STANDARD OPERATING PROCEDURE

**BUTYLTINS**
SOC-BUTYL
Revision 10

Effective date: January 20, 2012

| | | |
|---|---|---|
| Approved By: | Supervisor | 12/22/11 Date |
| | QA Manager | 12/22/11 Date |
| | Laboratory Director | 12/22/11 Date |

**COLUMBIA ANALYTICAL SERVICES, INC.**
1317 South 13th Avenue
Kelso, Washington 98626

© Columbia Analytical Services, Inc. 2011

| DOCUMENT CONTROL | |
|---|---|
| NUMBER: | |
| Initials: | Date: |

If this SOP is accessed electronically, it is an uncontrolled copy and will not be updated.



# BUTYLTINS

## 1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) describes the procedure used for the analysis of butyltins by GC-FPD. Concentrations of Tributyltin chloride ($Bu_3SnCl$) as well as butyltin trichloride ($BuSnCl_3$), dibutyltin dichloride ($Bu_2SnCl_2$), and tetrabutyltin ($Bu_4Sn$) in water, sediment and tissue can be determined by this method. The butyltin chloride salts of tributyltin, dibutyltin and monobutyltin are reported as butyltin cations. The current Method Reporting Limit (MRL) for each of these analytes is listed in Table 3. The Method Detection Limit (MDL) that has been obtained is also listed, and is subject to change as studies are repeated.

## 2. METHOD SUMMARY

This procedure is based on techniques described in various papers (Unger, et. al; Krone, et.al.) for performing the extraction, derivitization, and analysis of mono-, di-, tri-, and tetrabutyltin chloride, with use of certain modifications. This procedure involves a 0.1% tropolone in methylene chloride extraction of the analytes of interest from an acidified sample, followed by a Grignard reaction of the hexane extract with Hexylmagnesium bromide (HxMgBr). The extract is then eluted through silica and alumina cartridge columns for cleanup of soil extracts, or Florisil columns for cleanup of tissue and water extracts. Extracts are then analyzed by GC/FPD with a 610nm bandwidth filter. The extraction procedure used is outlined in the CAS SOP *SOC-OSWT*.

## 3. DEFINITIONS

**Analysis Sequence** - Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration followed by sample extracts interspersed with calibration standards. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

**Independent Calibration Verification (ICV)** - Verification of the ratio of instrument response to analyte amount as established during initial calibration. The verification is done by analyzing for target analytes in standards in an appropriate solvent. ICV solutions are made from neat standards whose source is different from that used to prepare calibration standards.

**Matrix Spike/Duplicate Matrix Spike Analysis** - In the matrix spike analysis, predetermined quantities of stock solutions of certain analytes are added to a sample matrix prior to sample extraction and analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the methods used for the analyses. Samples are split into duplicates, spiked, and analyzed. Percent recoveries are calculated for each of the analytes detected. The relative percent difference between the samples is calculated and used to assess analytical precision. The concentration of the spike should be at 5 to 10 times the MRL or at levels specified by a project analysis plan.

If this SOP is accessed electronically, it is an uncontrolled copy and will not be updated.



**Standard (Calibration) Curve** - A standard curve is a curve which plots concentrations of a known analyte standard versus the instrument response to the analyte.

**Surrogate** - Surrogates are organic compounds which are similar to analytes of interest in chemical composition, extraction, and chromatography, but which are not normally found in environmental samples. The purpose of the surrogates is to evaluate the preparation and analysis of samples. These compounds are spiked into all blanks, standards, samples, and spiked samples prior to analysis. Percent recoveries are calculated for each surrogate.

**Method Blank** - The method blank is an artificial sample designed to monitor introduction of artifacts into the process. The method blank is carried through the entire analytical procedure.

**Continuing Calibration Verification Standard (CCV)** - A mid-level standard injected into the instrument at specified intervals and is used to verify the ongoing accuracy of the initial calibration.

**Instrument Blank (CCB)** - The instrument blank (also called continuing calibration blank) is a volume of clean solvent analyzed on each GC column and instrument used for sample analysis. The purpose of the instrument blank is to determine the levels of contamination associated with the instrumental analysis itself, particularly with regard to the carry-over of analytes from standards or highly contaminated samples into other analyses.

**Laboratory Control Samples (LCS) –** The LCS is an aliquot of analyte free water or analyte free solid to which known amounts target analytes are added. The LCS is prepared and analyzed in exactly the same manner as the samples. The percent recovery is compared to established limits and assists in determining whether the batch is in control.

## 4. INTERFERENCES

4.1. Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines, causing misinterpretation of the chromatograms. All of these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by running method blanks.

4.2. Since this procedure is often applied to “trace level” analyses, particular attention should be paid to ensuring that standards are of acceptable quality and purity.

## 5. SAFETY

5.1. All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure. This includes the use of personnel protective equipment, such as, safety glasses, lab coat and the correct gloves.

If this SOP is accessed electronically, it is an uncontrolled copy and will not be updated.



5.2. Chemicals, reagents and standards must be handled as described in the CAS safety policies, approved methods and in MSDSs where available. Refer to the CAS Environmental, Health and Safety Manual and the appropriate MSDS prior to beginning this method.

## 6. SAMPLE COLLECTION, CONTAINERS, PRESERVATION, AND STORAGE

6.1. Containers used to collect samples for the determination of semivolatile organic compounds should be soap and water washed followed by methanol (or isopropanol) rinsing. The sample containers should be of glass or polycarbonate and have screw-top covers with teflon liners. Where teflon is not available, solvent-rinsed aluminum foil may be used as a liner. Highly acidic or basic samples may react with the aluminum foil, causing eventual contamination of the sample. Plastic containers or lids may <u>not</u> be used for the storage of samples due to the possibility of sample contamination from the phthalate esters and other hydrocarbons within the plastic.

6.2. Sample containers should be filled with care so as to prevent any portion of the collected sample coming in contact with the sampler's gloves, thus causing contamination. Samples should not be collected or stored in the presence of exhaust fumes. If the sample comes in contact with the sampler (e.g., if an automatic sampler is used), run reagent water through the sampler and use the rinsate as a field blank.

6.3. Water and soil samples must be iced or refrigerated at 4 ± 2□C from time of collection until extraction. Water samples should be extracted within 7 days and soil/sediment samples should be extracted within 14 days of collection. Tissue samples should be extracted within 1 year when stored frozen (< -10$^{o}$C) until extraction. Studies have not been done to determine sample or extract stability, however extracts should be analyzed within 40 days after extraction.

## 7. STANDARDS AND REAGENTS

7.1. Stock standard solutions may be purchased from a number of vendors. All reference standards, where possible, must be traceable to SI units or NIST certified reference materials. The preparation for all laboratory prepared reagents and solutions must be documented in a laboratory logbook. Refer to the SOP *Reagent/Standards Login and Tracking (ADM-RTL)* for the complete procedure and documentation requirements.

7.2. Stock Solutions - 2000 µg/mL

7.2.1. A certified butyltins stock solution containing Tetrabutyltin, Tributyltin, Dibutyltin, and Monobutyltin cations is purchased from Restek or equivalent at 2000ppm in methylene chloride.

7.2.2. Alternatively, a stock solution may be prepared from neat materials. Neat standards may be purchased from an approved vendor such as Aldrich, Alfa, or Acros. Prepare

If this SOP is accessed electronically, it is an uncontrolled copy and will not be updated.



by weighing out the following amounts of the neat standards and diluting to 10 mL in DCM. Replace stock solutions yearly, or sooner if there are signs of degradation.

| | |
|---|---|
| Tetrabutyltin | 20.0 mg |
| Tributyltin chloride | 22.4 mg |
| Dibutyltin dichloride | 26.1 mg |
| Butyltin trichloride | 32.1 mg |

7.2.3. The surrogate stock solution, tripropyltin chloride, is purchased as certified stock solution at 2000ppm (Restek or equivalent). Alternatively, the solution may be prepared by weighing 20 mg of the neat standard and diluting to 10 mL in DCM. The solution is good for 1 year, or as specified by the manufacturer. Tripentyltin chloride and tricyclohexyltin chloride may be used as alternate surrogates.

7.2.4. An ICV stock standard is purchased from a source different from the calibration standards (Accustandard or equivalent), and prepared at 2000ppm in DCM.

7.3. Spiking Standards

7.3.1. Butyltin Spike Standard - Prepare a 5 ug/mL solution by diluting the stock butyltin standard in acetone (2000 µg/mL x .125 mL/50 mL). Replace every 2 months.

7.3.2. Butyltin Surrogate Spike - Prepare a 5 ug/mL solution by diluting the stock butyltin standard in acetone (2000 µg/mL x .125 mL/50 mL). Replace every 2 months.

7.4. Calibration Standards

7.4.1. A 5ppm calibration intermediate standard mix is prepared by diluting .125 mL of the 2000ppm butyltins stock solution and .125 mL of 2000ppm surrogate stock solution into 5 mL hexane and derivitizing with Grignard reagent. The standard is brought to 50 mL final volume following alumina and silica gel cleanups. This standard can be prepared at the same time that a sample set is derivatized. Replace every 12 months.

7.4.2. Calibration standards are prepared by diluting the calibration intermediate mix into hexane at appropriate levels. A minimum of five concentrations are used to calibrate the instrument. Recommended concentrations are: 2, 5, 20, 50, 200, 500, and 1000 µg/L as cations. Replace every 6 months. To convert the butyltin cation concentration to the corresponding chloride salt concentration, divide the cation conc. by the following correction factors:

| | | |
|---|---|---|
| Tributyltin | = | 0.8910 |
| Dibutyltin | = | 0.7665 |
| Monobutyltin | = | 0.6230 |

If this SOP is accessed electronically, it is an uncontrolled copy and will not be updated.



7.5. ICV Standard Solution – Using the ICV stock standard, prepare the same as for the calibration intermediate standard (7.3.1). Replace every 12 months. From that solution, make an appropriate dilution to give an ICV concentration that is mid-range in the calibration.

7.6. Store all standards in a refrigerator or freezer (<4□C).

## 8. EQUIPMENT AND OPERATING CONDITIONS

8.1. Gas Chromatograph (GC) equipped with a flame photometric detector (FPD) and autosampler, HP 6890 with Enviroquant. A 610nm center wavelength, 10nm bandwidth filter for the FPD is required (purchased from Oriel, Stratford, Conn., Part No. 53295). The recommended GC columns and operating conditions are as follows:

8.1.1. Columns:

- Restek RTX-1, 30m x 0.32mm I.D., 1.0 µm film thickness, or equivalent.
- Restek RTX-35, 30m x 0.32mm I.D., 1.0 µm film thickness, or equivalent.

8.1.2. GC conditions:

| | |
|---|---|
| Carrier flow (column) | 2-5 mL/min. |
| Carrier + Makeup flow | 25 ml/min. |
| Hydrogen flow (detector) | 175 ml/min. |
| Air flow (detector) | 100 ml/min. |
| Temperature program (both columns): | |
| Injector Temp | 30□C, hold for .6 min., 250°C/min. to 325°C |
| Detector Temp | 250°C |
| Oven Temp | 120□C, hold for 1 minute, 20□C/minute to 280□C, hold for 3 minutes |

8.2. Data system - A computer system must be interfaced to the GC. The system must allow the continuous acquisition and storage on machine-readable media of all chromatographic data obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC data file and plot such response versus time. The data system must be capable of performing calibrations and quantitation calculations. HP Enviroquant is the current software in use.

8.3. Analytical balance (0.0001 g).

8.4. Volumetric flasks, syringes, vials, and bottles for standards preparation.

## 9. PREVENTIVE MAINTENANCE

If this SOP is accessed electronically, it is an uncontrolled copy and will not be updated.



9.1. All maintenance activities are recorded in a maintenance logbook kept for each instrument. Pertinent information (serial numbers, instrument I.D., etc.) must be in the logbook. This includes the routine maintenance described in section 9. The entry in the log must include: date of event, the initials of who performed the work, and a reference to analytical control.

9.2. Carrier gas - Inline purifiers or scrubbers should be in place for all sources of carrier gas. These are selected to remove water, oxygen, and hydrocarbons. Purifiers should be changed as recommended by the supplier.

9.3. Gas Chromatograph

9.3.1. Whenever GC maintenance is performed, care should be taken to minimize the introduction of air or oxygen into the column. Injection port maintenance includes changing the injection port liner, seal, washer, o-ring, septum, column ferrule, and autosampler syringe as needed. Liners and seals should be changed when recent sample analyses predict a problem with chromatographic performance. In some cases liners and seals may be cleaned and re-used.

9.3.2. Clipping off a small portion of the head of the column often improves chromatographic performance. When cutting off any portion of the column, make sure the cut is straight and "clean" (uniform, without fragmentation) by using the proper column cutting tool.

9.3.3. Over time, the column will exhibit poorer overall performance, as contaminated sample matrices are analyzed. The length of time for this to occur will depend on the samples analyzed. When a noticeable decrease in column performance is evident and other maintenance options do not result in improvement, the column should be replaced. This is especially true when evident in conjunction with calibration difficulties.

9.4. The autosampler should be cleaned periodically. This includes turret cleaning and cleaning or replacing the syringe. Refer to manufacturer's instructions for autosampler restarting.

9.5. The detector should be cleaned and serviced as specified by the manufacturer.

## 10. RESPONSIBILITIES

10.1. It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

If this SOP is accessed electronically, it is an uncontrolled copy and will not be updated.



10.2. It is the responsibility of the department supervisor/manager to document method proficiency and analyst training.

## 11. PROCEDURE

11.1. Refer to the SOP *Sample Batches* (*ADM-BATCH*) for guidance on analytical calibration and sample batches.

**Note:** Refer to the *SOP for Calibration of Instruments for Organics Chromatographic Analyses (SOC-CAL)*, where calibration procedures and policies are described. The calibration procedure(s) and options chosen must follow the SOP *SOC-CAL*. Any criteria described in the following sections takes precedence over the SOP SOC-CAL.

.

11.2. Initial Calibration

11.2.1. Calibrate the GC immediately prior to conducting any analyses, using the external standard technique. Starting with the standard of lowest concentration, analyze each calibration standard and tabulate response (peak area) versus the concentration in the standard. The ratio of the response to the amount injected, defined as the calibration factor (CF), is calculated for each analyte at each standard concentration.

11.2.2. If the percent relative standard deviation (%RSD) of the calibration factor is less than or equal to 20% over the working range, linearity through the origin can be assumed, and the average calibration factor may be used in place of a calibration curve. Other options for establishing the calibration are given in the *SOP for Calibration of Instruments for Organics Chromatographic Analyses (SOC-CAL).*

11.3. Prior to sample analysis; verify the calibration by analyzing the ICV standard immediately after the initial calibration. The acceptance criteria for the ICV are 75-125% of the true value. Values exceeding ± 20 %D should be scrutinized for possible error.

11.4. Calibration Verification

11.4.1. The start of any sequence must include a CCV checked against the Initial Calibration (curve or average calibration factors). For any analyte to "pass", the response (calculated concentration or calibration factor) must be within ± 25%D of the expected response. For this specific "passing" analyte, this CCV is valid for 12 hours and is considered an "Opening CCV". An Opening CCV must be run prior to (within 8 hours of the commencement of) any analytical sequence.

11.4.2. CCV standards must be analyzed at the start of each analytical sequence (except when the sequence is initiated with an ICAL and ICV).

11.4.3. CCV standards are analyzed at the following frequency:

If this SOP is accessed electronically, it is an uncontrolled copy and will not be updated.



11.4.3.1. CCV standards should be analyzed after every 10 injections of field and QC samples or every 12 hours, which ever is more frequent.

11.4.3.2. Samples with confirmed detections must be bracketed by acceptable CCV standards.

11.4.3.3. When a closing CCV standard is not acceptable, corrective action must be taken. A new CCV standard may be prepared and analyzed to demonstrate degradation of the standard as the cause of a CCV outlier. In this case, instrument stability will be verified and samples analyzed prior to this CCV can be reported. CCV standards that are reinjected after minor instrument maintenance (e.g., injection port maintenance, column bake-out, installation of a new trap, etc.) do not verify instrument stability. Samples analyzed prior to this CCV must be reanalyzed.

11.4.4. Any samples following a failing CCV must be rerun.

11.5. Retention Time Windows

11.5.1. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of 72 hours. Three times the standard deviation of a retention time is used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.5.2. Use the mid-level standards (CCVs) interspersed throughout the analysis sequence to evaluate the qualitative performance of the GC system. If any standard falls outside of their daily retention time window, evaluate the chromatogram for possible causes such as carryover from a highly contaminated sample. If a problem related to GC system has been determined to be the cause of retention time shift, perform whatever maintenance is necessary before reinjecting a CCV or recalibrating and proceeding with sample analysis.

11.6. Sample Analysis

11.6.1. Following calibration analyses, analyze samples in a set referred to as an analytical sequence. The sequence includes field samples and QC samples bracketed by CCVs. Using the data system, setup the data acquisition to acquire data for each analysis into a distinct folder. Refer to the SOP *Sample Batches* for guidance on setting up an analytical sequence.

11.6.2. Identification of Analytes

11.6.2.1. Identify a sample component by comparison of its retention time to the retention time of the daily standard chromatogram.

If this SOP is accessed electronically, it is an uncontrolled copy and will not be updated.



11.6.2.2. Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window. A tentatively identified compound is confirmed when the retention time for the compound on the confirmatory detector is within the retention time window on that system. Confirmation is routinely done using secondary column and/or GCMS techniques.

## 12. QA/QC REQUIREMENTS

12.1. The ability of each analyst/instrument to generate acceptable accuracy and precision must be documented prior to sample analysis (IPR study). This must be validated before analysis of samples, or whenever significant changes to the procedures have been made. To do this, four reagent water samples are spiked with each target analyte, extracted, and analyzed. Calculate the average percent recovery and standard deviation. Since no specific criteria are defined for this analysis, the section supervisor/manager should review this data for reasonableness.

12.2. Method Detection Limits

12.2.1. A method detection limit (MDL) study must be undertaken before analysis of samples can begin. To establish detection limits that are precise and accurate, the analyst must perform the following procedure. Spike a minimum of seven blank replicates with a MDL spiking solution (at a level below the MRL) for each target analyte, extract, and analyze. The MDL studies should be done for each matrix, prep method, and instrument. Refer to the CAS *SOP Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification.*

12.2.2. Calculate the average concentration found (x) in the sample concentration, and the standard deviation of the concentrations for each analyte. Calculate the MDL for each analyte using the correct T value for the number of replicates. The MDL must be verified annually (LOD) for each sample matrix or the MDL study repeated.

12.3. Limit of Quantitation (LOQ)

12.3.1. The LOQ must be verified annually for each quality system matrix. Any established LOQ must be above the LOD. Alternatively, the annual LOQ verification is not required if the LOD successfully meets the laboratory established acceptance limits.

12.4. Ongoing QC Samples required are described in the CAS-Kelso Quality Assurance Manual and in the SOP for *Sample Batches*. Routinely, these include:

12.4.1. Method blank - A method blank is extracted and analyzed with every batch of 20 or fewer samples to demonstrate that there are no method interferences. The method blank must demonstrate that interferences from the analytical and preparation steps

If this SOP is accessed electronically, it is an uncontrolled copy and will not be updated.



minimized. No target analytes should be detected above the MRL in the method blank.

**Note**: For DoD projects, no target analytes should be detected in the Method Blank above ½ the MRL. If this criterion is exceeded, the source of the contamination is investigated and steps are taken to correct, minimize, or eliminate the problem. The laboratory shall evaluate whether reprocessing of the samples is necessary.

12.4.2. A lab control sample (LCS) must be extracted and analyzed with every batch of 20 or fewer samples. The LCS is prepared by spiking a blank with the matrix spike solution, and going through the entire extraction and analysis. Calculate percent recovery (%R) as follows:

$$\%R = X/TV \times 100$$

Where X = Concentration of the analyte recovered
TV = True value of amount spiked

Acceptance criteria for lab control samples are listed in Attachment A. If the lab control sample (LCS) fails acceptance limits for any of the compounds, the analyst must evaluate the system and calibration. If no problems are found, corrective action must be taken.

12.4.3. A matrix spike/duplicate matrix spike (MS/DMS) must be extracted and analyzed with every batch of 20 or fewer samples. The MS is prepared by spiking a sample aliquot with the matrix spike solution, and going through the entire extraction and analysis. Calculate percent recovery (%R) as follows:

$$\%R = \frac{X - X1}{TV} \times 100$$

Where X = Concentration of the analyte recovered
X1 = Concentration of unspiked analyte
TV = True value of amount spiked

Calculate Relative Percent Difference (RPD) as:

$$RPD = \frac{R1 - R2}{(R1 + R2)/2} \times 100$$

Where R1 = % recovery of the MS
R2 = % recovery of the DMS

If this SOP is accessed electronically, it is an uncontrolled copy and will not be updated.



The acceptance limits for the MS/DMS are given in Attachment A. If the MS/DMS recovery is out of acceptance limits for reasons other than matrix effects, corrective action must be taken.

12.4.4. The acceptance limits for the surrogates are given in Attachment A. If surrogate recovery is outside acceptance criteria, the sample data must be closely evaluated for possible matrix interferences. If none are present, then corrective action must be identified.

12.5. Current acceptance criteria for matrix spikes, LCSs and surrogates are listed in Attachment A. The acceptance criteria listed are current criteria, but are subject to change as control limits are updated.

12.6. Additional QA/QC measures include control charting of QC sample results.

## 13. DATA REDUCTION AND REPORTING

13.1. Calculations

Sample results are calculated by the external standard method. If there are no interferences, results may also be calculated by the internal standard method, using $Pe_3SnCl$ as the internal standard, if the associated internal calibration is established. For external standard, use the following equations, for internal standard, use techniques described in EPA Method 8000B for quantification.

Aqueous Samples:

$$Conentration\ (\mu g / L) = \frac{(Cex)\ (vf)\ (D)}{Vs}\ x\ C$$

Where
Cex = Concentration in extract in µg/ml
VF = Final volume of extract in ml
D = Dilution factor
Vs = Volume of sample extracted, liters
C = Appropriate chloride-to-cation correction factor (Table 2)

Nonaqueous Samples:

$$Concentration\ (mg / Kg) = \frac{(Cex)\ (Vf)\ (D)\ x\ 1000}{(W)\ x\ 1000}\ x\ C$$

Cex = Concentration in extract in µg/ml
VF = Final volume of extract in ml
D = Dilution factor

If this SOP is accessed electronically, it is an uncontrolled copy and will not be updated.



W = Weight of sample extracted. The wet or dry weight may be used, depending upon the specific client requirements.
C = Appropriate chloride-to-cation correction factor (Table 2)

13.2. Data Review

Following primary data interpretation and calculations, all data is reviewed by a secondary analyst. Following generation of the report, the report is also reviewed. Refer to the SOP for *Laboratory Data Review Process (ADM-DREV)* for details.

13.3. Reporting

13.3.1. Reports are generated in the CAS LIMS by compiling the SMO login, sample prep database, instrument, date, and client-specified report requirements (when specified). This compilation is then transferred to a file that the Stealth reporting system uses to generate a report. The forms generated may be CAS standard reports, DOD, or client-specific reports. The compiled data from LIMS is also used to create EDDs.

13.3.2. As an alternative, reports are generated using Excel© templates located in R:\SVG\forms. The analyst should choose the appropriate form and QC pages to correspond to required tier level and deliverables requirements. The sample and QC results are then transferred, by hand or electronically, to the templates.

13.3.3. Sample concentrations are reported when all QC criteria for the analysis has been met or the results are qualified with an appropriate footnote.

## 14. CORRECTIVE ACTION

14.1. Refer to the SOP for Nonconformity and Corrective Action for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

14.2. Handling out-of-control or unacceptable data – see Table 2

14.2.1. On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, runlogs, for example.

14.2.2. Documentation of a nonconformity must be done using a Nonconformity and Corrective Action Report (NCAR) when:

- corrective action is not taken or not possible

If this SOP is accessed electronically, it is an uncontrolled copy and will not be updated.



- corrective action fails to correct an out-of-control problem on a laboratory QC or calibration analysis
- reanalysis corrects the nonconformity but is not a procedurally compliant analysis. See the SOP *Corrective Action (*ADM-CA) for corrective action procedures.

## 15. METHOD PERFORMANCE

Available method performance data is given in the reference method and determinative method. In addition, this procedure was validated through single laboratory studies of accuracy and precision as specified in the determinative procedures.

## 16. POLLUTION PREVENTION

It is the laboratory's practice to minimize the amount of solvents and reagents used to perform this method wherever technically sound, feasibly possible, and within method requirements. Standards are prepared in volumes consistent with laboratory use in order to minimize the volume of expired standards to be disposed of. The threat to the environment from solvents and/or reagents used in this method may be minimized when recycled or disposed of properly.

## 17. WASTE MANAGEMENT

17.1. The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the CAS EH&S Manual.

17.2. This method uses non-halogenated solvents and any waste generated from this solvent must be placed in the collection cans in the lab. The solvent will then be added to the hazardous waste storage area and disposed of in accordance with Federal and State regulations

## 18. TRAINING

18.1. Training outline

18.1.1. Review literature (see references section). Read and understand the SOP. Also review the applicable MSDS for all reagents and standards used. Following these reviews, observe the procedure as performed by an experienced analyst at least three times.

18.1.2. The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

18.1.3. Perform initial precision and recovery (IPR) study as described above for water samples. Summaries of the IPR are reviewed and signed by the supervisor. Copies

If this SOP is accessed electronically, it is an uncontrolled copy and will not be updated.



may be forwarded to the employee's training file. For applicable tests, IPR studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

18.2. Training is documented following the SOP for Documentation of Training.

NOTE: When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

## 19. REFERENCES

19.1. Unger, M.A.; MacIntyre, W.G. Greaves, J.; Huggett, R.J., *GC Determination of Butyltins in Natural Waters by Flame Photometric Detection of Hexane Derivatives with Mass Spectrometric Confirmation, Chemosphere,* 1986, 16 (4): 461-470.

19.2. Krone, C.A.; Brown, D.W.; Burrows, D.G.; Bogar, R.G.; Chan, S.; Varanasi, U., *A Method for Analysis of Butyltin Species and Measurement of Butyltins in Sediment and English Sole Livers from Puget Sound,* Environmental Conservation Division, Northwest and Alaska Fisheries Center, National Marine Fisheries Service, NOAA, November, 1988.

If this SOP is accessed electronically, it is an uncontrolled copy and will not be updated.



## 20. METHOD MODIFICATIONS

20.1. This procedure is based upon procedures published in literature referenced in section 19.
20.2. Krone uses GC/MS for analysis, this procedure uses GC/FPD as described in the Unger reference.
20.3. The procedure in Krone addressed tissue and sediment matrices. This procedure applies to all matrices.

## 21. CHANGES SINCE THE LAST REVISION

21.1. Sec 1 – added *water* to third sentence and rewrote the first two sentences for clarity
21.2. Sec 6.3 – replaced -18 C with < -10C
21.3. Sec 7.1 updated
21.4. Sec 7.2.4 – remove the word 'Independent Calibration Verification Stock Standard'
21.5. Sec 9.1 updated
21.6. Sec 20 is new

If this SOP is accessed electronically, it is an uncontrolled copy and will not be updated.



## TABLE 1 CONVERSION FACTORS

| Compound | Salt Cation | Cation - Sn |
|---|---|---|
| Tetrabutyltin | 1 | 0.3419 |
| Tributyltin | 0.8911 | 0.4092 |
| Dibutyltin | 0.7666 | 0.5095 |
| Monobutyltin | 0.6230 | 0.6751 |

## TABLE 2

| Summary of Corrective Actions | | | | |
|---|---|---|---|---|
| **Method Reference** | **Control** | **Specification and Frequency** | **Acceptance Criteria** | **Corrective Action** |
| SOC-Butyl | ICAL | Prior to sample analysis | % RSD ≤ 25% or see SOC-CAL | Correct problem then repeat ICAL |
| SOC-Butyl | ICV | After ICAL | ± 25% | Correct problem and verify second source standard; rerun second source verification. If fails, correct problem and repeat initial calibration. |
| SOC-Butyl | Method Blank | Include with each analysis batch (up to 20 samples) | <MRL | If target < 20x MB re-extract and re-analyze. |
| SOC-Butyl | Matrix Spike | Include with each analysis batch (up to 20 samples) | See Table3 | Evaluate data to determine if the there is a matrix effect or analytical error |
| SOC-Butyl | Lab Control Sample | Include with each analysis batch (up to 20 samples) | See Table 3 | Re-extract and re-analyze. |

If this SOP is accessed electronically, it is an uncontrolled copy and will not be updated.



# TABLE 3

**CAS/KELSO DATA QUALITY OBJECTIVES**

| METHOD | ANALYTE | CAS No. | MATRIX | MDLa | MRL | LODb | LOQc | UNITS | Accuracy (LCS %Rec.) | Matrix Spike (%Rec.) | Precision (% RPD) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| SOC-Butyl | Di-n-butyltin | 14488-53-0 | Soil | 0.19 | 1 | 0.6 | 1 | ug/kg | 12-136 | 10-133 | 40 |
| SOC-Butyl | n-Butyltin | 78763-54-9 | Soil | 0.26 | 1 | 0.5 | 1 | ug/kg | 10-150 | 10-124 | 40 |
| SOC-Butyl | Tetra-n-butyltin | 1461-25-2 | Soil | 0.44 | 1 | 0.8 | 1 | ug/kg | 19-130 | 16-126 | 40 |
| SOC-Butyl | Tri-n-butyltin | 36643-28-4 | Soil | 0.43 | 1 | 0.7 | 1 | ug/kg | 10-122 | 10-115 | 40 |
| SOC-Butyl | Tripropyltin (Surr.) | | Soil | NA | NA | NA | NA | % | 10-120 | NA | NA |
| SOC-Butyl | Di-n-butyltin | 14488-53-0 | Tissue | 0.11 | 1 | 0.4 | 1 | ug/kg | 24-155 | 10-154 | 40 |
| SOC-Butyl | n-Butyltin | 78763-54-9 | Tissue | 0.18 | 1 | 0.3 | 1 | ug/kg | 27-141 | 10-152 | 40 |
| SOC-Butyl | Tetra-n-butyltin | 1461-25-2 | Tissue | 0.15 | 1 | 0.5 | 1 | ug/kg | 26-136 | 10-123 | 40 |
| SOC-Butyl | Tri-n-butyltin | 36643-28-4 | Tissue | 0.11 | 1 | 0.4 | 1 | ug/kg | 25-124 | 10-128 | 40 |
| SOC-Butyl | Tripropyltin (Surr.) | | Tissue | NA | NA | NA | NA | % | 23-145 | NA | NA |
| SOC-Butyl | Di-n-butyltin | 14488-53-0 | Water | 0.0073 | 0.05 | | | ug/L | 17-140 | 18-148 | 30 |
| SOC-Butyl | n-Butyltin | 78763-54-9 | Water | 0.029 | 0.05 | | | ug/L | 32-177 | 24-180 | 30 |
| SOC-Butyl | Tetra-n-butyltin | 1461-25-2 | Water | 0.038 | 0.05 | | | ug/L | 26-110 | 10-121 | 30 |
| SOC-Butyl | Tri-n-butyltin | 36643-28-4 | Water | 0.012 | 0.05 | | | ug/L | 32-122 | 17-142 | 30 |
| SOC-Butyl | Tripropyltin (Surr.) | | Water | NA | NA | NA | NA | % | 31-137 | NA | NA |

a Method Detection Limits are subject to change as new MDL studies are completed.
a MDL is the smallest analyte concentration that can be demonstrated to be different from zero with 99% confidence
b The LOD is the smallest amount of a substance that must be present in a sample in order to be detected with 99% confidence.
Verification is acceptable if the response is > 3x instrument noise & 2nd column confirmed or pattern.