

METHOD 3541

AUTOMATED SOXHLET EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 Method 3541 describes the extraction of organic analytes from soil, sediment, sludges, and waste solids. The method uses a commercially available, unique, three stage extraction system to achieve analyte recovery comparable to Method 3540, but in a much shorter time. There are two differences between this extraction method and Method 3540. In the initial extraction stage of Method 3541, the sample-loaded extraction thimble is immersed into the boiling solvent. This ensures very rapid intimate contact between the specimen and solvent and rapid extraction of the organic analytes. In the second stage the thimble is elevated above the solvent, and is rinse-extracted as in Method 3540. In the third stage, the solvent is evaporated, as would occur in the Kuderna-Danish (K-D) concentration step in Method 3540. The concentrated extract is then ready for cleanup (Method 3600) followed by measurement of the organic analytes.

1.2 The method is applicable to the extraction and concentration of water insoluble or slightly water soluble polychlorinated biphenyls (PCBs) in preparation for gas chromatographic determination using either Method 8080 or 8081. This method is applicable to soils, clays, solid wastes and sediments containing from 1 to 50 µg of PCBs (measured as Arochlors) per gram of sample. It has been statistically evaluated at 5 and 50 µg/g of Arochlors 1254 and 1260, and found to be equivalent to Method 3540 (Soxhlet Extraction). Higher concentrations of PCBs are measured following volumetric dilution with hexane.

1.3 The method is also applicable the extraction and concentration of semivolatile organics in preparation for GC/MS analysis by Method 8270 or by analysis using specific GC or HPLC methods.

2.0 SUMMARY OF METHOD

2.1 PCBs: Moist solid samples (e.g., soil/sediment samples) may be air-dried and ground prior to extraction or chemically dried with anhydrous sodium sulfate. The prepared sample is extracted using 1:1 (v/v) acetone:hexane in the automated Soxhlet following the same procedure as outlined for semivolatile organics in Sec. 2.1. The extract is then concentrated and exchanged into pure hexane prior to final gas chromatographic PCB measurement.

2.2 Other semivolatile organics: A 10-g solid sample (the sample is pre-mixed with anhydrous sodium sulfate for certain matrices) is placed in an extraction thimble and usually extracted with 50 mL of 1:1 (v/v) acetone/hexane for 60 minutes in the boiling extraction solvent. The thimble with sample is then raised into the rinse position and extracted for an additional 60 minutes. Following the extraction steps, the extraction solvent is concentrated to 1 to 2 mL.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

3.2 The extraction thimble and the o-rings used to seal the extraction cup are both a source of interference. Both should be checked by including a method blank and following the extraction procedure as written. Solvent rinsing or extraction, prior to use, may be necessary to eliminate or reduce interferences. Viton seals contributed least to the interference problem, however, even they contributed some interference peaks when the extraction solvent was analyzed by the electron capture detector. Use of butyl or EPDM rings are not recommended since they were found to contribute significant background when the extraction solvent was 1:1 v/v hexane/acetone or 1:1 v/v methylene chloride/acetone.

4.0 APPARATUS AND MATERIALS

4.1 Automated Soxhlet Extraction System - with temperature-controlled oil bath (Soxtec, or equivalent). Tecator bath oil (catalog number 1000-1886) should be used with the Soxtec. Silicone oil must not be used because it destroys the rubber parts. See Figure 1. The apparatus is used in a hood.

4.2 Accessories and consumables for the automated Soxhlet system. (The catalog numbers are Fisher Scientific based on the use of the Soxtec HT-6, however, other sources that are equivalent are acceptable.)

4.2.1 Cellulose extraction thimbles - 26 mm ID x 60 mm contamination free, catalog number 1522-0034, or equivalent.

4.2.2 Glass extraction cups (80 mL) - (set of six required for the HT-6), catalog number 1000-1820.

4.2.3 Thimble adapters - (set of six required for the HT-6), catalog number 1000-1466.

4.2.4 Viton seals - catalog number 1000-2516.

4.3 Syringes - 100 and 1000 μ L and 5 mL.

4.4 Apparatus for Determining Percent Dry Weight

4.4.1 Drying Oven.

4.4.2 Desiccator.

4.4.3 Crucibles, porcelain.

4.4.4 Balance, analytical.

4.5 Apparatus for grinding - Fisher Cyclotec, Fisher Scientific catalog number 1093, or equivalent.

4.6 Spatula

4.7 Graduated cylinder - 100 mL.

4.8 Aluminum weighing dish - VWR Scientific catalog number 25433-008 or equivalent.

4.9 Graduated, conical-bottom glass tubes - 15 mL, Kimble catalog number 45166 or equivalent, or 10 mL KD concentrator tube.

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 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. A method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.4 Extraction solvents:

5.4.1 Organochlorine pesticides/PCB extraction:

5.4.1.1 Acetone/hexane (1:1 v/v), $\text{CH}_3\text{COCH}_3/\text{C}_6\text{H}_{14}$. Pesticide quality or equivalent.

5.4.2 Semivolatile organics extraction:

5.4.2.1 Acetone/hexane (1:1 v/v), $\text{CH}_3\text{COCH}_3/\text{C}_6\text{H}_{14}$. Pesticide quality or equivalent.

5.4.2.2 Acetone/methylene chloride (1:1 v/v), $\text{CH}_3\text{COCH}_3/\text{CH}_2\text{Cl}_2$. Pesticide quality or equivalent.

5.5 Hexane, C_6H_{14} . 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.

7.0 PROCEDURE

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.

7.1.1.1 PCBs or high-boiling organochlorine pesticides - Air-dry the sample at room temperature for 48 hours in a glass tray or on hexane-cleaned aluminum foil, or dry the sample by mixing with anhydrous sodium sulfate until a free-flowing powder is obtained (see Sec. 7.2).

NOTE: Dry, finely ground soil/sediment allows the best extraction efficiency for non-volatile, non-polar organics, e.g., PCBs, 4,4'-DDT, etc. Air-drying is not appropriate for the analysis of the more volatile organochlorine pesticides (e.g. the BHCs) or the more volatile of the semivolatile organics because of losses during the drying process.

7.1.2 Dried sediment/soil and 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 20 g after grinding. Disassemble grinder between samples, according to manufacturer's instructions, and clean with soap and water, followed by acetone and hexane rinses.

NOTE: The same warning on loss of volatile analytes applies to the grinding process. Grinding should only be performed when analyzing for non-volatile organics.

7.1.3 Gummy, fibrous, or oily materials not amenable to grinding should be cut, shredded, or otherwise broken up to allow mixing, and maximum exposure of the sample surfaces for extraction. If grinding of these materials is preferred, the addition and mixing of anhydrous sodium sulfate with the sample (1:1) may improve grinding efficiency. The professional judgment of the analyst is required for handling such difficult matrices.

7.1.4 Multiple phase waste samples - Samples consisting of multiple phases must be prepared by the phase separation method in Chapter Two before extraction. This procedure is for solids only.

7.2 For sediment/soil (especially gummy clay) that is moist and cannot be air-dried because of loss of volatile analytes - Mix 5 g of sample with 5 g of anhydrous sodium sulfate in a small beaker using a spatula. Use this approach for any solid sample that requires dispersion of the sample particles to ensure greater solvent contact throughout the sample mass.

7.3 Determination of sample percent dry weight - In certain cases, sample results are desired based on dry weight basis. When such data are desired, a portion of sample for this determination 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 the drying of a heavily contaminated hazardous waste sample.

7.3.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

7.4 Check the heating oil level in the automated Soxhlet unit and add oil if needed. See service manual for details. Set the temperature on the service unit at 140°C when using hexane-acetone (1:1, v/v) as the extraction solvent.

7.5 Press the "MAINS" button; observe that the switch lamp is now "ON".

7.6 Open the cold water tap for the reflux condensers. Adjust the flow to 2 L/min to prevent solvent loss through the condensers.

7.7 Weigh 10 g of sample into extraction thimbles. For samples mixed with anhydrous sodium sulfate, transfer the entire contents of the beaker (Sec. 7.2) to the thimble. Add surrogate spikes to each sample and the matrix spike/matrix spike duplicate to the selected sample.

NOTE: When surrogate spikes and/or matrix spikes contain relatively volatile compounds (e.g., trichlorobenzenes, BHCs, etc.), steps 7.8, 7.9, and 7.10 must be performed quickly to avoid evaporation losses of these compounds. As the spike is added to the sample in each thimble, the thimble should immediately be transferred to the condenser and lowered into the extraction solvent.

7.8 Immediately transfer the thimbles containing the weighed samples into the condensers. Raise the knob to the "BOILING" position. The magnet will now fasten to the thimble. Lower the knob to the "RINSING" position. The thimble will now hang just below the condenser valve.

7.9 Insert the extraction cups containing boiling chips, and load each with 50 mL of extraction solvent (normally 1:1 (v/v) hexane:acetone, see Sec. 5.4). Using the cup holder, lower the locking handle, ensuring that the safety catch engages. The cups are now clamped into position. (The seals must be pre-rinsed or pre-extracted with extraction solvent prior to initial use.)

7.10 Move the extraction knobs to the "BOILING" position. The thimbles are now immersed in solvent. Set the timer for 60 minutes. The condenser valves must be in the "OPEN" position. Extract for the preset time.

7.11 Move the extraction knobs to the "RINSING" position. The thimbles will now hang above the solvent surface. Set timer for 60 minutes. Condenser valves are still open. Extract for the preset time.

7.12 After rinse time has elapsed, close the condenser valves by turning each a quarter-turn, clockwise.

7.13 When all but 2 to 5 mL of solvent have been collected, open the system and remove the cups.

7.14 Transfer the contents of the cups to 15 mL graduated, conical-bottom glass tubes. Rinse the cups using hexane (methylene chloride if 1:1 methylene chloride-acetone was used for extraction and analysis is by GC/MS) and add the rinsates to the glass tubes. Concentrate the extracts to 1 to 10 mL. The final volume is dependent on the determinative method and the quantitation limit required. Transfer a portion to a GC vial and store at 4°C until analyses are performed.

NOTE: The recovery solvent volume can be adjusted by adding solvent at the top of the condensers. For more details concerning use of the extractor, see the operating manual for the automated extraction system.

7.15 Shutdown

7.15.1 Turn "OFF" main switch.

7.15.2 Turn "OFF" cold water tap.

7.15.3 Ensure that all condensers are free of solvent. Empty the solvent that is recovered in the evaporation step into an appropriate storage container.

7.16 The extract is now ready for cleanup or analysis, depending on the extent of interfering co-extractives. See Method 3600 for guidance on cleanup methods and Method 8000 for guidance on determinative methods. Certain cleanup and/or determinative methods may require a solvent exchange prior to cleanup and/or determination.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for general quality control procedures and to Method 3500 for specific extraction and sample preparation QC procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of an organic-free solid matrix (e.g., reagent sand) method blank that all glassware and reagents are interference-free. Each time a set of samples is extracted, or when 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. This is especially important because of the possibility of interferences being extracted from the extraction cup seal.

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 method 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. Also, routinely check the integrity of the instrument seals.

8.4 Surrogate standards must be added to all samples when specified in the appropriate determinative method.

9.0 METHOD PERFORMANCE

9.1 Multi-laboratory accuracy and precision data were obtained for PCBs in soil. Eight laboratories spiked Arochlors 1254 and 1260 into three portions of 10 g of Fuller's Earth on three non-consecutive days followed by immediate extraction using Method 3541. Six of the laboratories spiked each Arochlor at 5 and 50 mg/kg and two laboratories spiked each Arochlor at 50 and 500 mg/kg. All extracts were analyzed by Oak Ridge National Laboratory, Oak Ridge, TN, using Method 8081. These data are listed in a table found in Method 8081, and were taken from Reference 1.

9.2 Single-laboratory accuracy data were obtained for chlorinated hydrocarbons, nitroaromatics, haloethers, and organochlorine pesticides in a clay soil. The spiking concentrations ranged from 500 to 5000 µg/kg, depending on the sensitivity of the analyte to the electron capture detector. The spiking solution was mixed into the soil during addition and then immediately transferred to the extraction device and immersed in the extraction solvent. The data represents a single determination. Analysis was by capillary column gas chromatography/electron capture detector following Methods 8081 for the organochlorine pesticides, 8091 for the nitroaromatics, 8111 for the hydrocarbons, and 8121 for the chlorinated hydrocarbons. These data are listed in a table located in their respective methods and were taken from Reference 2.

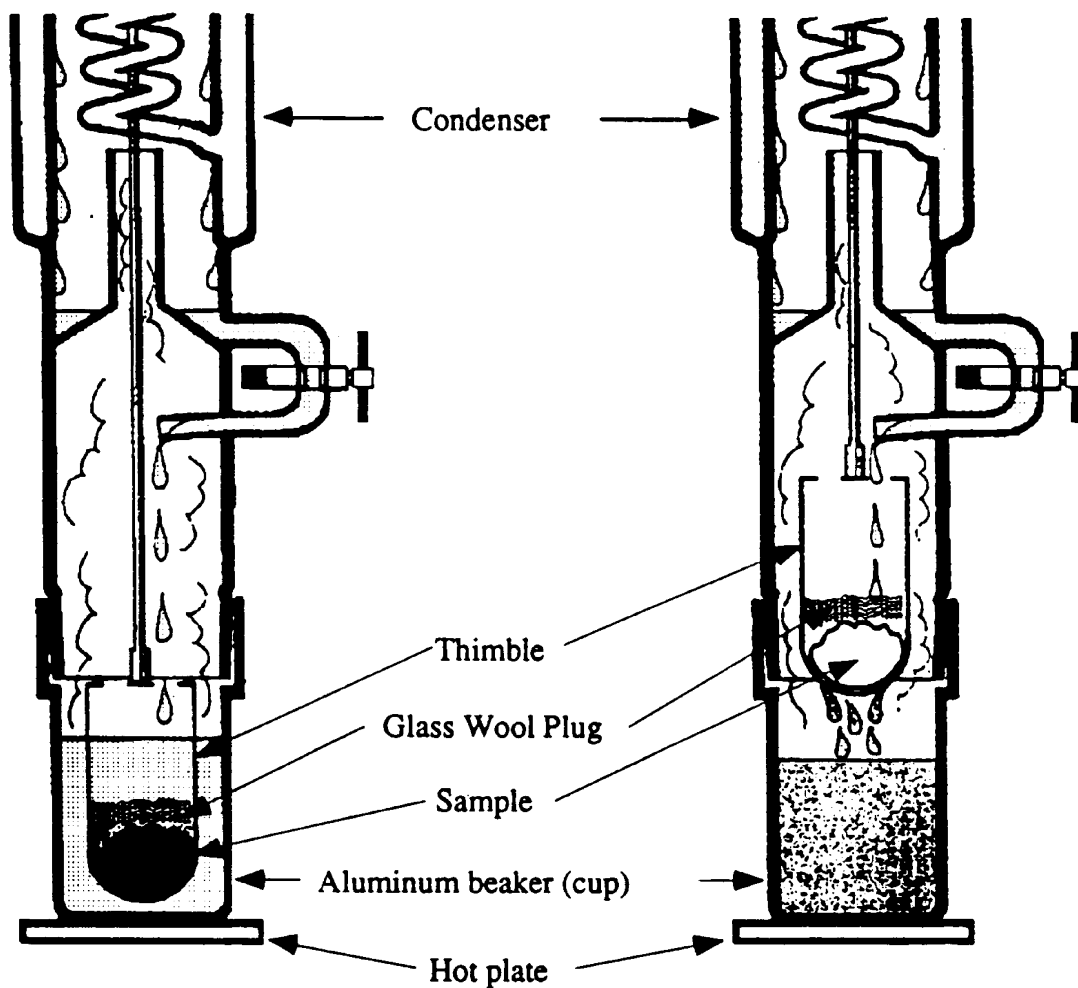
9.3 Single-laboratory accuracy and precision data were obtained for semivolatile organics in soil by spiking at a concentration of 6 mg/kg for each compound. The spiking solution was mixed into the soil during addition and then allowed to equilibrate for approximately 1 hr prior to extraction. Three 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 a Table located in Method 8270 and were taken from Reference 2.

10.0 REFERENCES

1. Stewart, J. "Intra-Laboratory Recovery Data for the PCB Extraction Procedure"; Oak Ridge National Laboratory, Oak Ridge, TN, 37831-6138; October 1989.

2. Lopez-Avila, V. (Beckert, W., Project Officer), "Development of a Soxtec Extraction Procedure for Extracting Organic Compounds from Soils and Sediments", EPA 600/X-91/140, US EPA, Environmental Monitoring Systems Laboratory-Las Vegas, October 1991.

Figure 1
Automated Soxhlet Extraction System



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