SUPERCRITICAL FLUID EXTRACTION OF POLYCHLORINATED BIPHENYLS (PCBs) AND ORGANOCHLORINE PESTICIDES

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method describes the use of supercritical fluids for the extraction of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) from soils, sediments, fly ash, solid-phase extraction media, and other solid materials which are amenable to extraction with conventional solvents. This method is suitable for use with any supercritical fluid extraction (SFE) system that allows extraction conditions (e.g., pressure, temperature, flow rate) to be adjusted to achieve separation of the PCBs and OCPs from the matrices of concern. The following compounds have been extracted by this method during validation studies. Similar compounds not listed should also be amenable to this extraction.

Compound	CAS Registry No.	IUPAC No.
2,4,4'-Trichlorobiphenyl	7012-37-5	28
2,2',5,5'-Tetrachlorobiphenyl	35693-99-3	52
2,2',4,5,5'-Pentachlorobiphenyl	37680-73-2	101
2,3,3',4,4'-Pentachlorobiphenyl	32598-14-4	105
2,3',4,4',5-Pentachlorobiphenyl	31508-00-6	118
2,2',3,3',4,4'-Hexachlorobiphenyl	38380-07-3	128
2,2',3,4,4',5'-Hexachlorobiphenyl	35065-28-2	138
2,2',3,4',5',6-Hexachlorobiphenyl	38380-04-0	149
2,2',4,4',5,5'-Hexachlorobiphenyl	35065-27-1	153
2,3,3',4,4',5'-Hexachlorobiphenyl	38380-08-4	156
2,2',3,3',4,4',5-Heptachlorobiphenyl	35065-30-6	170
2,2',3,4,4',5,5'-Heptachlorobiphenyl	35065-29-3	180
Aldrin	309-00-2	
β-Hexachlorocyclohexane (β-BHC)	319-85-7	
δ-Hexachlorocyclohexane (δ-BHC)	319-86-8	
γ-Hexachlorocyclohexane (γ-BHC, or Lindane)	58-89-9	

Compound	CAS Registry No.	IUPAC No.
α-Chlordane	5103-71-9	
4,4'-DDD	72-54-8	
4,4'-DDE	72-55-9	
4,4'-DDT	50-29-3	
Dieldrin	60-57-1	
Endosulfan II	33213-65-9	
Endrin	72-20-8	
Endrin aldehyde	7421-93-4	
Heptachlor	76-44-8	
Heptachlor epoxide	1024-57-3	

1.2 This method is not suitable for the extraction of PCBs or organochlorine pesticides from liquid samples without some treatment of the liquid before introduction into the SFE to "stabilize" the liquid. Otherwise, the sample may be extruded through the end pieces of the extraction vessel without the benefit of SFE. The use of solid-phase extraction (SPE) media, as described in Method 3535, is one way to stabilize a liquid sample and it allows an easy coupling of two selective sample preparation techniques. The use of large diameter (ca. 90 mm) SPE disks coupled with SFE allows large volumes of aqueous samples to be prepared without the need for organic solvent elution. Furthermore, SFE may allow an in-line cleanup to be performed, thus eliminating the need for separate column cleanup and subsequent solvent concentration steps.

1.3 The extraction conditions listed in this procedure (see Sec. 11.7) employed a variable restrictor and solid trapping media. Other extraction conditions and equipment are acceptable once appropriate method performance is demonstrated. The method applicability demonstration should be based on the extraction of a certified reference sample or an environmentally-contaminated sample, not on spiked soil/solids, whenever possible. It should be noted that there are currently no "certified" samples for organochlorine pesticides. An authentic, weathered, environmental sample which has been extracted by a traditional sample preparation technique should be used as the reference for these compounds.

1.4 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 3500, 3600, 5000, and 8000) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.5 Use of this method is restricted to use by, or under supervision of, appropriately experienced and trained personnel. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 In order to assure a homogeneous sample and minimum subsampling errors, at least 100 g of sample are homogenized with an equal volume of solid CO_2 "snow." An aliquot of this mixture is packed into a stainless steel SFE extraction vessel. Copper powder may be added to the cell to remove sulfur from the sample extract. Surrogates and/or internal standards are added to the portion of the sample in the cell and the cell is placed in the SFE extraction device.

2.2 The sample is extracted using supercritical carbon dioxide with no modifiers. Samples to be analyzed for PCBs are subjected to a 10-min static extraction, followed by a 40-min dynamic extraction. Samples for organochlorine pesticides are subjected to a 20-min static extraction, followed by a 30-min dynamic extraction.

2.3 The sample extract is trapped on a solid-phase sorbent (Florisil® for PCBs and octadecyl silane for pesticides). The trapping material is then rinsed with solvent to collect the analytes of interest and reactivate the trapping material for reuse.

2.4 The sample extracts may be subjected to additional cleanup steps (see Method 3600) and then analyzed by the appropriate determinative methods.

3.0 DEFINITIONS

See the "Glossary" at the end of this method. Also refer to Chapter One and the manufacturer's instructions for other definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware that make up the supercritical fluid extraction system may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. To do this, perform a simulated extraction using an empty extraction vessel and a known amount of CO_2 under the same conditions as those used for sample extraction, and determine the background contamination by analyzing the extract by the determinative method that will be used for sample analysis. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Four for general guidance on the cleaning of glassware.

4.2 The extraction vessel(s), the end-frits, the nozzle restrictor(s), and the multi-port valve(s) may retain solutes whenever high-concentration samples are extracted. Therefore, it is good practice to clean the extraction system after such extractions. Suspect parts of the system should be replaced when reagent blanks indicate carryover. At least one reagent blank should be prepared and analyzed daily when the instrument is in use. Furthermore, reagent blanks should be prepared and analyzed after each extraction of a high-concentration sample (high part per million range). If reagent blanks continue to indicate contamination, even after replacement of the extraction vessel (and the restrictor, if a fixed restrictor system is used), then

the multi-port valve must be cleaned. The operator must be ever vigilant against impurities arising from liquid solvents and CO_2 itself. Avoid any apparatus, valves, solenoids, and other hardware that contain lubricants or chlorofluorohydrocarbon materials that can serve as background contaminant sources.

4.3 No modifier was employed in the development of this method for either PCBs or organochlorine pesticides. Use of a modifier may cause many other problems in these samples. If this method is modified by the user to include an on-line modifier, or pre-mixed tanks of CO_2 and modifier, considerable effort must be made to validate this change.

4.4 Refer to Method 3500 for general extraction interference guidance.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2 SFE involves the use of high pressure gases. Typical SFE systems have maximum operating pressures of approximately 400 atm (6000 psi). Great care must be taken to ensure that *all* components of the system are capable of withstanding such pressures.

5.3 SFE also involves heating portions of the system above ambient temperature, resulting in further increases in pressure. The combined effects of the starting pressure and temperature increase must be taken into account when evaluating the capabilities of system components.

5.4 SFE devices typically employ gases at high pressure directly from a tank, with no pressure regulator. In addition to making it difficult to monitor the level of gas in the tank, the lack of a regulator means that system leaks may involve gases at 2000 psi or more.

5.5 A safety feature to prevent over-pressurization is required on the extractor. This feature should be designed to protect the laboratory personnel and the instrument from possible injuries or damage resulting from equipment failure under high pressure.

5.6 When liquid CO_2 comes in contact with skin, it can cause "burns" because of its low temperature (-70 EC). Burns are especially severe when $C0_2$ is modified with organic liquids.

5.7 The extraction fluid usually exhausts through an exhaust gas and liquid waste port on the rear of the panel of the extractor. This port must be connected to a chemical fume hood to prevent contamination of the laboratory atmosphere.

5.8 Combining modifiers with supercritical fluids needs an understanding and evaluation of the potential chemical interaction between the modifier and the supercritical fluid, and between the supercritical fluid and/or modifier and the analyte(s) or matrix.

5.9 When CO_2 is used for cryogenic cooling, typical coolant consumption is 5 L/min, which results in a CO_2 level of 900 ppm for a room of 4.5 m x 3.0 m x 2.5 m, assuming 10 air exchanges per hr.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list common laboratory glassware (e.g., beakers and flasks).

6.1 Supercritical fluid extractor and associated hardware -- Any supercritical fluid extraction system that can achieve the extraction conditions and performance specifications detailed in this procedure may be used. Also see Figure 1 of Method 3561 for a schematic of a typical supercritical fluid extraction system.

WARNING: A safety feature to prevent over-pressurization is necessary on the extractor. This feature should be designed to protect the laboratory personnel and the instrument from possible injuries or damage resulting from equipment failure under high pressure.

6.1.1 Extraction vessel -- Stainless-steel vessel equipped with end fittings with 2-µm frits. Use the extraction vessel supplied by the manufacturer of the SFE system being used. The vessels may be constructed of stainless steel, polyether ether ketone (PEEK), or other suitable materials. Fittings used for the extraction vessel must be capable of withstanding the designated extraction pressures. The maximum operating pressure for most extractors is 400 atm. Pressures above 400 atm, especially at elevated temperatures, are likely to exceed the ratings of standard chromatography tubing and fittings. Check with the manufacturer of the particular extraction system and especially the tubing manufacturer for the maximum operating pressure and temperature for that system. Make sure that the extraction vessels are rated for such pressures and temperatures.

6.1.2 Restrictor -- This method was developed using continuously variable nozzle restrictors whereby the operator does not need to take steps to remove water from the sample. If a fixed restrictor is used, additional validation must be done to verify that moisture from the sample does not adversely affect the chromatography of the determinative step.

6.1.3 Collection device -- This method is based on a solid trap used at sub-ambient and above ambient temperatures for the different classes of analytes (PCBs vs. OCPs). However, a liquid (solvent) trap may also be used.

6.1.3.1 Use Florisil®, 30-40 µm particle diameter (commonly used in SPE cartridges), as a solid trap for the PCBs.

6.1.3.2 For organochlorine pesticides, octadecyl silane (ODS) may be used as a solid trap, although the use of Florisil® is also possible.

6.1.3.3 Analytes may be collected in a small volume of solvent in a suitable vial, however, great care must be taken to recover the most volatile compounds. The use of a glass wool plug in the inner tube of the collection vial improves recoveries. Gas flow must not be so high as to evaporate the collection solvent to dryness. A 15-mL collection solvent volume is recommended.

6.2 CO_2 cylinder balance (optional) -- Balances from Scott Specialty Gases, Model 5588D, or equivalent, may be used to monitor the fluid usage. Such a device is useful because CO_2 tanks used for SFE are not equipped with regulators, and it is difficult to determine when the tank needs to be replaced.

6.3 Glass microfiber filter paper disks -- Cored out of Whatman QF/F filter paper (Whatman No. 1825021), or equivalent. A disk is placed at both ends of the sample. This ultra-fine filter paper has good retentive properties for particulate matter down to 0.7 µm and is easy to core. The normal background is insignificant, but blanks need to be run on each batch.

7.0 REAGENTS AND STANDARDS

7.1 Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that 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. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

7.2 CO_2 -- SFE-grade CO_2 is absolutely necessary for use in SFE. Aluminum cylinders are preferred to steel cylinders. The cylinders must be fitted with eductor tubes.

7.3 CO_2 for cryogenic cooling -- Certain parts of some models of extractors (i.e., the high-pressure pump head and the analyte trap) must be cooled during use. The CO_2 used for this purpose must be supplied in tanks with a full-length eductor tube, but need not be SFE-grade. A low-cost industrial grade is acceptable.

7.4 Reconstitution solvents -- The reconstitution solvents dispensed by the SFE instruments that use solid-phase trapping may be the same solvent that is used for liquid trapping. This method was developed with only sub-ambient solid trapping. Liquid trapping will work for this method as well. However, the trapping volume is typically ten times larger than that with a solid trap. Further, the use of liquid trapping will likely necessitate the use of manual Florisil® or silica cleanup. These manual cleanup steps will also make it necessary to concentrate the solvent after the cleanup, a step that can be avoided through use of solid-phase trapping.

7.5 Internal standards -- Refer to the appropriate determinative method for information of the choice of internal standards, where applicable. However, note that for PCBs, certain ethers work well as internal standards, but do not survive the SFE extraction particularly well.

7.5.1 Internal standards for PCBs -- Internal standards that have been evaluated using this method include PCB 35, PCB 36, PCB 169, 2,4-dichlorobenzyl hexyl ether, 2,4-dichlorobenzyl heptyl ether, 1,2,3,4-tetrachloronaphthalene, hexabromobenzene, and octachloronaphthalene.

7.5.2 Internal standard for organochlorine pesticides -- Pentachloronitrobenzene

7.6. Surrogate standards -- Refer to the appropriate determinative method for information of the choice of surrogates. Surrogates that have been evaluated using this method include hexabromobenzene, PCB 35, PCB 36, PCB 169, 1,2,3,4-tetrachloronaphthalene, and octachloronaphthalene. Prepare a stock solution of 10 mg/mL. Apply 150-µL aliquots to the soil samples within the extraction vessels at the exit end of the flow-through vessels. It has

been observed that a very small volume (10 µL) of a concentrated surrogate mixture often gives poor recoveries, while adding a larger volume of more dilute surrogate standard to the sample matrix achieved the expected recoveries.

7.7 Copper powder -- Electrolytic grade. Added to samples that contain elemental sulfur. The powder is pretreated by rinsing 20 g with 150 mL organic-free reagent water, 150 mL acetone, 150 mL of hexane, and drying in a rotary evaporator. The powder is kept under argon or helium until used. Copper powder must have a shiny bright appearance to be effective. If it has oxidized and turned dark, it should not be used.

7.8 Sodium sulfate, Na_2SO_4 -- Anhydrous (12-60 mesh), Baker Analyzed grade, or equivalent.

7.9 Celite® 545 -- 60/80 mesh, J. T. Baker, or equivalent. Prepare a reagent blank to assure that no background contaminants are present.

7.10 Elution solvents -- Used for eluting the analytes of interest from the solid trapping material and rinsing the trapping material prior to reuse.

The choice of solvent will depend on the analytes of interest and no single solvent is universally applicable to all analyte groups. Whatever solvent system is employed, *including* those specifically listed in this method, the analyst *must* demonstrate adequate performance for the analytes of interest, at the levels of interest. At a minimum, such a demonstration will encompass the initial demonstration of proficiency described in Method 3500, using a clean reference matrix. Method 8000 describes procedures that may be used to develop performance criteria for such demonstrations as well as for matrix spike and laboratory control sample results.

All solvents should be pesticide-grade or equivalent. Solvents may be degassed prior to use.

7.10.1 n-Heptane, C_7H_{16}

7.10.2 Methylene chloride, CH_2Cl_2

7.10.3 Acetone, CH_3COCH_3

7.11 Florisil® -- Pesticide residue grade.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to Chapter Four, "Organic Analytes," Method 3500, and the specific determinative methods to be employed.

8.2 Solid samples to be extracted by this procedure should be collected and stored as any other solid samples containing semivolatile organics.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter

One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Initial demonstration of proficiency

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

9.3 Initially, before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a method blank. As a continuing check, each time samples are extracted, cleaned up, and analyzed, and when there is a change in reagents, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination.

9.4 Any method blanks, matrix spike samples, or replicate samples should be subjected to the same analytical procedures (Sec. 11.0) as those used on actual samples.

9.5 Standard quality assurance practices should be used with this method as included in appropriate systematic planning documents and laboratory SOPs. All instrument operating conditions should be recorded.

9.6 Also refer to Method 3500 for extraction and sample preparation quality control procedures and the determinative methods to be used for determinative QC procedures.

9.7 When listed in the appropriate determinative method, surrogate standards should be added to all samples prior to extraction. See Methods 3500 and 8000, and the appropriate determinative methods for more information.

9.8 As noted earlier, use of any extraction technique, including supercritical fluid extraction, should be supported by data that demonstrate the performance of the specific extraction fluid(s) and operating conditions for the analytes of interest, at the levels of interest, in the sample matrix.

10.0 CALIBRATION AND STANDARDIZATION

There are no calibration or standardization steps directly associated with this sample extraction procedure, other than establishing the extraction conditions in Sec. 11.7.

11.0 PROCEDURE

11.1 Sample handling -- Decant and discard any water layer on a sediment sample. Discard any foreign objects such as pieces of wood, glass, leaves and rocks.

11.2 Determination of percent dry weight -- When sample results are to be calculated on a dry weight basis, a separate portion of sample for this determination should be weighed out at the same time as the portion used for analytical determination.

CAUTION: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

11.2.1 Immediately after weighing the sample aliquot to be extracted, weigh an additional 5 - 10 g aliquot of the sample into a tared crucible. Dry this aliquot overnight at 105 EC. Allow to cool in a desiccator before weighing.

11.2.2 Calculate the % dry weight as follows:

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

This oven-dried aliquot is not used for the extraction and should be appropriately disposed of once the dry weight is determined.

11.3 Safety considerations -- Read Sec. 5.0, "Safety," before attempting to perform this procedure.

11.4 Sample grinding and homogenization

NOTE: Sample grinding is a critical step in the SFE process. The soil/solid must be a fine particle to ensure efficient extraction.

11.4.1 Mix at least 100 g of sample with an equal volume of CO_2 solid "snow" prepared from the extraction grade CO_2. Place this mixture in a small food-type chopper, and grind for 2 min. Place the chopped sample on a clean surface and allow the CO_2 to sublime away. As soon as the sample appears free-flowing and solid CO_2 is no longer visible, weigh the sample and place it in the extraction vessel. This procedure will ensure the homogeneity of the sample without loss of the volatile analytes and also retains the original moisture content of the sample.

11.4.2 Weigh 1.0 to 5.0 g of the homogenized sample from Sec. 11.4.1 into a pre-cleaned aluminum dish. For samples in the mg/kg (ppm) concentration range, use a 0.1-g sample after carefully homogenizing (Sec. 11.4.1) the bulk sample, to avoid sub-sampling errors.

11.5 For samples known to contain elemental sulfur, use copper powder (Sec. 7.7) to remove the dissolved sulfur from the sample and CO_2 eluant. The copper powder (1 to 2 g per sample) can be mixed with the sample in the extraction vessel itself, or packed in a separate vessel between the extraction vessel and the nozzle (restrictor). The addition of copper to samples is a useful precaution, whether or not one suspects the presence of elemental sulfur. In tests, no adverse effect from the addition of copper was observed and it appears that finely

divided copper may enhance the dispersion of CO_2. If copper powder is added to the samples, it must also be added to the method blank.

11.6 Packing the extraction cell

The procedure used for a 7.0-mL SFE extraction vessel with sample and copper powder is as follows:

11.6.1 Place a small disk of fiber glass filter paper at the bottom of the extraction vessel to protect the end frits from particulate matter (this makes the cleanup very easy between samples and lessens any chance of plugging of the frits).

11.6.2 Place approximately 2 g of anhydrous sodium sulfate on top of this disk in the extraction vessel. Weigh 1.0 g of solid waste sample into a weighing dish. Add 2 g of electrolytic grade copper powder to the same weighing dish, followed by 7 g of anhydrous sodium sulfate. Mix the weighed material. Transfer the entire homogeneous mixture to the extraction vessel on top of the existing small layer of sodium sulfate. Finally, place a top layer (2 g) of sodium sulfate on top of the mixture. The densities of the respective materials are such that this still leaves a small volume at the top of a 7-mL vessel. These ratios may be adjusted for different sample sizes and vessel sizes, but should be kept consistent among samples and blanks.

11.6.3 If a surrogate is being added, transfer half of the weighed sample to the extraction vessel. Add 150 µL of surrogate standard to the sample in the vessel and then add the remainder of the sample material.

11.6.4 To ensure efficient extraction, fill the extraction vessel completely, avoiding any dead volume. If any dead volume remains, fill the space with an inert, porous material, e.g., pre-cleaned Pyrex glass wool, Celite®, etc.

11.7 Sample extraction conditions

11.7.1 Recommended conditions for PCBs

11.7.1.1 Extraction conditions

Pressure:	4417 psi (305 bar)
Extraction chamber temperature:	80 EC
Density:	0.75 g/mL
Extraction fluid composition:	CO_2
Static equilibration time:	10 min
Dynamic extraction time:	40 min
Extraction fluid flow rate:	2.5 mL/min

The resultant thimble volume swept is 17.6 times the volume of the cell at 1 bar (this is equivalent to 100 mL of liquid CO_2 at a reference temperature of 4.0 EC and a density of 0.92 g/mL, or 92 g of CO_2).

11.7.1.2 Collection conditions (during extraction)

Trap packing:	Florisil®
Trap temperature:	15 - 20 EC
Nozzle temperature:	45 - 55 EC (variable restrictor)

11.7.1.3 Reconstitution conditions for collected extracts

The reconstitution process consists of four rinse steps. The first rinse is used to elute the analytes of interest from the trapping material. All four rinse steps are performed with a recommended trap temperature of 38 EC, a nozzle temperature of 30 EC, and a flow rate of 1.0 mL/min.

Rinse substep 1:

Rinse solvent	n-Heptane
Collected rinse volume:	1.6 mL

Rinse substep 2 – This second rinse step is an "insurance rinse." The vial is usually not analyzed unless there is a need or desire to assure that the entire sample is rinsed in substep 1:

Rinse solvent	n-Heptane
Collected rinse volume:	1.6 mL

Rinse substep 3 – This third rinse step provides a means of rinsing the solid Florisil® trap to remove interfering compounds such as lipids, hydrocarbons, and PAHs. The rinse solvent is then discarded:

Rinse solvent	Methylene chloride:acetone (1:1)
Collected rinse volume:	4.0 mL (to waste)

Rinse substep 4 – This fourth rinse step provides a means of regenerating the solid Florisil® trap to prepare it (reactivate) for reuse:

Rinse solvent	n-Heptane
Collected rinse volume:	3.0 mL (to waste)

11.7.2 Recommended conditions for organochlorine pesticides

11.7.2.1 Extraction conditions

Pressure:	4330 psi (299 bar)
Extraction chamber temperature:	50 EC
Density:	0.87 g/mL
Extraction fluid composition:	CO_2
Static equilibration time:	20 min
Dynamic extraction time:	30 min
Extraction fluid flow rate:	1.0 mL/min

The resultant thimble volume swept is 4.6 times the volume of the cell at 1 bar (this is equivalent to 30 mL of liquid CO_2 at a reference temperature of 4.0 EC and a density 0.92 g/mL, or 28 g of CO_2).

11.7.2.2 Collection conditions (during extraction)

Trap packing:	ODS
Trap temperature:	20 EC
Nozzle temperature:	50 EC (variable restrictor)

11.7.2.3 Reconstitution conditions for collected extracts

The extraction of organochlorine pesticides utilizes only a single rinse step.

Rinse solvent:	n-Hexane
Collected fraction volume:	1.3 mL
Trap temperature:	50 EC
Nozzle temperature:	30 EC (variable restrictor)
Rinse solvent flow rate:	2 mL/min

NOTE: If a fixed restrictor and liquid trapping are used, a restrictor temperature between 100 EC and 150 EC is recommended.

11.8 Label the extract with the fraction designation and vial number.

11.9 If the copper powder was not added to the sample prior to loading the cell, additional sulfur cleanup of the extracts may be necessary prior to analysis.

11.10 SFE system maintenance

11.10.1 Depressurize the system following the manufacturer's instructions.

11.10.2 After extraction of an especially "tarry" sample, the end-frits of the extraction vessel may need extensive cleanup or replacement to ensure adequate flow of extraction fluid without an excessive pressure drop. In addition, very fine particles may clog the exit frit, necessitating its replacement. By placing a layer of inert material such as Celite® or sand between the sample and the exit frit (and placing disks of filter paper or glass fiber filter on top of the inert material), this maintenance may be delayed.

11.10.3 Clean the extraction vessel after each sample extraction. The cleaning procedure depends upon the type of sample. After removing the bulk of the extracted sample from the extraction vessel, the cell and end-frits should be scrubbed with a solution of detergent and water using a stiff brush. Placing the parts in an ultrasonic bath with a warm detergent solution may help. Rinse the parts with organic-free reagent water. Repeat the ultrasonic bath treatment with either methyl alcohol, or acetone, or both, followed by air drying.

12.0 DATA ANALYSIS AND CALCULATIONS

There are no calculations explicitly associated with this extraction procedure. See the appropriate determinative method for the calculation of final sample results.

13.0 METHOD PERFORMANCE

13.1 Refer to the appropriate determinative method for performance data examples and guidance. Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance goals for users of the methods. Instead, performance goals should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 Tables in Method 8081 contain example single laboratory performance data for the organochlorine pesticides using supercritical fluid extraction according to this method. Sample extracts were analyzed using an HP 7680, GC/ELCD. The method was performed using a variable restrictor and solid trapping material. Three different soil samples were spiked at 5 and 250 ug/kg. Soil 1 (Delphi) is described as loamy sand, with 2.4% clay, 94% sand, 0.9% organic matter, 3.4% silt, and 0.1% moisture. Soil 2 (McCarthy) is described as sandy-loam, with 11% clay, 56% sand, 22% organic matter, 33% silt, and 8.7% moisture. Soil 3 (Auburn) is described as clay loam, with 32% clay, 21% sand, 5.4% organic matter, 46% silt, and 2.2% moisture. Seven replicate extractions were made of each soil at the 2 concentrations. These data are provided for guidance purposes only.

13.3 Tables in Method 8082 contain laboratory performance data for several PCB congeners using supercritical fluid extraction according to this method followed by analysis using an HP 7680, GC/ELCD. Seven replicate extractions on each sample were performed. The method was performed using a variable restrictor and solid trapping material (Florisil®). The following soil samples were used for this study:

13.3.1 Two field-contaminated certified reference materials were extracted by a single laboratory. One of the materials was a lake sediment from Environment Canada (EC-5). The other material was soil from a dump site and was provided by the National Science and Engineering Research Council of Canada (EC-1). The average recoveries for EC-5 are based on the certified value for that sample. The average recoveries for EC-1 are based on the certified value of the samples or a Soxhlet value, if a certified value was unavailable for a specific analyte. These data are provided for guidance purposes only.

13.3.2 Four certified reference materials were extracted by two independent laboratories. The materials included a marine sediment from NIST (SRM 1941), a fish tissue from NIST (SRM 2974), a sewage sludge from BCR European Union(CRM 392), and a soil sample from BCR European Union (CRM 481). The average recoveries are based on the certified value of the samples or a Soxhlet value, if a certified value was unavailable for a specific analyte. These data are provided for guidance purposes only.

13.3.3 A weathered sediment sample from Michigan (Saginaw Bay) was extracted by a single laboratory. Soxhlet extractions were carried out on this sample and the SFE recovery is relative to that for each congener. The average recoveries are based on the certified value of the samples. Additional data is shown in the tables for some congeners that were not certified. These data are provided for guidance purposes only.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical management for Waste*

Reduction available from the American Chemical Society, Department of Government Relations and Science Policy, 1155 16th Street, NW, Washington, DC, 20036, http://www.acs.org.

14.3 Extraction of organic compounds using supercritical fluid extraction conforms with EPA's pollution prevention goals. The volumes of solvent employed, if any, are significantly smaller than with other extraction procedures. Minimal waste is generated.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. D. Gere, "Final Deliverables for PCB/OCP SFE Draft Method," letter to B. Lesnik, April 15, 1995.

17.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

There are no tables or figures associated with this method. The following page contains a glossary of terms specific to this procedure.

1. Dynamic extraction -- An application of SFE in which the supercritical extraction fluid flows through the sample and out of the extraction cell to a collection device during the extraction. Dynamic extraction is contrasted with static extraction (see below).

2. Modifier -- A liquid or gaseous component added to the supercritical fluid to change its extraction capabilities, often through changes in the solvation power of the extraction fluid. Modifiers may be polar or nonpolar.

3. Supercritical fluid -- A gas maintained above its critical temperature through the application of pressure.

4. Supercritical fluid extraction (SFE) -- The use of a gas maintained above its critical temperature as an extraction fluid.

5. Static extraction -- An application of SFE in which the supercritical extraction fluid is held in the extraction vessel during the entire procedure, and is then released to a collection device. Static extraction is contrasted with dynamic extraction (see above).