# Microscale Solvent Extraction (MSE)

References: **EPA Method 3570,** Test Methods for Evaluating Solid Waste, SW-846, November 2002, Revision 0, (USEPA, Office of Solid Waste and Emergency Response, Washington, DC).

**Method 3500B,** Test Methods for Evaluating Solid Waste, SW-846, Third Edition, Final Update III, December 1996, Revision 2, (USEPA, Office of Solid Waste and Emergency Response, Washington, DC)

**Method 8081B**, Reference: SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update IV, February 2007.

**Method 8082A**, Reference: SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update IV, February 2007.

**Method 8270D,** Reference: SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update IV, February 2007

## 1. Scope and Application

**Matrices:** This method is applicable to solid samples (soils, sludges, tissues, sediments, and solids).

**Definitions:** Refer to Alpha Analytical Quality Manual.

This method is recommended for the extraction of the organic compound classes in solids. This method may be used on a project specific basis as determined by the Project Manager and the Laboratory Director. This method is appropriate when the sample size maybe limited due to uncontrollable factors.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one or more of the following laboratory personnel before performing the modification: Area Supervisor, Department Supervisor, Laboratory Director, or Quality Assurance Officer.

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 by performing an initial demonstration of capability, analyzing a proficiency test sample and completing the record of training.

After initial demonstration, ongoing demonstration is based on acceptable laboratory performance of at least a quarterly laboratory control sample or acceptable performance from an annual proficiency test sample. A major modification to this procedure requires demonstration of performance. The identification of major method modification requiring performance demonstration is directed by the Quality Assurance Officer and/or Laboratory Director on a case-by-case basis.

## 2. Summary of Method

Samples are weighed on an appropriate balance (analytical or top loading), spiked with surrogate, and prepared by shake or spin extraction with an organic solvent in a sealed vessel. Sample extracts

are dried and concentrated using either the Kuderna-Danish (K-D) or TurboVap method, and brought to the appropriate analytical final volume.

### 2.1 Method Modifications from Reference

**2.1.1** Acetone is used as the first extraction solvent.

**2.1.2** Extraction time is reduced from three 4 hour extractions, to one 30 minute, one 4 hour and one 1 hour extraction.

## 3. Reporting Limits

Refer to analytical SOPs for Reporting Limit information.

## 4. Interferences

**4.1** Solvents, reagents and glassware may introduce interferences. These must be demonstrated to be free of interferences by the analysis of a method blank. See the *Reagent, Solvent and Standard Control* SOP (G-008) and *Laboratory Glassware Cleaning* SOP (G-002), for additional details.

**4.2** Many interferences can be removed by sample cleanup. Other cleanup methods performed include the following: *Alumina Column Cleanup of Organic Extracts* (OP-009), *Sulfur Cleanup* (OP-007), *Sulfuric Acid* (OP-010), and *GPC Cleanup* (OP-006). Only appropriate cleanup techniques must be performed based on the suspected interference and the compounds of interest. For example, sulfuric acid cleanup is not applicable to samples requiring pesticide analysis because this rigorous cleanup will destroy the majority of pesticides.

**4.3** Soapy residue may result in basic conditions on glassware and may cause degradation of the pesticides Aldrin and Heptachlor, and some organophosphorous pesticides. All glassware must be rinsed thoroughly with deionized water and solvent to remove soapy residue. See the *Laboratory Glassware Cleaning* SOP (G-002), for additional details.

**4.4** Phthalate esters can be a major source of contamination if any material containing plasticizers (phthalates) comes in contact with the sample during the extraction process. Use of plastic or any material containing plasticizers (phthalates) should be avoided during extraction, cleanup, or analysis.

## 5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

**5.1** Lab coats, safety glasses, and gloves must be worn when handling samples, extracts, standards or solvents and when washing glassware.

**5.2** All extract concentration steps must be performed in the extraction hoods. All solvent and extract transfers must also be handled in the hood.

**5.3** All expired stock standards, working standards, and spent sample extracts must be placed into the waste bucket in the lab, for future disposal by the Hazardous Waste Manager. The container must be properly labeled with hazard warning labels indicating the container contents.

**5.4** Bottles containing flammable solvents must be stored in the flammables cabinet or in the vented cabinets found under the hoods.

**5.5** All waste solvents must be transferred to the satellite waste storage containers located in the extraction lab. Separate containers are provided for chlorinated and non-chlorinated solvents and must be used accordingly. Under no circumstances are solvents to be poured down the sink drains.

**5.6** Inspect all glassware prior to use. Do not use any glassware that is chipped, cracked or etched if it could present a safety hazard. Damaged glassware is put aside for repair, otherwise discard the piece.

# 6. Sample Collection, Preservation, Shipping and Handling

## 6.1 Sample Collection

Sample collection and preservation requirements are described in the various analytical method SOPs.

## 6.2 Sample Preservation

None.

## 6.3 Sample Shipping

No specific requirements.

## 6.4 Sample Handling

The samples must be refrigerated and maintained at 4°C ±2°C until extraction and analysis. All solid/tissue samples must be extracted within 14 days from the date of collection. Alternatively, samples may be stored frozen at -15°C±5°C for up to one year if the project specifies. This effectively arrests the hold time until samples are thawed for extraction. Sample extracts must be refrigerated and maintained at 4°C ±2°C until analysis. Sample extracts must be analyzed within 40 days from date of extraction.

# 7. Equipment and Supplies

**7.1 Vials:** 40, 60mL, pre-cleaned, open-top screw cap with PTFE-lined silicone septum.

**7.2 Balances**

**7.2.1 Top-loading:** Capable of weighing to 0.01g

**7.2.2 Analytical:** Capable of weighing to 0.0001g.

**7.3 Spatulas:** Stainless steel and Teflon

**7.4 Syringes:** 1-5 mL, varying volumes.

### 7.5 Custom Tumbler Set-up

### 7.6 Brady Labeling System

### 7.7 Kuderna-Danish (KD) Apparatus:

**7.7.1 Evaporation Flask:** 250 and 500mL KD flasks.

**7.7.2 Concentrator Tube:** 10mL, graduated.

**7.7.3 3-Ball Macro Snyder Column**

**7.7.4 Plastic clips.**

**7.8 Boiling Chips:** Solvent rinsed, approximately 10/40 mesh (silicon carbide, or equivalent).

**7.9 N-EVAP:** Organomation; utilized for micro blow down.

**7.10 Glass vials and Screw caps:** 2, 4, 10mL volume

**7.11 Powder Funnels:** Glass or stainless steel

**7.12 Glass wool:** Purified by heating to 400°C for 4 hours.

**7.13 Disposable Glass Transfer Pipets.**

## 8. Reagents and Standards

Pesticide or reagent grade chemicals are used in all tests. All reagents 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.

**8.1 Reagent Water:** All references to water in this method refer to reagent water from Alpha's DI water treatment system.

**8.2 Methylene Chloride (DCM):** Pesticide quality or equivalent.

**8.3 Acetone:** Pesticide quality or equivalent.

**8.4 Hexane:** Pesticide quality or equivalent.

**8.5 Sodium Sulfate ($Na_2SO_4$):** Granular anhydrous; purified by baking at 400ºC for 4 hours in a shallow tray. Store in closed glass containers. All references to sodium sulfate in this method refer to this prepared reagent.

**8.6 Copper:** Granular, 20-30 mesh

**8.7 Spiking Solutions:** There are various surrogate and LCS/MS spiking solutions used in the extraction steps. The preparation of these solutions is described in the analytical SOPs.

# 9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

Each extraction batch contains various QC samples used to ensure the validity of the sample results. The particular QC elements performed for a given extraction batch are determined by the requirements of the determinative method. The purpose and definition of the QC samples performed are listed below.

## 9.1 Blank

A method blank must be prepared in sodium sulfate once per every 20 samples or per extraction batch, whichever is more frequent. If samples will be extracted for a variety of determinative analyses (*i.e.,* PAH, Pesticide and PCBs within the same extraction batch) a method blank for *each* analysis must be prepared and carried through the same extraction procedures as the samples.

## 9.2 Laboratory Control Sample / Laboratory Control Sample Duplicate (LCS/LCSD)

Laboratory control samples (LCS/LCSD) must be prepared once per every 20 samples or per extraction batch, whichever is more frequent, in sodium sulfate and spiked with a solution prepared from a second source or lot number, other than the source used to verify the accuracy of the standard curve for the determinative analytical method. The LCS/LCSD contains all target compounds of interest, and is extracted along with the samples as verification of the accuracy of the entire extraction procedure. If samples will be extracted for a variety of determinative analyses (*i.e.,* PAH, Pesticide and PCBs within the same extraction batch) a LCS/LCSD for *each* analysis must be prepared and carried through the same procedures as the samples.

## 9.3 Initial Calibration Verification (ICV)

Not Applicable.

## 9.4 Continuing Calibration Verification (CCV)

Not Applicable.

## 9.5 Matrix Spike

Matrix spike / matrix spike duplicate (MS/MSD) samples are performed once per 20 samples (5% frequency) per client request. If samples will be extracted for a variety of determinative analyses (*i.e.,* PAH, Pesticide and PCBs within the same extraction batch) a MS/MSD pair for *each* analysis must be prepared and carried through the same procedures as the samples. If less than 20 samples are prepared in a one-week time frame, a MS/MSD pair will be extracted at the beginning of each week.

## 9.6 Laboratory Duplicate

Duplicate analyses (matrix or sample duplicate) are performed once per 20 samples (5% frequency) per client request. For Organic analyses, the matrix duplicate is usually in the form of the matrix spike duplicate, see Section 9.5.

## 9.7 Method-specific Quality Control Samples

### 9.7.1 Surrogates

Surrogates are compounds specified by the analytical method that are added to all samples and QC samples prior to beginning the extraction process. Surrogate recoveries are calculated and serve as a sample specific quantitative check of the extraction. The various spiking solutions are prepared according to the directions found in the analytical SOPs.

## 9.8 Method Sequence

See Section 10.

# 10. Procedure

Samples are prioritized by the Organic Department Manager or Preparation Group Leader for extraction based on hold time and client due date. If tissue samples will be extracted, refer to the *Tissue Preparation and Homogenization* SOP (OP-003) for initial sample processing details that must be employed prior to MSE extraction.

## 10.1 Sample Preparation and Extraction

**10.1.1** Using a solvent cleaned spatula, weigh approximately 3 to 10 grams of homogenized sample into a pre-labeled 40mL VOA vial. For QC samples use sodium sulfate. Smaller sample weights may be used, depending upon the sample volume received. Sample weights of less than 1.0g must be weighed on the Analytical balance. See MSE Extraction Method Notes (Form No.: 102-21) for additional details as needed.

**10.1.2** Spike all samples with the appropriate volume of surrogate solution, and spike all QC samples with the appropriate MS and/or LCS solution. See Organic Prep Lab Spiking Solutions (Form 102-19) for specific spiking details. All sample spiking must be “witnessed” for validity by a second analyst. Add 7mLs of Acetone to each sample. For sediment samples, add approximately 5g of activated copper with the acetone. If the sample turns the copper black add more copper until is the sample no longer turns black.This copper addition will aid in the reduction of sulfur in the sediment samples. For the preparation, storage, and expiration of activated copper, see the Sulfur Cleanup SOP (OP-007

**10.1.3** Samples spin the vials for 30 minutes on the automated tumbler, and then allow them to settle.

**10.1.4** Decant the Acetone layer directly into a pre-labeled 60mL VOA vial, and cap the vial. Centrifuge the VOA vials if there is a suspension and the Acetone cannot be decanted.

**10.1.5** Add 7mLs of Methylene Chloride to the samples. The volume may vary, however the samples must be completely covered with Methylene Chloride.

**10.1.6** Tumble the samples on the automated tumbler for at least 4 hours, then let the samples and Methylene Chloride settle. Alternatively, samples can be tumbled for at least 1 hour (Section 10.1.8).

**10.1.7** Decant the Methylene Chloride layer into the pre-labeled 60mL VOA vial, adding this Methylene Chloride aliquot to the Acetone aliquots from 10.1.4 and cap. Centrifuge the VOA vials if there is a suspension and the Methylene Chloride cannot be decanted.

**10.1.8** Repeat steps 10.1.5 thru 10.1.7, this time tumbling the samples for at least 1 hour. If samples were tumbled for only 1 hour in section 10.1.6, then the samples are to tumble for at least 4 hours.

**10.1.9** Samples are now ready for concentration by KD. Samples are not concentrated immediately are stored in a refrigerator.

## 10.2 Initial Concentration: KD Technique

**10.2.1** Assemble the Kuderna-Danish (KD) apparatus (Section 7.8) by attaching a 10mL KD tube to a 250 or 500mL KD flask. Rinse the apparatus completely. Add 5mL DCM to the assembled apparatus to check for leaks or cracks prior to transferring the sample. If the apparatus is leak free, discard the DCM.

**10.2.2** Place a DCM rinsed filter funnel containing glass wool and sodium sulfate on top of the KD apparatus. Transfer the sample extract from the collection flask through the filter funnel and into the 250 or 500-mL K-D flask with the 10mL concentrator tube clipped to the bottom. Rinse the filter funnel three times with 20mL of DCM. Place the K-D flask on the water bath with 1-2 boiling chips in the bottom of the tube and the macro Snyder column on top. The bath temperature should be 80 $\pm$ 5°C. Macro-concentrate the sample to less than 10mL. This will take approximately 35-40 minutes. At the proper rate of distillation, the balls of the column will chatter, but the column should not flood with condensed solvent.

**10.2.3** If the extract appears extremely viscous and reduces in volume very slowly, a final volume of greater than 10mL may be used to ensure that there is no loss of surrogates or the compounds of interest. See the Section Supervisor or Laboratory Director for additional guidance on troublesome matrices. See Organic Prep Lab Final Volumes (Form No.:102-20) for guidance on sample final volumes.

**10.2.4** Remove the sample from the bath and allow it to drain and cool for approximately 10 minutes, unless the sample requires solvent exchange. See Table I, Section 16 for solvent exchange information.

**10.2.5** Move the cooled sample, still in the 10mL concentrator tube, to the N-EVAP unit for micro-concentration, and bring the extract to the final volume required before cleanup. The extract must be concentrated under a *gentle* steady stream of nitrogen. The internal walls of the concentrator tube must be rinsed periodically with the appropriate solvent during evaporation. The solvent level of the sample must be positioned to prevent water from condensing into the sample (*i.e.,* the solvent level should be below the level of the water in the bath). If the sample requires solvent exchange, add 10mL of the exchange solvent to the concentrator tube. Move samples to a 67C N-evap to finish the solvent exchange. Concentrate the solvent exchanged sample to less than 2mL, repeat the exchange for a second time. Re-concentrate to the final volume according to the Organic Prep Lab Final Volumes (Form No.:102-20).

**10.2.6** If the extract appears extremely viscous and reduces in volume very slowly then a final volume of 5-10 mL should be used to ensure that there is no loss of surrogates or the compounds of interest. Note: Micro-concentration may not be needed depending upon the determinative analytical method. Client specifications may be different than this SOP. Always see the Section Supervisor or Laboratory Director for additional guidance when needed. See Organic Prep Lab Final Volumes (Form No.: 102-20) for guidance on sample final volumes.

**10.2.7** If the sample in the 10mL concentrator tube is dark and viscous, an “auto-vial”, pre-fitted with a filtration disk, can be employed to remove particulate material. This is particularly evident in heavily contaminated petroleum samples. Reduce the extract to just less than

10mL. Remove it from the concentrator tube with an appropriate size syringe. Pass it through the auto-vial, and back into the concentrator tube. Rinse the syringe, tube and auto-vial as needed to ensure a thorough transfer. The extract may now concentrate more easily with the majority of the particulate matter removed. However, do not force the concentration as this may jeopardize the surrogate and the compounds of interest recoveries.

**10.2.8** In some heavily contaminated petroleum extracts, it is possible to perform an extra step of hexane exchange to remove the asphaltene material that precipitates out in hexane. This decision must be made with the Department Supervisor approval. This may preserve the integrity of surrogates and the compounds of interest. This extract can also be auto-vialed to further remove any unwanted particulate materials. Micro-concentration may then continue.

**10.2.9** Transfer the sample extract from the concentrator tube to a vial of the appropriate final volume size. The sample may now undergo any necessary cleanup that may be required prior to analysis. If the sample does not require cleanup, it may be directly transferred at the correct final volume, with copies of the sample preparation extraction log.

### 10.3 Preventive Maintenance

#### 10.3.1 Water Bath

**10.3.1.1** The water bath should be kept full at all times. Add reagent water as necessary.

**10.3.1.2** Keep unit clean. Avoid solvent spills on or around unit. Clean periodically with a damp cloth.

## 11. Data Evaluation, Calculations and Reporting

Not Applicable.

## 12. Contingencies for Handling Out-of-Control Data or Unacceptable Data

Holding time exceedence, improper preservation and observed sample headspace are noted on the nonconformance report form.

When analysis of samples indicates possible extraction problems, such as poor surrogate recoveries, poor LCS/MS/MSD recoveries, or suspected contamination in blanks or samples, re-extractions are required. Depending on the particular failure, the re-extraction may be of a specific sample or the entire extraction batch.

The analyst that determines the need for re-extraction must fill out a sample re-extract request form. This form notes the reason for the re-extraction request along with any special requirements, and the date and time that the re-extract is needed. Re-extraction request forms are maintained on file to help track the cause for re-extractions, and to be used as a tool in improving systems to minimize the need for re-extractions.

Depending on the results of the re-extraction, the first, second, or both sets of results may be reported to the client, along with a narrative report detailing the problems encountered and the resolution.

# 13. Method Performance

## 13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/08-05. These studies performed by the laboratory are maintained on file for review.

## 13.2 Demonstration of Capability Studies

Refer to Alpha SOP/08-12 for further information regarding IDC/DOC Generation.

### 13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

### 13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

# 14. Pollution Prevention and Waste Management

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

# 15. Referenced Documents

Chemical Hygiene Plan
SOP/01-01 Sample Receipt & Log-In
SOP/08-05 MDL/LOD/LOQ Generation
SOP/08-12 IDC/DOC Generation
SOP/G-006 Hazardous Waste and Sample Disposal
SOP/G-008 Reagent, Solvent and Standard Control
SOP/G-002 Laboratory Glassware Cleaning
SOP/OP-003 Tissue Preparation and Homogenization
SOP/OP-006 GPC Cleanup
SOP/OP-007 Sulfur Cleanup
SOP/OP-009 Alumina Column Cleanup of Organic Extracts
SOP/OP-010 Sulfuric Acid
Form/102-19 Organic Prep Lab Spiking Samples
Form/102-20 Organic Prep Lab Final Volumes
Form/102-21 MSE Extraction Method Notes

# 16. Attachments

Table 1: Solvent Exchange per Method

# Table 1

## Solvent Exchange per Method

| Method | Exchange Solvent |
|---|---|
| 8081A | HEXANE |
| 8081A-low | HEXANE |
| 8082 | HEXANE |
| 8082-low | HEXANE |
| Congener | HEXANE |
| Homolog | HEXANE |
| 209 PCB | HEXANE |
| 8270C | NONE |
| PAH-SIM | NONE |