
Geochemical and Environmental Research Group
STANDARD OPERATING PROCEDURES

SOP-9805

**EXTRACTING SEDIMENT SAMPLES USING ACCELERATED SOLVENT
EXTRACTOR FOR THE ANALYSES OF ORGANOCHLORINE PESTICIDES,
POLYCHLORINATED BIPHENYLS AND AROMATIC HYDROCARBONS**

This document presents the procedures, materials, and quality control used in the performance of the above preparation activities.


Quality Assurance Manager


Date

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1.0 PURPOSE

This document provides the procedures for the extraction of sediment samples using the Accelerated Solvent Extractor (ASE) and the subsequent concentration of the extracts for environmental trace analysis which are used by the staff of the Geochemical and Environmental Research Group (GERG) of the College of Geosciences at Texas A&M University.

1.1 Summary of the Method

This procedure uses matrix-specific extraction and analyte-specific concentration steps to allow the determination of organochlorine pesticides (OCs), polychlorinated biphenyls (PCBs), and polynuclear aromatic hydrocarbons (PAHs) in environmental samples. With modification, this method may be used for the extraction of other types of matrices and for other types of analytes.

The sediment samples are weighed and placed into extraction cells. The desired solvent is placed into the solvent reservoir of the ASE 200. The method for extraction is selected and initiated. The extract is released into collection vials. The extracts are then concentrated on a water bath. The concentrated extract is purified by column chromatography using appropriate GERG SOPs.

1.2 Application of Method

- 1.2.1** The extraction method described in this standard operation procedure is applicable to wet and dried sediment samples that require measurement of aliphatic hydrocarbons, OCs, PCBs, and PAHs. With modification to the extraction conditions, other types of compounds, such as herbicides, organophosphorus pesticides, and dioxin/furans from various types of matrices may be extracted by this technique.

2.0 SAFETY

The hazards, toxicity or carcinogenicity of each compound or reagent used in GERG standard operating procedures have 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. The laboratory maintains Material Safety Data Sheets

(MSDS) which contain information regarding the safe handling of chemicals used at GERG facilities. A reference file of MSDS is available to all personnel involved with these materials. All laboratory personnel should direct any questions regarding safety issues to their supervisors or the Safety Officer.

3.0 QUALITY CONTROL REQUIREMENTS

The quality control samples routinely used at GERG include a method blank (BLANK), a sample duplicate (DUP), a matrix spike (MS), and a matrix spike duplicate (MSD) per batch of 20 or less samples. The number and type of QC samples may be modified to satisfy client's requests and sample availability. A laboratory blank spike (LBS) and standard reference material (SRM) may be included in each extraction batch.

3.1 Method Blank (BLANK)

A Method Blank is used to demonstrate that the analytical method is free of contaminating interference. The BLANK is prepared by executing all of the specified extraction and extract purification steps except for the introduction of a sample. The BLANK is spiked with Surrogate Standard Solution (SU) and the Internal Standard (IS) at the appropriate stages of the preparation.

3.2 Laboratory Blank Spike (LBS)

A Laboratory Blank Spike is used to demonstrate accuracy of the method. It is prepared by executing all of the specific extraction and extraction purification steps except for the introduction of a sample. The LBS is spiked with the Surrogate Standard Solution (SU), the matrix spike standard (MA), and the Internal Standard (IS) at the appropriate stages of the preparation.

3.3 Matrix Spike (MS) and Matrix Spike Duplicate (MSD)

Matrix Spike/Matrix Spike Duplicate are used to demonstrate accuracy and precision of the sample processing method in the presence of a representative matrix. MS/MSD are prepared by executing all of the specified extraction and purification steps on a selected sample. The MS/MSD are spiked with the Surrogate Spiking Solution (SU), the Matrix Spike Standard (MA) and the Internal Standard (IS) at the appropriate stages of the preparation.

3.4 Duplicate (DUP)

A sample Duplicate is used to demonstrate matrix homogeneity and analytical precision in the presence of a representative matrix. A DUP is prepared by executing all of the specified

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extraction and purification steps on replicate portions of a selected sample. The DUP is spiked with the Surrogate Standard Solution (SU) and the Internal Standard (IS) at the appropriate stages of the preparation.

3.5 Standard Reference Material (SRM)

A standard reference material (SRM) is used to demonstrate the relative accuracy of the sample processing and analytical methods in the presence of a representative matrix.

4.0 APPARATUS AND MATERIALS

3.1 Glassware and Hardware

The following laboratory glassware and hardware is needed to perform the extraction and concentration procedures:

Stainless steel forceps
Flat-bottomed Flasks: 250 mL
Collection Vials and Caps : 60 mL capacity
Beakers: 50 mL
Stainless Steel Extraction Cells and Caps : 22 or 33 mL capacity, Dionex
Water Bath: Heated to 40-50° C
Balance: Top Loading, 0.001 g accuracy
Funnels
Glass Wool

4.2 Instrumentation

Accelerated Solvent Extractor: ASE 200, Dionex

5.0 REAGENTS AND CONSUMABLE MATERIALS

5.1 Reagents

5.1.1 Hydrochloric Acid: 38%; VWR Scientific, Cat. HX0603-3 or equivalent.

5.1.2 Solvents: Equivalent solvents from other source may be used after lot testing. Methylene Chloride: Burdick and Jackson; Cat# 300-4, High Purity, Pesticide grade or equivalent.
Hexane: Burdick and Jackson; Cat# GC60394-4, Capillary GC/GC-MS solvent or equivalent.

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Acetone: Burdick and Jackson; Cat# 010-4, High purity solvent or equivalent.

Methanol: Burdick and Jackson; Cat# 230-4, pesticide grade or equivalent.

5.1.3 Nitrogen Gas: Compressed nitrogen

5.1.4 Sand: White quartz, Sigma, combusted at 440°C for 4 hours

5.1.5 Copper, Granular: 20-30 mesh: J.T. Baker

5.1.6 Glass Microfibre Filters; GF/B: 21mm; Whatman Cat# 1821-021, combusted at 440°C for 4 hours

5.1.7 Sodium sulfate, J. T. Baker; analytical grade, combusted at 440°C for 4 hours

5.2 Analytical Standards

Appropriate analytical standards are specified on the Analysis Request Form and are prepared according to GERG SOPs. When not in use, standards are stored at 4°C in a refrigerator.

6.0 EXTRACTION PROCEDURE

6.1 Reagent and Apparatus Preparation

6.1.1 Preparation of Activated Copper:

6.1.1.1 Pour desired amount of granular copper into a beaker. Add enough amount of diluted 1:1 hydrochloric acid to the beaker to cover the copper. The acid is diluted in the hood by slowly adding an equal volume of acid to the water with stirring. Let the copper stand in acid for approximately 2-5 minutes.

6.1.1.2 Slowly decant the acid into the acid container. Add baking soda to another beaker. Add water to the copper, stir, and decant the liquid onto the baking soda. Continue the water rinsing process until the acid is neutralized (no bubbling when added to the baking soda).

6.1.1.3 Wash the copper with methanol three times, or until the methanol wash is clear, by adding methanol into the beaker and stirring. Decant the methanol into an appropriate waste container.

6.1.1.4 Wash the copper with methylene chloride three times, or until the methylene chloride wash is clear, by adding methylene chloride to the beaker and stirring. Decant the methylene chloride into an appropriate waste container. Transfer the copper into a clean beaker and cover with hexane.

6.1.2 Clean Extraction Cell Tube

Disassemble the extraction cell by unscrewing the cap. Wash the extraction cell tube with soap and water using a brush. After rinsing with water, rinse the inside of the tube with acetone or methanol, followed by methylene chloride.

6.1.3 Clean Cell Caps

Wash the cell caps with water. Rinse the caps with methanol, followed by methylene chloride. Before assembling, carefully check the inside of the caps. Make sure there is no sand, copper, sediment, or any other residual dirt inside the cap, particularly around the brown PEEK seal. If there is any, disassemble the cap and clean it.

6.2 SAMPLE PREPARATION

6.2.1 Calibrate Balance

6.2.1.1 Tare the balance. Place a standard weight (100 g) on the weighing pan. Press CAL button. Record the weight displayed. If the weight differs from the standard by 0.005 g, re-calibrate the balance by pressing CAL button. If the reading is still out of the range of 99.995 g to 100.005 g, notify your supervisor.

6.2.2 Aliquot a 20 gram subsample into a clean jar. If the sample contains greater than 30% of water, partially dry the sample at 40°C for 3-5 hours.

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- 6.2.3** Mix the sample with 15-20 gram anhydrous sodium sulfate. Stir the sample/sodium sulfate constantly until the mixture free flows. Assemble the 33 mL extraction cell body tube and bottom cap, hand tight. Rinse with methanol and methylene chloride.
- 6.2.4** Insert a combusted filter into the cell and push down with a rod. Make sure the filter is flat and covers the bottom fully.
- 6.2.5** Using a funnel, add one scoop of the activated copper to the extraction cell.
- 6.2.6** Using a funnel, add the sample/sodium sulfate mixture into the extraction cell.
- 6.2.7** Prepare a Blank and Spiked Blank sample (if required) by preparing a cell filled with sand along with copper and filter.
- 6.2.8** Rinse a micropipette with methylene chloride in the hood at least five times. Spike all samples with the appropriate amount of the required surrogate standards.
- 6.2.9** Rinse the micropipette five times again and spike the appropriate samples with the required amount of spiking standards.
- 6.2.10** Using caps that have been rinsed with methanol/methylene chloride, screw the top cap onto the cell hand tight.
- 6.3 Extraction**

 - 6.3.1** Place the assembled extraction cells onto the top cell tray on the ASE 200 in numerical order according to slots.
 - 6.3.2** Place labeled 60 mL collection vials in the bottom collection tray to coincide with the top tray.
 - 6.3.3** Fill the solvent reservoir with methylene chloride, or other solvent if specified.
 - 6.3.4** Make sure the solvent waste/rinse collection vial inside the chamber of the reservoir is empty, as well as the rinse vial on the sample collection tray (R1, R2).

6.3.5 Press *RINSE* button on the control panel.

6.3.6 As the status returns to *IDLE* after instrumental rinse, press *MENU* and choose the first selection *LOAD METHOD/SCHEDULE* to designate the method. Enter the desired method number, press *ENTER*, and then press *START*. This will start the instrument extraction beginning with the first extraction cell.

The conditions used for the extraction of the environmental sediment are:

Temperature	100°C
Pressure	1500 psi
Heating time	5 minutes
Flush volume	90%
Cycles	2

If required, the extraction may be started from cells other than the first cell. If so desired, press *MENU* and choose the first selection *LOAD METHOD/SCHEDULE* to designate the method. Move the cursor to the third entry field and enter the vial number you wish to begin with. Move the cursor to *METHOD NUMBER* and enter the method number. Press *ENTER*. Press *START* and the extraction process should begin.

While the extraction is in progress, check the collected solvent volume in the sample collection vial. The vial should be more than half full for the 33 mL extraction tubes. Check for leaking cells by listening to the pump action. If the pump is continuously activated while the machine is in *STATIC*, or if the pressure reading is constantly below the setting (1500 psi) then there is probably a leak. If this occurs, stop the extraction by pressing the *ABORT* button on the control panel.

6.4 Concentration

6.4.1 Filter the sample extract by pouring it through a sodium sulfate filtration funnel into a 250 mL flask.

6.4.2 Add some activated copper to the sample extract. If the gloss and color of the copper darkens, add additional copper to the extract until the copper does not change color.

- 6.4.3** Add boiling chips to the flask and concentrate the sample extract to about 1-2 mL on a water bath at 60°C.
- 6.4.4** Exchange the solvent of the extract to hexane by gradually adding small amount of hexane to the extract while the sample extract is being concentrated on the water bath. When the solvent in the extract is exchanged to hexane (no apparent boiling), purify the sample extract using the column chromatography procedures of the appropriate GERG SOP.

7.0 DOCUMENTATION REQUIREMENTS

Copies of the following applicable documents should accompany the sample set in a labeled manila folder:

- Chain of Custody documents
- Sample Information Sheet
- Analysis Request Form
- Laboratory Bench Sheet
- Sample Dry Weight Sheets
- Sample Action Request Form, if applicable
- Other miscellaneous information