3.3	0.05
Benzene	0.5	1.5	3.2	0.05
cis-1,3-Dichloropropene	1.4	1.7	3.0	0.04
Bromoform	1.8	1.5	4.0	0.05
2-Hexanone	4.6	3.6	8.0	INT[h]
4-Methyl-2-pentanone	3.5	4.6	8.0	INT[h]
Tetrachloroethene	1.4	1.6	4.0	0.10
Toluene	1.0	3.3	2.5	0.05
Chlorobenzene	1.4	1.4	2.8	0.06
Ethylbenzene	1.5	2.8	3.5	0.04
Styrene	1.4	1.4	3.3	0.18
p-Xylene	1.5	2.9	3.5	0.20
o-Xylene	1.7	3.4	4.7	0.07

Footnotes are found on the following page.

[a] Quantitation was performed using GC/MS Method 8260 and chromatographic separation with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness. Method detection limits are the average MDLs for studies on three non-consecutive days.

[b] Method detection limits are the average MDLs for studies of three non-consecutive days. Daily studies were seven replicated analyses of 5 mL aliquots of 4 ppb soil. Daily MDLs were three times the standard deviation.

[c] Daily studies were seven replicated analyses of 10 g fish tissue spiked at 5 ppb. Daily MDLs were three times the standard deviation. Quantitation was performed using GC/MS Method 8260 and chromatographic separation with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness.

[d] Method detection limits are estimated analyzing 1 g of cod liver oil samples spiked at 250 ppm. Five replicates were analyzed using Method 8260.

[e] No analyses.

[f] Contamination of sample by analyte prevented determination.

[g] Interference by co-eluting compounds prevented accurate quantitation.

TABLE 25

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES
(METHOD 5032) (EXTERNAL STANDARD METHOD)[a]

Compound	Water[b] (µg/L)	Soil[c] (µg/kg)	Tissue[d] (µg/kg)	Oil[e] (mg/kg)
Chloromethane	3.1	8.6[f]	7.8	N/A[g]
Bromomethane	2.5	4.9[f]	9.7	N/A[g]
Vinyl chloride	4.0	7.1[f]	9.5	N/A[g]
Chloroethane	6.1	7.5[f]	9.2	N/A[g]
Methylene chloride	3.1	3.3	CONT[h]	0.08
Acetone	33.0[f]	CONT[h]	CONT[h]	0.12
Carbon disulfide	2.5	3.2	5.4	0.19
1,1-Dichloroethene	3.4	3.8	4.0	0.19
1,1-Dichloroethane	2.3	1.7	4.0	0.13
trans-1,2-Dichloroethene	3.0	3.2	4.4	0.09
cis-1,2-Dichloroethene	2.4	2.7	4.7	0.08
Chloroform	2.7	2.6	5.6	0.06
1,2-Dichloroethane	1.6	1.7	3.3	0.06
2-Butanone	57.0[f]	INT[i]	INT[i]	INT[i]
1,1,1-Trichloroethane	1.6	2.4	1.1	0.08
Carbon tetrachloride	1.5	1.7	3.2	0.15
Vinyl acetate	23.0[f]	INT[i]	INT[i]	INT[i]
Bromodichloromethane	2.0	2.3	3.2	0.05
1,1,2,2-Tetrachloroethane	3.6	3.2	4.4	0.09
1,2-Dichloropropane	2.9	3.7	3.8	0.12
trans-1,3-Dichloropropene	2.3	2.4	3.8	0.08
Trichloroethene	2.5	3.0	3.1	0.06
Dibromochloromethane	2.1	2.9	3.5	0.04
1,1,2-Trichloroethane	2.7	2.8	4.4	0.07
Benzene	1.7	2.9	3.6	0.03
cis-1,3-Dichloropropene	2.1	2.5	3.5	0.06
Bromoform	2.3	2.5	4.9	0.10
2-Hexanone	4.6	4.6	7.7	INT[i]
4-Methyl-2-pentanone	3.8	3.9	7.5	INT[i]
Tetrachloroethene	1.8	2.6	4.3	0.12
Toluene	1.8	4.4	3.0	0.09
Chlorobenzene	2.4	2.6	3.3	0.07
Ethylbenzene	2.4	4.1	3.6	0.09
Styrene	2.0	2.5	3.5	0.16
p-Xylene	2.3	3.9	3.7	0.18
o-Xylene	2.4	4.1	3.3	0.08

[a] Method detection limits are the average MDLs for studies on three non-consecutive days. Daily studies were seven replicate analyses of 5-mL aliquots of water spiked at 4 ppb. Daily MDLs were three times the standard deviation.

[b] Daily studies were seven replicate analyses of 5-mL aliquots of water spiked at 4 ppb.

[c] These studies were seven replicate analyses of 5-g aliquots of soil spiked at 4 ppb.

[d] These studies were seven replicate analyses of 10-g aliquots of fish tissue spiked at 5 ppb.

[e] Method detection limits were estimated by analyzing cod liver oil samples spiked at 250 ppb. Five replicates were analyzed using Method 8260.

[f] Method detection limits were estimated by analyzing replicate 50 ppb standards five times over a single day.

[g] No analyses.

[h] Contamination of sample by analyte prevented determination.

[i] Interference by co-eluting compound prevented accurate quantitation.

TABLE 26

VOLATILE ORGANIC ANALYTE RECOVERY FROM OIL
USING VACUUM DISTILLATION (METHOD 5032)[a]

Compound	Recovery Mean (%)	RSD (%)
Chloromethane	N/A[b]	
Bromomethane	N/A[b]	
Vinyl chloride	N/A[b]	
Chloroethane	N/A[b]	
Methylene chloride	62	32
Acetone	108	55
Carbon disulfide	98	46
1,1-Dichloroethene	97	24
1,1-Dichloroethane	96	22
trans-1,2-Trichloroethene	86	23
cis-1,2-Dichloroethene	99	11
Chloroform	93	14
1,2-Dichloroethane	138	31
2-Butanone	INT[c]	
1,1,1-Trichloroethane	89	14
Carbon tetrachloride	129	23
Vinyl acetate	INT[c]	
Bromodichloromethane	106	14
1,1,2,2-Tetrachloroethane	205	46
1,2-Dichloropropane	107	24
trans-1,3-Dichloropropene	98	13
Trichloroethene	102	8
Dibromochloromethane	168	21
1,1,2-Trichloroethane	95	7
Benzene	146	10
cis-1,3-Dichloropropene	98	11
Bromoform	94	18
2-Hexanone	INT[c]	
4-Methyl-2-pentanone	INT[c]	
Tetrachloroethene	117	22
Toluene	108	8
Chlorobenzene	101	12
Ethylbenzene	98	10
Styrene	120	46
p-Xylene	87	23
o-Xylene	90	10

TABLE 26 (cont.)

Compound	Recovery Mean (%)	RSD (%)
Surrogates		
1,2-Dichloroethane	137	30
Toluene-d_8	84	6
Bromofluorobenzene	48	2

[a] Results are for 10 min. distillation times and condenser temperature held at -10°C. Five replicates of 10-g fish aliquots spiked at 25 ppb were analyzed. Quantitation was performed with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness. Standards and samples were replicated and precision value reflects the propagated errors. Vacuum distillation efficiencies (Method 5032) are modified by internal standard corrections. Method 8260 internal standards may bias for some analytes. See Method 5032 to identify alternate internal standards with similar efficiencies to minimize bias.

[b] Not analyzed.

[c] Interference by co-evaluating compounds prevented accurate measurement of analyte.

TABLE 27

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES IN OIL (METHOD 5032)[a]

Compound	Method Detection Limit (ppb) External Standard Method	Internal Standard Method
Chloromethane	N/A[b]	N/A[b]
Bromomethane	N/A[b]	N/A[b]
Vinyl chloride	N/A[b]	N/A[b]
Chloroethane	N/A[b]	N/A[b]
Methylene chloride	80	50
Acetone	120	60
Carbon disulfide	190	180
1,1-Dichloroethene	190	180
1,1-Dichloroethane	130	140
trans-1,2-Dichloroethene	90	100
cis-1,2-Dichloroethene	80	70
Chloroform	60	70
1,2-Dichloroethane	60	60
2-Butanone	INT[c]	INT[c]
1,1,1-Trichloroethane	80	100
Carbon tetrachloride	150	130
Vinyl acetate	INT[c]	INT[c]
Bromodichloromethane	50	60
1,1,2,2-Tetrachloroethane	90	20
1,2-Dichloropropane	120	150
trans-1,3-Dichloropropene	80	50
Trichloroethene	60	40
Dibromochloromethane	40	70
1,1,2-Trichloroethane	70	50
Benzene	30	50
cis-1,3-Dichloropropene	60	40
Bromoform	100	50
2-Hexanone	INT[c]	INT[c]
4-Methyl-2-pentanone	INT[c]	INT[c]
Tetrachloroethene	120	100
Toluene	90	50
Chlorobenzene	70	60
Ethylbenzene	90	40
Styrene	160	180
p-Xylene	180	200
o-Xylene	80	70

TABLE 27 (cont.)

[c] Method detection limits are estimated as the result of five replicated analyses of 1 g cod liver oil spiked at 25 ppb. MDLs were calculated as three times the standard deviation. Quantitation was performed using a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness.

[d] No analyses.

[e] Interference by co-eluting compounds prevented accurate quantitation.

TABLE 28

INTERNAL STANDARDS FOR ANALYTES AND SURROGATES PREPARED USING EQUILIBRIUM HEADSPACE ANALYSIS (METHOD 5021)

Chloroform-d_1	1,1,2-TCA-d_3	Bromobenzene-d_5
Dichlorodifluoromethane	1,1,1-Trichloroethane	Chlorobenzene
Chloromethane	1,1-Dichloropropene	Bromoform
Vinyl chloride	Carbon tetrachloride	Styrene
Bromomethane	Benzene	iso-Propylbenzene
Chloroethane	Dibromomethane	Bromobenzene
Trichlorofluoromethane	1,2-Dichloropropane	n-Propylbenzene
1,1-Dichloroethene	Trichloroethene	2-Chlorotoluene
Methylene chloride	Bromodichloromethane	4-Chlorotoluene
trans-1,2-Dichloroethene	cis-1,3-Dichloropropene	1,3,5-Trimethylbenzene
1,1-Dichloroethane	trans-1,3-Dichloropropene	tert-Butylbenzene
cis-1,2-Dichloroethene	1,1,2-Trichloroethane	1,2,4-Trimethylbenzene
Bromochloromethane	Toluene	sec-Butylbenzene
Chloroform	1,3-Dichloropropane	1,3-Dichlorobenzene
2,2-Dichloropropane	Dibromochloromethane	1,4-Dichlorobenzene
1,2-Dichloroethane	1,2-Dibromoethane	p-iso-Propyltoluene
	Tetrachloroethene	1,2-Dichlorobenzene
	1,1,2-Trichloroethane	n-Butylbenzene
	Ethylbenzene	1,2-Dibromo-3-chloropropane
	m-Xylene	1,2,4-Trichlorobenzene
	p-Xylene	Naphthalene
	o-Xylene	Hexachlorobutadiene
	1,1,2,2-Tetrachloroethane	1,2,3-Trichlorobenzene
	1,2,3-Trichloropropane	

TABLE 29

PRECISION AND MDL DETERMINED FOR ANALYSIS OF FORTIFIED SAND[a] (METHOD 5021)

Compound	% RSD	MDL (µg/kg)
Benzene	3.0	0.34
Bromochloromethane	3.4	0.27
Bromodichloromethane	2.4	0.21
Bromoform	3.9	0.30
Bromomethane	11.6	1.3
Carbon tetrachloride	3.6	0.32
Chlorobenzene	3.2	0.24
Chloroethane	5.6	0.51
Chloroform	3.1	0.30
Chloromethane	4.1	3.5[b]
1,2-Dibromo-3-chloropropane	5.7	0.40
1,2-Dibromoethane	3.2	0.29
Dibromomethane	2.8	0.20
1,2-Dichlorobenzene	3.3	0.27
1,3-Dichlorobenzene	3.4	0.24
1,4-Dichlorobenzene	3.7	0.30
Dichlorodifluoromethane	3.0	0.28
1,1-Dichloroethane	4.5	0.41
1,2-Dichloroethane	3.0	0.24
1,1-Dichloroethene	3.3	0.28
cis-1,2-Dichloroethene	3.2	0.27
trans-1,2-Dichloroethene	2.6	0.22
1,2-Dichloropropane	2.6	0.21
1,1-Dichloropropene	3.2	0.30
cis-1,3-Dichloropropene	3.4	0.27
Ethylbenzene	4.8	0.47
Hexachlorobutadiene	4.1	0.38
Methylene chloride	8.2	0.62[c]
Naphthalene	16.8	3.4[c]
Styrene	7.9	0.62
1,1,1,2-Tetrachloroethane	3.6	0.27
1,1,2,2-Tetrachloroethane	2.6	0.20
Tetrachloroethene	9.8	1.2[c]
Toluene	3.5	0.38
1,2,4-Trichlorobenzene	4.2	0.44
1,1,1-Trichloroethane	2.7	0.27
1,1,2-Trichloroethane	2.6	0.20
Trichloroethene	2.3	0.19

TABLE 29 (cont.)

Compound	% RSD	MDL (µg/kg)
Trichlorofluoromethane	2.7	0.31
1,2,3-Trichloropropane	1.5	0.11
Vinyl chloride	4.8	0.45
m-Xylene/p-Xylene	3.6	0.37
o-Xylene	3.6	0.33

[a] Most compounds spiked at 2 ng/g (2 µg/kg)
[b] Incorrect ionization due to methanol
[c] Compound detected in unfortified sand at >1 ng

TABLE 30

RECOVERIES IN GARDEN SOIL FORTIFIED AT 20 µg/kg (ANALYSIS BY METHOD 5021)

Compound	Recovery per Replicate (ng) Sample 1	Sample 2	Sample 3	Mean (ng)	RSD	Recovery (%)
Benzene	37.6	35.2	38.4	37.1	3.7	185[a]
Bromochloromethane	20.5	19.4	20.0	20.0	2.3	100
Bromodichloromethane	21.1	20.3	22.8	21.4	4.9	107
Bromoform	23.8	23.9	25.1	24.3	2.4	121
Bromomethane	21.4	19.5	19.7	20.2	4.2	101
Carbon tetrachloride	27.5	26.6	28.6	27.6	3.0	138
Chlorobenzene	25.6	25.4	26.4	25.8	1.7	129
Chloroethane	25.0	24.4	25.3	24.9	1.5	125
Chloroform	21.9	20.9	21.7	21.5	2.0	108
Chloromethane	21.0	19.9	21.3	20.7	2.9	104[a]
1,2-Dibromo-3-chloro-propane	20.8	20.8	21.0	20.9	0.5	104
1,2-Dibromoethane	20.1	19.5	20.6	20.1	2.2	100
Dibromomethane	22.2	21.0	22.8	22.0	3.4	110
1,2-Dichlorobenzene	18.0	17.7	17.1	17.6	2.1	88.0
1,3-Dichlorobenzene	21.2	21.0	20.1	20.8	2.3	104
1,4-Dichlorobenzene	20.1	20.9	19.9	20.3	2.1	102
Dichlorodifluoromethane	25.3	24.1	25.4	24.9	2.4	125
1,1-Dichloroethane	23.0	22.0	22.7	22.6	1.9	113
1,2-Dichloroethane	20.6	19.5	19.8	20.0	2.3	100
1,1-Dichloroethene	24.8	23.8	24.4	24.3	1.7	122
cis-1,2-Dichloroethene	21.6	20.0	21.6	21.1	3.6	105
trans-1,2-Dichloroethene	22.4	21.4	22.2	22.0	2.0	110
1,2-Dichloropropane	22.8	22.2	23.4	22.8	2.1	114
1,1-Dichloropropene	26.3	25.7	28.0	26.7	3.7	133
cis-1,3-Dichloropropene	20.3	19.5	21.1	20.3	3.2	102
Ethylbenzene	24.7	24.5	25.5	24.9	1.7	125
Hexachlorobutadiene	23.0	25.3	25.2	24.5	4.3	123
Methylene chloride	26.0	25.7	26.1	25.9	0.7	130[a]
Naphthalene	13.8	12.7	11.8	12.8	6.4	63.8[a]
Styrene	24.2	23.3	23.3	23.6	1.8	118
1,1,1,2-Tetrachloroethane	21.4	20.2	21.3	21.0	2.6	105
1,1,2,2-Tetrachloroethane	18.6	17.8	19.0	18.5	2.7	92.3
Tetrachloroethene	25.2	24.8	26.4	25.5	2.7	127
Toluene	28.6	27.9	30.9	29.1	4.4	146[a]
1,2,4-Trichlorobenzene	15.0	14.4	12.9	14.1	6.3	70.5
1,1,1-Trichloroethane	28.1	27.2	29.9	28.4	4.0	142
1,1,2-Trichloroethane	20.8	19.6	21.7	20.7	4.2	104

TABLE 30 (cont.)

Compound	Recovery per Replicate (ng) Sample 1	Sample 2	Sample 3	Mean (ng)	RSD	Recovery (%)
Trichloroethene	26.3	24.9	26.8	26.0	3.1	130
Trichlorofluoromethane	25.9	24.8	26.5	25.7	2.7	129
1,2,3-Trichloropropane	18.8	18.3	19.3	18.8	2.2	94.0
Vinyl chloride	24.8	23.2	23.9	24.0	2.7	120
m-Xylene/p-Xylene	24.3	23.9	25.3	24.5	2.4	123
o-Xylene	23.1	22.3	23.4	22.9	2.0	115

* Compound found in unfortified garden soil matrix at >5 ng.

TABLE 31

METHOD DETECTION LIMITS AND BOILING POINTS
FOR VOLATILE ORGANICS (ANALYSIS BY METHOD 5041)[a]

Compound	Detection Limit (ng)	Boiling Point (°C)
Chloromethane	58	-24
Bromomethane	26	4
Vinyl chloride	14	-13
Chloroethane	21	13
Methylene chloride	9	40
Acetone	35	56
Carbon disulfide	11	46
1,1-Dichloroethene	14	32
1,1-Dichloroethane	12	57
trans-1,2-Dichloroethene	11	48
Chloroform	11	62
1,2-Dichloroethane	13	83
1,1,1-Trichloroethane	8	74
Carbon tetrachloride	8	77
Bromodichloromethane	11	88
1,1,2,2-Tetrachloroethane[b]	23	146
1,2-Dichloropropane	12	95
trans-1,3-Dichloropropene	17	112
Trichloroethene	11	87
Dibromochloromethane	21	122
1,1,2-Trichloroethane	26	114
Benzene	26	80
cis-1,3-Dichloropropene	27	112
Bromoform[b]	26	150
Tetrachloroethene	11	121
Toluene	15	111
Chlorobenzene	15	132
Ethylbenzene[b]	21	136
Styrene[b]	46	145
Trichlorofluoromethane	17	24
Iodomethane	9	43
Acrylonitrile	13	78
Dibromomethane	14	97
1,2,3-Trichloropropane[b]	37	157
total Xylenes[b]	22	138-144

Footnotes are found on the following page.

TABLE 31 (cont.)

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* The method detection limit (MDL) is defined in Chapter One. The detection limits cited above were determined according to 40 CFR, Part 136, Appendix B, using standards spiked onto clean VOST tubes. Since clean VOST tubes were used, the values cited above represent the best that the methodology can achieve. The presence of an emissions matrix will affect the ability of the methodology to perform at its optimum level.

** Boiling Point greater than 130 °C. Not appropriate for quantitative sampling by Method 0030.

TABLE 32

VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION (METHOD 5041)

Bromochloromethane	1,4-Difluorobenzene
Acetone	Benzene
Acrylonitrile	Bromodichloromethane
Bromomethane	Bromoform
Carbon disulfide	Carbon tetrachloride
Chloroethane	Chlorodibromomethane
Chloroform	Dibromomethane
Chloromethane	1,2-Dichloropropane
1,1-Dichloroethane	cis-1,3-Dichloropropene
1,2-Dichloroethane	trans-1,3-Dichloropropene
1,2-Dichloroethane-d_4 (surrogate)	1,1,1-Trichloroethane
1,1-Dichloroethene	1,1,2-Trichloroethane
Trichloroethene	
trans-1,2-Dichloroethene	
Iodomethane	
Methylene chloride	
Trichlorofluoromethane	
Vinyl chloride	

Chlorobenzene-d_5
4-Bromofluorobenzene (surrogate)
Chlorobenzene
Ethylbenzene
Styrene
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
Toluene-d_8 (surrogate)
1,2,3-Trichloropropane
Xylenes

TABLE 33

METHOD 0040 - COMPOUNDS DEMONSTRATED TO BE APPLICABLE TO THE METHOD

Compound	Boiling Point (°C)	Condensation Point at 20°C (%)	Estimated Detection Limit* (ppm)
Dichlorodifluoromethane	-30	Gas	0.20
Vinyl chloride	-19	Gas	0.11
1,3-Butadiene	-4	Gas	0.90
1,2-Dichloro-1,1,2,2-tetrafluoroethane	4	Gas	0.14
Methyl bromide	4	Gas	0.14
Trichlorofluoromethane	24	88	0.18
1,1-Dichloroethene	31	22	0.07
Methylene chloride	40	44	0.05
1,1,2-Trichloro-trifluoroethane	48	37	0.13
Chloroform	61	21	0.04
1,1,1-Trichloroethane	75	13	0.03
Carbon tetrachloride	77	11	0.03
Benzene	80	10	0.16
Trichloroethene	87	8	0.04
1,2-Dichloropropane	96	5	0.05
Toluene	111	3	0.08
Tetrachloroethene	121	2	0.03

* Since this value represents a direct injection (no concentration) from the Tedlar® bag, these values are directly applicable as stack detection limits.

FIGURE 1
GAS CHROMATOGRAM OF VOLATILE ORGANICS

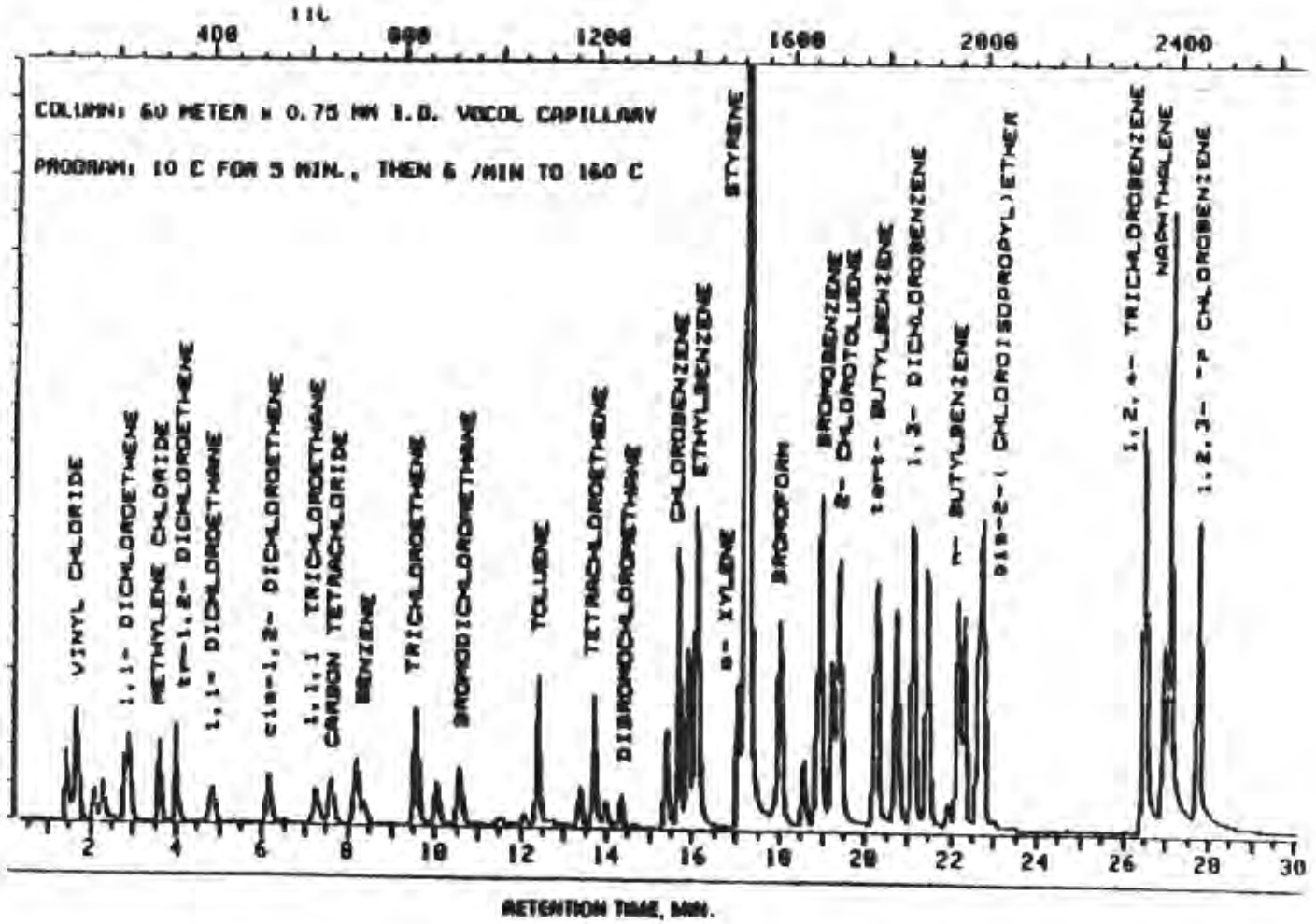


FIGURE 2
GAS CHROMATOGRAM OF VOLATILE ORGANICS

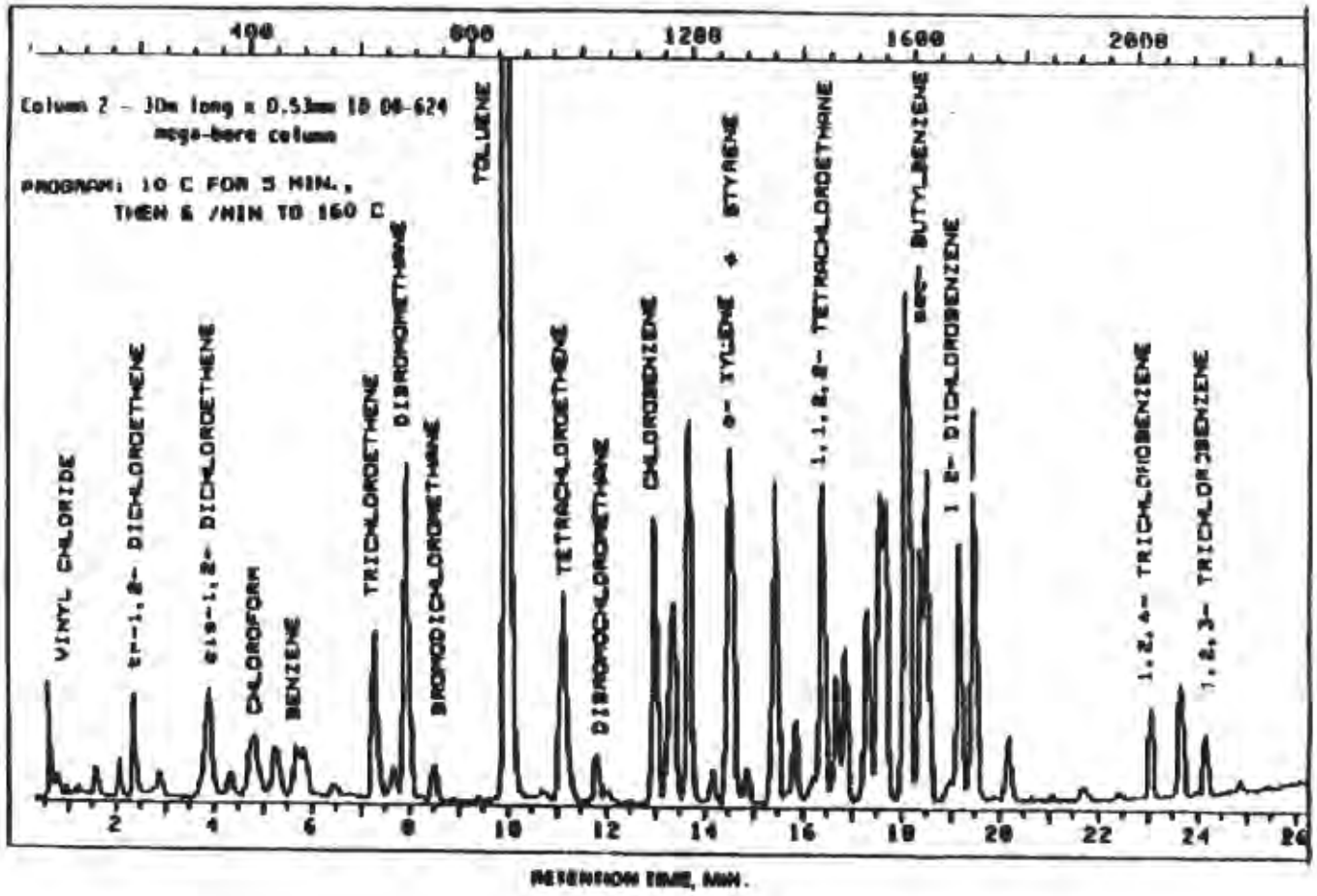


FIGURE 3
GAS CHROMATOGRAM OF VOLATILE ORGANICS

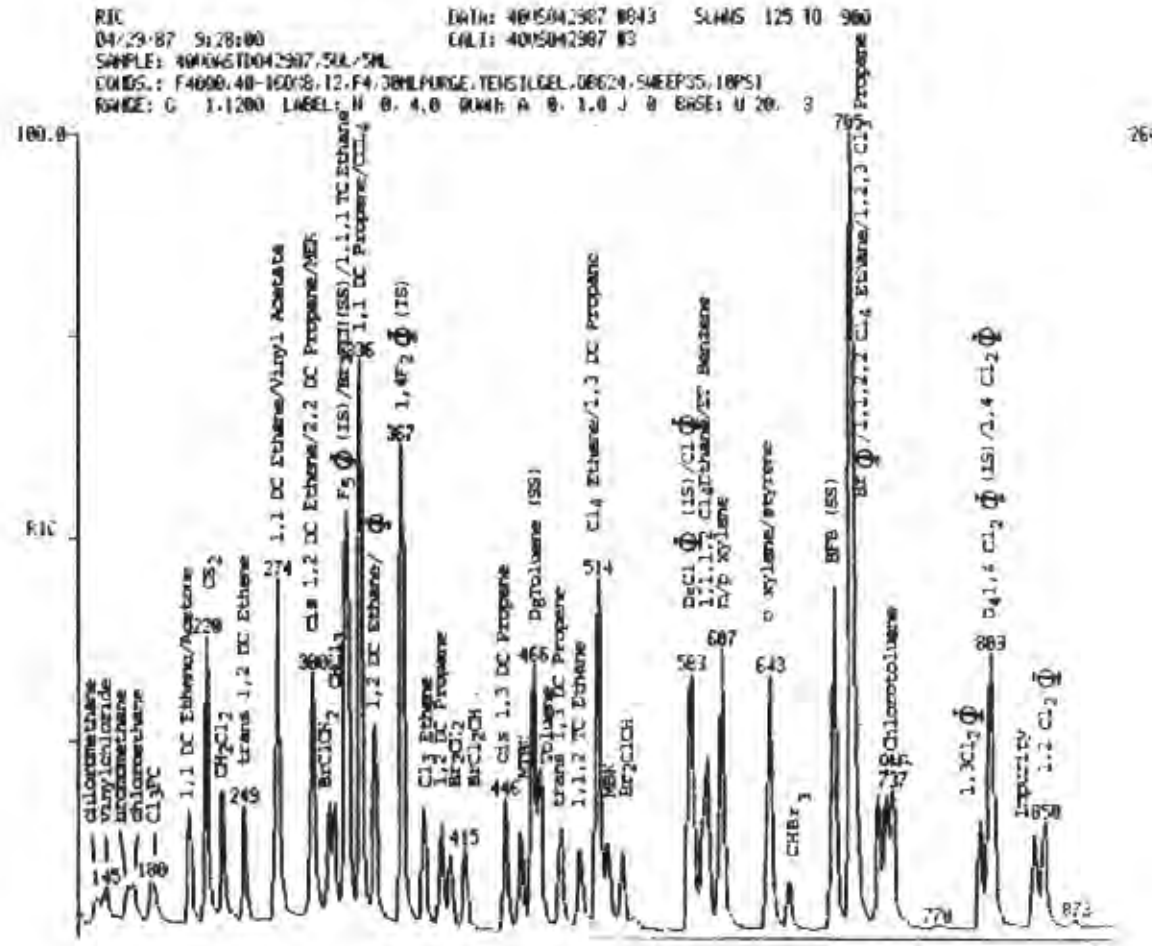
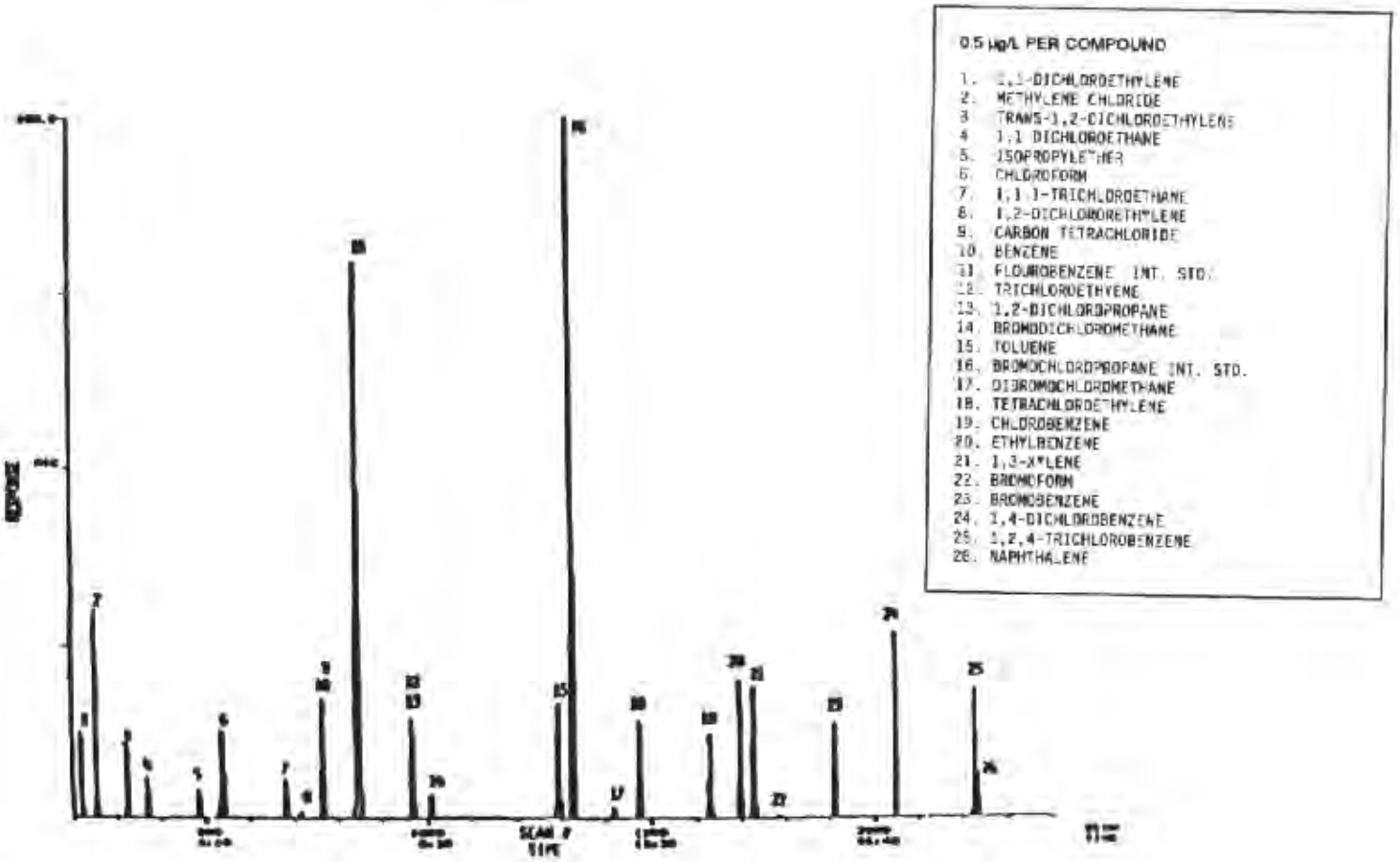
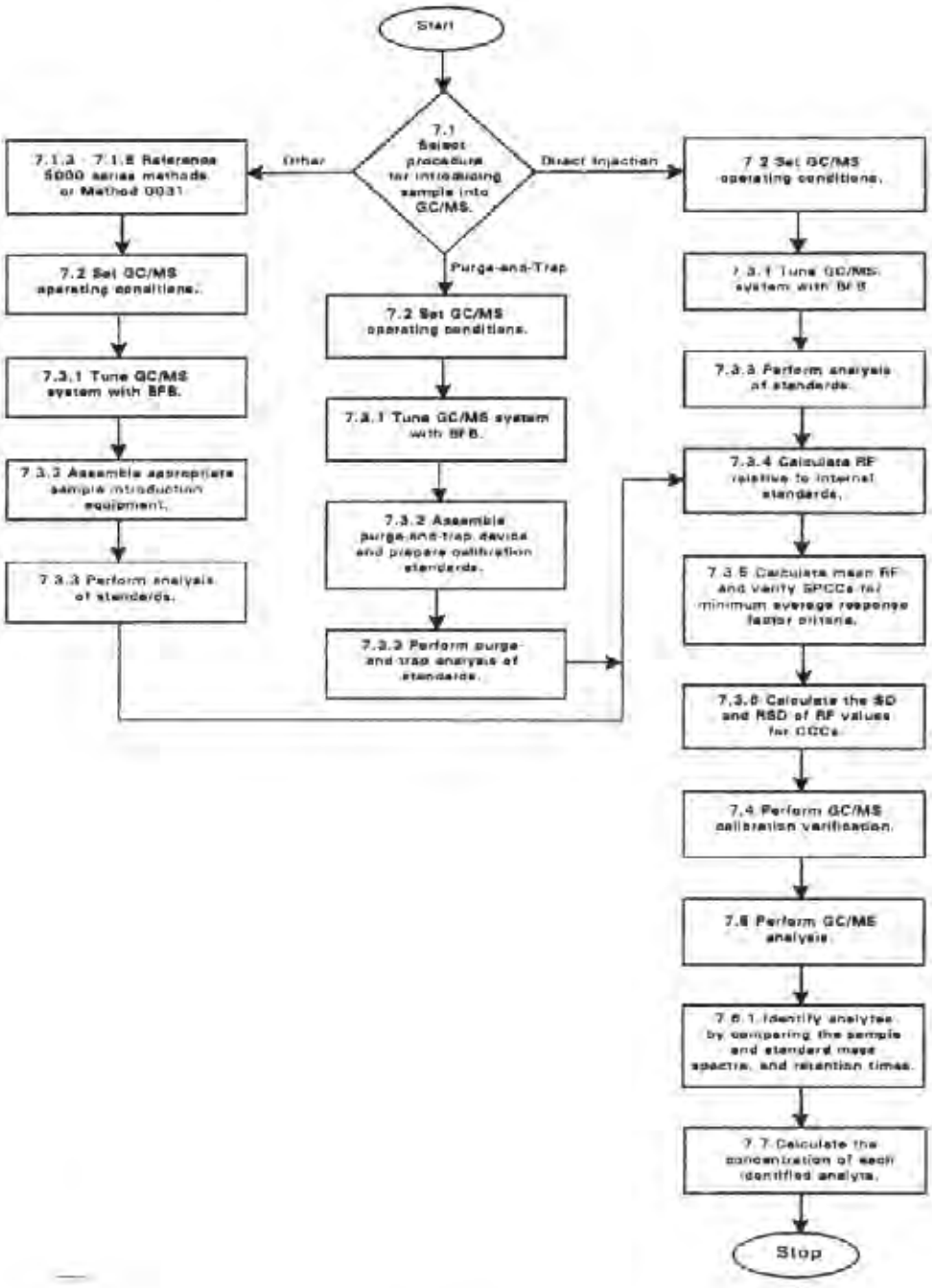


FIGURE 4
GAS CHROMATOGRAM OF TEST MIXTURE




Start
7.1 Select procedure for introducing sample into GC/MS.
Other
Purge-and-Trap
Direct Injection
7.1.2 - 7.1.5 Reference 5000 series methods or Method 0031
7.2 Set GC/MS operating conditions.
7.3.1 Tune GC/MS system with BFB.
7.3.3 Assemble appropriate sample introduction equipment.
7.3.3 Perform analysis of standards.
7.2 Set GC/MS operating conditions.
7.3.1 Tune GC/MS system with BFB.
7.3.2 Assemble purge-and-trap device and prepare calibration standards.
7.3.3 Perform purge-and-trap analysis of standards.
7.2 Set GC/MS operating conditions.
7.3.1 Tune GC/MS system with BFB
7.3.3 Perform analysis of standards.
7.3.4 Calculate RF relative to internal standards.
7.3.5 Calculate mean RF and verify SPCCs for minimum average response factor criteria.
7.3.6 Calculate the SD and RSD of RF values for CCCs.
7.4 Perform GC/MS calibration verification.
7.6 Perform GC/MS analysis.
7.6.1 Identify analytes by comparing the sample and standard mass spectra, and retention times.
7.7 Calculate the concentration of each identified analyte.
Stop