METHOD 3545A

PRESSURIZED FLUID EXTRACTION (PFE)

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 is a procedure for extracting water insoluble or slightly water soluble organic compounds from soils, clays, sediments, sludges, and waste solids. This method uses elevated temperature (100-180 EC) and pressure (1500-2000 psi) to achieve analyte recoveries equivalent to those from Soxhlet extraction, using less solvent and taking significantly less time than the Soxhlet procedure. This procedure was developed and validated on a commercially-available, automated extraction system.

1.2 This method is applicable to the extraction of semivolatile organic compounds, organophosphorus pesticides, organochlorine pesticides, chlorinated herbicides, polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs/PCDFs), and diesel range organics (DRO), which may then be analyzed by a variety of chromatographic procedures. The quantitative analysis of DRO is operationally defined on the basis of the retention times of characteristic components. This definition can be found in Method 8015. This method may also be applicable for the extraction of additional target analytes, provided that the analyst demonstrates adequate performance for the intended application (see Method 3500 and Chapter Two).

1.3 This method has been validated for solid matrices containing from 250 to 12,500 µg/kg of semivolatile organic compounds, 250 to 2500 µg/kg of organophosphorus pesticides, 5 to 250 µg/kg of organochlorine pesticides, 50 to 5000 µg/kg of chlorinated herbicides, 1 to 1400 µg/kg of PCBs, 1 to 2500 ng/kg of PCDDs/PCDFs, and 5 to 2000 mg/kg of DRO.

This method may be applicable to samples containing these analytes at higher concentrations and may be employed after adequate performance has been demonstrated for the concentrations of interest (see Method 3500). It may also be applicable to classes of analytes, to fuel types, and to petroleum fractions other than those listed in Sec 1.2. However, in order to be used for additional analytes, fuel types, petroleum fractions, or different concentrations, the analyst must demonstrate that the extraction conditions are appropriate for the analytes of interest. The analyst must also perform the initial demonstration of proficiency described in Sec. 9.3 and Methods 3500 and 8000. If this method is expanded to address other fuel types or petroleum hydrocarbons, the boiling point range or carbon number range of the material also needs to be carefully defined and the quantitation approach be modified to match

such ranges. Analysts are advised to consult authoritative sources, such as the American Petroleum Institute (API), for appropriate definitions of other fuel types or petroleum fractions.

NOTE: Mention of the analyses of other fuel types and petroleum fractions does *not* imply a regulatory requirement for such analyses, using this or any other method.

1.4 This method is only applicable to solid samples, and is most effective on dry materials with small particle sizes. Therefore, waste samples must undergo phase separation, as described in Chapter Two, and only the solid-phase material is to be extracted by this procedure. If possible, soil/sediment samples may be air-dried and ground to a fine powder prior to extraction. Alternatively, if worker safety or the loss of analytes during drying is a concern, soil/sediment samples may be mixed with anhydrous sodium sulfate or pelletized diatomaceous earth. (Drying and grinding samples containing PCDDs/PCDFs is *not* recommended, due to safety concerns.) The total mass of material to be prepared depends on the specifications of the determinative method and the sensitivity necessary for the analysis, but an amount of 10-30 g of material is usually necessary and can be accommodated by this extraction procedure.

1.5 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.

1.6 Use of this method is restricted to use by, or under the 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 Samples are prepared for extraction either by air drying and grinding, or by mixing the samples with anhydrous sodium sulfate or pelletized diatomaceous earth. The sample is then loaded into the extraction cell.

WARNING: The drying and grinding of samples containing PCDDs/PCDFs is *not* recommended, due to safety concerns. Grinding may also be a concern for other more volatile analytes (see Sec. 11.1).

2.2 The extraction cell containing the sample is heated to the extraction temperature (see Sec. 11.8), pressurized with the appropriate solvent system, and extracted for 5-10 minutes (or as recommended by the instrument manufacturer). Multiple extractions are

recommended for some groups of analytes. The solvent systems used for this procedure vary with the analytes of interest and are described in Sec. 7.7.

2.3 The solvent is collected away from the heated extraction vessel and allowed to cool. Since the extraction cells contain frits, no filtration of the extracts is needed. However, for the extraction of very wet samples (e.g., $30% moisture), it may be necessary that the extract be dried with sodium sulfate (see note in Sec. 11.6).

2.4 The extract may be concentrated, if necessary, and, as needed, exchanged into a solvent compatible with the cleanup or determinative step being employed.

3.0 DEFINITIONS

Refer to Chapter One and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware 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. 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 Refer to Method 3500 for information regarding interferences.

4.3 If necessary, Florisil and/or sulfur cleanup procedures may be employed. In such cases, proceed with Method 3620 and/or Method 3660.

4.4 Samples for PCDD/PCDF analysis should be subjected to the various cleanup procedures described in the determinative methods (Methods 8280 and 8290).

4.5 Samples for the analysis of DRO may be subjected to a sodium sulfate/silica gel cleanup procedure to remove non-petroleum hydrocarbon interferences (see Sec. 11.12.2).

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 The use of organic solvents, elevated temperatures, and high pressures in this method present potential safety concerns in the laboratory. Common sense laboratory practices can be employed to minimize these concerns. The sections to follow describe additional steps that should be taken.

5.3 Extraction cells in the oven are hot enough to burn unprotected skin. Allow the cells to cool for 10-15 min before removing them from the oven or use appropriate protective equipment (e.g., insulated gloves or tongs), as recommended by the manufacturer.

5.4 During the gas purge step, some solvent vapors may exit through a vent port in the instrument. Follow the manufacturer's directions regarding connecting this port to a fume hood or other means to prevent release of solvent vapors to the laboratory atmosphere.

5.5 The instrument may contain flammable vapor sensors and should be operated with all covers in place and doors closed to ensure proper operation of the sensors. Follow the manufacturer's directions regarding replacement of extraction cell seals to ensure against vapor leaks.

5.6 The drying or grinding of samples for PCDDs/PCDFs generally is not recommended due to safety concerns regarding worker exposure to analytes.

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 Pressurized fluid extraction device

6.1.1 Dionex Accelerated Solvent Extractor® with appropriately-sized extraction cells. Currently, cells are available that will accommodate 1-g, 5-g, 10-g, 20-g and 30-g samples. Cells should be made of stainless steel or other material capable of withstanding the pressure levels (2000+ psi) necessary for this procedure.

6.1.2 Other system designs may be employed, provided that adequate performance can be demonstrated for the analytes and matrices of interest.

6.2 Apparatus for determining percent dry weight

6.2.1 Drying oven

6.2.2 Desiccator

6.2.3 Crucibles, porcelain or disposable aluminum

6.3 Apparatus for grinding, capable of reducing particle size to < 1 mm.

6.4 Analytical balance, capable of weighing to 0.01 g.

6.5 Vials for collection of extracts -- 40-mL or 60-mL, pre-cleaned, open-top screw-cap with polytetrafluoroethylene (PTFE)-lined silicone septum (Dionex 049459, 049460, 049461, 049462 or equivalent).

6.6 Filter disk -- 1.983-cm, cellulose or glass fiber (Dionex 049458 or 047017, or equivalent).

6.7 Cell cap sealing disk (Dionex 49454, 49455, or equivalent).

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 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

7.3 Drying agents

7.3.1 Sodium sulfate (granular anhydrous), Na_2SO_4.

7.3.2 Pelletized diatomaceous earth.

7.3.3 The drying agents should be purified by heating at 400 EC for 4 hrs in a shallow tray, or by extraction with methylene chloride. If extraction with methylene chloride is employed, then a reagent blank should be prepared to demonstrate that the drying agent is free of interferences.

7.3.4 See the note in Sec. 11.6 regarding the use of drying agents for very wet samples (#30% moisture).

7.4 Quartz sand -- Clean sand may be used to facilitate grinding of some sample matrices, to fill void volumes in the extraction cell, and to increase the flow of solvent through the sample. It may be prepared as described in Sec. 7.3.3. Sand with a small particle size should not be used, as the fine particles can stick to the threads of the cell, resulting in leaks and damage to the threads. Ottawa sand, with a particle size of 20-30 mesh, has been found to work well and it is readily available from suppliers (e.g., Fisher Scientific, S23-3, or equivalent).

7.5 Silica gel for DRO cleanup -- 100/200 mesh, Davisil sorbent, Grade 634 (60 A pores) or equivalent. Before use, activate for at least 16 hrs at 130 EC in a shallow glass tray, loosely covered with foil.

7.6 Acids

7.6.1 Phosphoric acid solution used for extraction of chlorinated herbicides (see Sec. 7.7.5). Prepare a 1:1 (v/v) solution of 85% phosphoric acid (H_3PO_4) in organic-free reagent water.

7.6.2 Trifluoroacetic acid solution used for extraction of chlorinated herbicides (see Sec. 7.7.5). Prepare a 1% (v/v) solution of trifluoroacetic acid in acetonitrile.

7.6.3 Glacial acetic acid used for extraction of PCDDs/PCDFs (see Sec. 7.7.6).

7.7 Extraction solvents

Samples should be extracted using a solvent system that gives optimum, reproducible recovery of the analytes of interest from the sample matrix, at the concentrations of interest. The choice of extraction 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.

Many of the solvent systems described below include the combination of a water-miscible solvent, such as acetone, and a water-immiscible solvent, such as methylene chloride or hexane. The purpose of the water-miscible solvent is to facilitate the extraction of wet solids by allowing the mixed solvent to penetrate the layer of water on the surface of the solid particles. The water-immiscible solvent extracts organic compounds with similar polarities. Thus, a non-polar solvent such as hexane is often used for non-polar analytes such as PCBs, while a polar solvent such as methylene chloride may be used for polar analytes. The polarity of acetone may also help extract polar analytes in mixed solvent systems.

CAUTION: When extracting very wet samples (e.g., $30% moisture), large amounts of water may be collected along with the extracts if a mixed solvent containing acetone is used (also see the first note of Sec. 11.6).

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

7.7.1 Organochlorine pesticides may be extracted with acetone/hexane (1:1, v/v), CH_3COCH_3/C_6H_{14}, or acetone/methylene chloride (1:1, v/v), CH_3COCH_3/CH_2Cl_2.

7.7.2 Semivolatile organics may be extracted with acetone/methylene chloride (1:1, v/v), CH_3COCH_3/CH_2Cl_2, or acetone/hexane (1:1, v/v), CH_3COCH_3/C_6H_{14}.

7.7.3 PCBs may be extracted with acetone/hexane (1:1, v/v), CH_3COCH_3/C_6H_{14}, acetone/methylene chloride (1:1, v/v), CH_3COCH_3/CH_2Cl_2, or hexane, C_6H_{14}.

7.7.4 Organophosphorus pesticides may be extracted with methylene chloride, CH_2Cl_2, or acetone/methylene chloride (1:1, v/v), CH_3COCH_3/CH_2Cl_2.

7.7.5 Chlorinated herbicides may be extracted with an acetone/methylene chloride/phosphoric acid solution (250:125:15, v/v/v), $CH_3COCH_3/CH_2Cl_2/H_3PO_4$, or an acetone/methylene chloride/trifluoroacetic acid solution (250:125:1, v/v/v), $CH_3COCH_3/CH_2Cl_2/CF_3COOH$. (If the second option is used, the trifluoroacetic acid solution should be prepared by mixing 1% trifluoroacetic acid in acetonitrile.) Make fresh solutions before each batch of extractions.

7.7.6 PCDDs/PCDFs may be extracted with toluene, $C_6H_5CH_3$. Fly ash samples to be extracted for PCDDs/PCDFs may be extracted with a toluene/acetic acid solution (5% v/v glacial acetic acid in toluene) in lieu of the HCl pretreatment described in Methods 8280 and 8290.

7.7.7 DRO may be extracted with acetone/methylene chloride (1:1, v/v), CH_3COCH_3/CH_2Cl_2, acetone/hexane (1:1, v/v), CH_3COCH_3/C_6H_{14}, or acetone/heptane (1:1, v/v), CH_3COCH_3/C_7H_{16}.

7.7.8 Other solvent systems may be employed, provided that the analyst can demonstrate adequate performance for the analytes of interest in the sample matrix (see Sec. 7.7 above and Method 3500).

7.8 High-purity gases such as nitrogen, carbon dioxide, or helium are used to purge and/or pressurize the extraction cell. Follow the instrument manufacturer's recommendation for the choice of gases.

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 like 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 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. For this method, this can be accomplished through the analysis of a solid matrix method blank (e.g., clean sand). 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 QC 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 pressurized fluid extraction, should be supported by data that demonstrate the performance of the specific solvent system and operating conditions for the analytes of interest, at the levels of interest, and 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. 11.9.

11.0 PROCEDURE

11.1 Sample preparation

As is the case for many other extraction procedures, pressurized fluid extraction performs best on dry, finely-ground solids. However, the processes of sample drying and grinding involve the potential for a loss of analytes, the introduction of other contaminants into the sample, the contamination of the laboratory environment, and exposure of the analyst to environmental contaminants. Therefore, the analyst must determine the most appropriate approach to be used for each combination of sample matrix and analytes of interest, balancing analytical accuracy, practicality, and worker safety. No single approach should be expected to work for all matrices or analytes. The following sections describe the general procedures that may be applied to different matrices, types of solid samples, and/or samples for specific classes of analytes.

WARNING: *The drying or grinding of samples for PCDDs/PCDFs generally is not recommended, due to safety concerns regarding worker exposure to these analytes.*

11.1.1 Sediment/wet soil samples

Decant and discard any water layer on a sediment sample. Discard any foreign objects such as sticks, leaves, and rocks. Mix the sample thoroughly, especially composited samples. When practical, air dry the sample at room temperature for 48 hrs in a glass tray or on hexane-rinsed aluminum foil. See the note in Sec. 11.6.

CAUTION: Dry, finely-ground soil/sediment allows the best extraction efficiency for nonvolatile, non-polar organic compounds, e.g., 4,4'-DDT, PCBs, etc. Air-drying may not be appropriate for the analysis of the more volatile organochlorine pesticides (e.g., the BHCs) or the more volatile of the semivolatile organic compounds, because of losses during the drying process. Worker safety may be an issue with the drying of soils containing PCDDs/PCDFs as well. Oven-drying during this step is not recommended for any analytes.

CAUTION: Drying should always be performed in a hood, to avoid contamination of the laboratory.

11.1.2 Waste samples

Multiphase waste samples must be prepared by the phase separation method in Chapter Two before extraction. *This extraction procedure is for solids only.*

11.1.3 Dry sediment/soil and dry waste samples amenable to grinding

Visually inspect the samples to determine approximate particle size. For many samples, pretreatment prior to loading into the extraction cells is not necessary, other than mixing with diatomaceous earth. If the sample particle size is too large, grind or otherwise reduce the particle size of the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole, using the procedures described in Sec. 11.2.

CAUTION: The first caution in Sec. 11.1.1 also applies to the grinding process.

11.1.4 Gummy, fibrous, or oily materials not amenable to grinding

Cut, shred, or otherwise reduce in size the samples to allow mixing and maximum exposure of the sample surfaces for the extraction. If necessary, mix drying agents in the samples to make them more amenable to grinding, as described in Sec. 11.2.

11.1.5 Carefully mix solid samples for PCDD/PCDF analysis, breaking up lumps with a spatula or other suitable tool.

11.1.6 Fly ash samples may be pretreated with an HCl solution prior to extraction (see Method 8280 or 8290). Alternatively, the samples may be extracted with the toluene/acetic acid solution described in Sec. 7.7.6. Fly ash samples do not need grinding.

11.2 Sample grinding

11.2.1 If the sample was air-dried (see Sec. 11.1.1) or was already dry enough for grinding (see Sec. 11.1.3), then grind at least enough of the sample to yield the sample weight needed for the determinative method (usually 10-30 g). Grind the sample until it passes through a 10-mesh sieve.

WARNING: *Grinding of samples for PCDDs/PCDFs generally is not recommended, due to safety concerns with samples containing these analytes.*

11.2.2 For gummy, fibrous, or oily materials, the analyst may add anhydrous sodium sulfate, pelletized diatomaceous earth, sand, or other clean, dry reagents to the sample to make it more amenable to grinding. Grind the sample until it passes through a 10-mesh sieve.

NOTE: If this approach is used, then in order to obtain accurate results, the weights of the sample aliquot and the drying agent must be carefully measured prior to mixing and the total volume of the combined material must not exceed the capacity of the extraction cell. Otherwise, it will not be possible to determine the weight of the actual field sample that was extracted.

11.2.3 Disassemble the grinder between samples, according to the manufacturer's instructions, and wash it with soap and water, followed by acetone and hexane rinses. Other cleaning procedures may be employed, provided that the analyst can demonstrate through the analysis of method blanks that the procedures are effective at preventing cross-contamination between samples.

11.3 Weighing the sample

If the sample was ground, then weigh the appropriate aliquot of the ground sample needed for the determinative method and the sensitivity needed for the project into the extraction cell of the appropriate size for the aliquot plus any other reagents, or into another clean container. For samples for PCDD/PCDF analysis and other samples that have not been ground, weigh the appropriate aliquot of the well-homogenized sample into the extraction cell or other clean container.

NOTE: The weight of a specific sample that a cell will contain depends on the bulk density of the sample and the amount of drying agent that must be added to the sample in order to make it suitable for extraction. Generally, an 11-mL cell will hold about 10 g of material, a 22-mL cell will hold about 20 g of material, and a 33-mL cell will hold about 30 g of material. Analysts should ensure that the sample aliquot extracted is large enough to provide the necessary sensitivity and choose the extraction cell size accordingly.

If the sample is weighed in the extraction cell, then prepare the cell by placing a disposable cellulose or glass fiber filter in the cell outlet before adding the sample. Record the weight of the empty cell and the weight of the sample and the cell. Determine the weight of the sample by difference.

11.4 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 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 drying a heavily contaminated sample.

Immediately after weighing the sample for extraction, weigh an additional 5- to 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. 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.

11.5 Adding surrogates and other spiked compounds

Add the surrogates (or labeled internal standards for PCDDs/PCDFs) listed in the determinative method to each sample in its extraction cell or in another clean container. Consult Method 3500 and the determinative method for information on appropriate surrogates and internal standards.

Stir the mixture well and allow it to stand while the spiking solvent evaporates. Add the matrix spike/matrix spike duplicate compounds listed in the determinative method to the two additional aliquots of the sample selected for spiking.

CAUTION: The utility of the data for the matrix spike compounds, as well as the surrogates and any other compounds spiked into any sample, depends on the degree to which the spiked compounds mimic the compounds already present in a field sample. Therefore, it is CRITICAL that any compounds added to a sample, including the surrogates, are added to the sample aliquot PRIOR TO any additional processing steps. This means that the matrix spike and surrogate compounds should be added to the sample PRIOR TO adding drying agents such as sodium sulfate to solid samples. It is also CRITICAL that the spiked compounds be in the same chemical form as the target compounds, e.g., DO NOT spike the methyl esters of the phenoxy acid herbicides, but rather, spike the phenoxy acids themselves.

11.6 After spiking the surrogates or other compounds, if needed, add sufficient drying agent to the sample in order to make it suitable for extraction (see the note in Sec. 11.3). Some samples may not need any drying agent. Very wet samples may need twice the weight of the sample in drying agent. Carefully mix the sample and the drying agent in the cell, using a clean spatula or other suitable tool.

If the sample was spiked in a container other than the extraction cell, then add a weighed amount of the drying agent to that container and carefully mix it with the sample. Weigh the empty cell, transfer the mixture to the cell, and reweigh the cell. Determine the weight of the

sample *plus* the drying agent by difference. Determine the weight of the actual sample by assuming that the mixture that was transferred to the cell was composed of the original ratio of sample material and drying agent (e.g., if the mixture was made of 10 g of sample and 12 g of drying agent, then assume that 10/22th of the material in the cell is the original sample).

NOTE: The use of sodium sulfate as a drying agent with very wet samples (e.g., $30% moisture) can lead to clogging of the frits in the cell with recrystallized sodium sulfate, particularly if a mixed solvent containing acetone is used. In these cases, pelletized diatomaceous earth and not sodium sulfate should be used as a drying agent. (Alternatively, pelletized diatomaceous earth may be used as a drying agent in the cell in place of sodium sulfate for all levels of moisture.) For very wet samples, regardless of the drying agent used, it will be necessary to add sodium sulfate to the vials after collection and to pass the extracts through a drying column or drying cartridge to dry the extract completely. Due to the high temperatures used, more water will be coextracted than with other extraction procedures. The analyst must make sure that adequate attention is given to rinsing the sodium sulfate in the vial and the clean up column to ensure good analyte recovery (see Secs. 11.12.1 and 11.12.2).

If no drying agent is needed, then clean sand may be used to fill any void volume in the extraction cells. Follow the manufacturer's recommendations regarding the need to fill void volumes.

NOTE: Since the sand is not intended to dry the sample, it need not be mixed with the sample, but can be placed at one end of the cell.

11.7 Seal the extraction cell according to the manufacturer's instructions. Use disposable cellulose or glass fiber filters in the cell outlets. Place the extraction cell into the instrument or autosampler tray, as described by the instrument manufacturer.

11.8 Place a precleaned collection vessel in the instrument for each sample, as described by the instrument manufacturer. The total volume of the collected extract will depend on the specific instrumentation and the extraction procedure recommended by the manufacturer and may range from 0.5 to 1.4 times the volume of the extraction cell. Ensure that the collection vessel is sufficiently large to hold the extract.

NOTE: The volume of solvent used for each extraction is a function of the size of the extraction cell, not the weight of the sample. Consult the manufacturer's instructions for the appropriate volume of solvent to employ for a given cell size and the necessary collection vessel volume.

11.9 Recommended extraction conditions

See the introductory material in Sec. 7.7 regarding the choice of solvents.

11.9.1 Semivolatiles, organophosphorus pesticides, organochlorine pesticides, herbicides, and PCBs

Oven temperature:	100 EC
Pressure:	1500-2000 psi
Static time:	5 min (after 5-min pre-heat equilibration)
Flush volume:	60% of the cell volume

Nitrogen purge:	60 sec at 150 psi (purge time may be extended for larger cells)
Static cycles:	1

11.9.2 PCDDs/PCDFs

Oven temperature:	150-175 EC
Pressure:	1500-2000 psi
Static time:	5-10 min (after 7- to 8-min pre-heat equilibration)
Flush volume:	60-75% of the cell volume
Nitrogen purge:	60 sec at 150 psi (purge time may be extended for larger cells)
Static cycles:	2 or 3

11.9.3 DRO

Oven temperature:	175 EC
Pressure:	1500-2000 psi
Static time:	5-10 min (after 7- to 8-min pre-heat equilibration)
Flush volume:	60-75% of the cell volume
Nitrogen purge:	60 sec at 150 psi (purge time may be extended for larger cells)
Static cycles:	1

11.9.4 Optimize the conditions, as needed, according to the manufacturer's instructions. In general, the pressure is not a critical parameter, as the purpose of pressurizing the extraction cell is to prevent the solvent from boiling at the extraction temperature and to ensure that the solvent remains in intimate contact with the sample. Any pressure in the range of 1500-2000 psi should suffice.

11.9.5 Once established, the same pressure should be used for all samples extracted for the same type of analysis.

11.10 Begin the extraction according to the manufacturer's instructions. For PCDD/PCDF extraction, 2 to 3 static extractions are recommended.

11.11 Collect each extract in a clean vial (see Sec. 11.8). Generally, the extracts are near room temperature upon collection.

11.12 The extract is now ready for concentration, cleanup, or analysis, depending on the extent of interferants and the determinative method to be employed. Refer to Method 3600 for guidance on selecting appropriate cleanup methods. Excess water present in extracts may be removed by filtering the extract through a bed of anhydrous sodium sulfate. Certain cleanup and/or determinative methods may need a solvent exchange prior to cleanup and/or sample analysis.

11.12.1 When extracting very wet samples (e.g., $30% moisture) with acetone-containing solvents, it is often necessary to add sodium sulfate to the collection vials after extraction to remove excess water. Amounts of 1 to 10 g may need to be added

depending on the amount of water in the sample. It is important that the vial and sodium sulfate be thoroughly rinsed to ensure complete analyte recovery.

11.12.2 For DRO-containing samples, a column cleanup procedure may be necessary to remove coextracted interferants. Place 2 to 10 g of activated silica gel (Sec. 7.5) in a 10-mm ID glass chromatographic column and top it with 4 to 5 cm of sodium sulfate (see Method 3630 for guidance). The amount of silica gel needed will depend on the size of sample extracted. The amount of sodium sulfate will depend on the moisture content of the sample. Transfer the sample extract onto the column. Rinse the collection vial two or three times and transfer each rinse to the column. Elute the column with sufficient hexane or methylene chloride to ensure recovery of the analytes. (See Method 8440 for a procedure to calibrate the silica gel cleanup.) After cleanup, the samples are ready for volume adjustment and analysis.

11.13 If the phosphoric acid solution in Sec. 7.6 is used for the extraction of chlorinated herbicides, then the extractor should be rinsed by pumping acetone through all the lines of the system. The use of other solvents for these analytes may not need this rinse step.

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

13.2 Chlorinated pesticides and semivolatile organics

Single-laboratory accuracy data were obtained for chlorinated pesticides and semivolatile organics at three different spiking concentrations in three different soil types. Spiking concentrations ranged from 5 to 250 µg/kg for the chlorinated pesticides and from 250 to 12500 µg/kg for the semivolatiles. Spiked samples were extracted both by the Dionex Accelerated Solvent Extraction system and by a Perstorp Environmental Soxtec (automated Soxhlet). Extracts were analyzed either by Method 8270 or Method 8081. Method blanks, spikes and spike duplicates were included for the low concentration spikes; matrix spikes were included for all other concentrations. The data are reported in detail in Reference 1, and represent seven replicate extractions and analyses for each sample. Data summary tables are included in Methods 8270 and 8081, for guidance purposes only.

13.2 Organophosphorus pesticides and chlorinated herbicides

Single-laboratory accuracy data were obtained for organophosphorus pesticides (OPPs) and chlorinated herbicides at two different spiking concentrations in three different soil types. Spiking concentrations ranged from 250 to 2500 µg/kg for the OPPs and from 50 to 5000 µg/kg

for the chlorinated herbicides. Chlorinated herbicides were spiked with a mixture of the free acid and the ester (1:1). Spiked samples were extracted both by the Dionex Accelerated Solvent Extractor and by Soxhlet for the OPPs. Extracts were analyzed by Method 8141. Spiked chlorinated herbicides were extracted by the Dionex Accelerated Solvent Extractor and by the shaking method described in Method 8151. Extracts were analyzed by Method 8151. Method blanks, spikes and spike duplicates were included for the low concentration spikes; matrix spikes were included for all other concentrations. The data are reported in detail in Reference 2, and represent seven replicate extractions and analyses for each sample. Data summary tables are included in Methods 8141 and 8151, for guidance purposes only.

13.3 PCBs

Single-laboratory accuracy data were obtained for PCBs from a soil sample with PCB content certified by NIST (Standard Reference Material, SRM 1939, River Sediment). A PCB-contaminated soil was purchased from a commercial source. Spiking or certified concentrations ranged from 1 to 1400 µg/kg. Samples were extracted by the Dionex Accelerated Solvent Extractor and by Soxtec (Perstorp Environmental). Extracts were analyzed using Method 8082. Method blanks, spikes and spike duplicates were included. The data are reported in Reference 2, and represent seven replicate extractions and analyses for each sample. Data summary tables are included in Method 8082, for guidance purposes only.

13.4 PCDDs/PCDFs

Single-laboratory data were obtained for PCDDs/PCDFs from ground chimney brick, urban dust, fly ash, a relatively highly contaminated soil sample (EC-2, National Water Research Institute, Burlington, Ontario, Canada), a low-level sediment sample (HS-2, National Research Council Institute of Marine Biosciences, Halifax, Nova Scotia, Canada) and various field-contaminated soils and sediments. Concentrations of PCDDs/PCDFs ranged from low ng/kg to mid µg/kg levels. Samples were extracted by the Dionex Accelerated Solvent Extractor and by traditional Soxhlet techniques. Extracts were analyzed by a high resolution mass spectrometric method employing isotope dilution quantitation. The data are reported in Reference 3. Data summary tables are included in Method 8290, for guidance purposes only.

13.5 DRO

Single-laboratory data were obtained for DRO at two different spiking concentrations in three different soil types. Spiking concentrations ranged from 5 to 2000 mg/kg. Spiked samples were extracted by the Dionex Accelerated Solvent Extractor. Extracts were analyzed by GC using Method 8015. Method blanks, spikes and spike duplicates were included for the low concentration spikes; matrix spikes were included for the high concentration spikes. The data are reported in detail in Reference 4, and represent seven replicate extractions and analyses for each sample. The data are summarized in Method 8015, 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's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

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. B. Richter; J. Ezzell; and D. Felix; "Single Laboratory Method Validation Report. Extraction of TCL/PPL (Target Compound List/Priority Pollutant List) BNAs and Pesticides Using Accelerated Solvent Extraction (ASE) with Analytical Validation by GC/MS and GC/ECD;" Document 116064.A; Dionex Corporation; June 16, 1994.

2. B. Richter; J. Ezzell; and D. Felix; "Single Laboratory Method Validation Report. Extraction of TCL/PPL (Target Compound List/Priority Pollutant List) OPPs, Chlorinated Herbicides and PCBs Using Accelerated Solvent Extraction (ASE);" Document 101124, Dionex Corporation, December 2, 1994.

3. B. E. Richter, *et al.*, "Extraction of Polychlorinated Dibenzo-*p*-Dioxins and Polychlorinated Dibenzofurans from Environmental Samples Using Accelerated Solvent Extraction (ASE)," *Chemosphere*, 34(5-7), pp. 975-987, 1997.

4. B. E. Richter, "Single Laboratory Method Validation Report. Extraction of Diesel Range Organics (DRO), Waste Oil Organics (WOO), and Total Petroleum Hydrocarbons (TPH) using Accelerated Solvent Extraction (ASE) with Analytical Validation by GC," Document 118357, Dionex Corporation, June 21, 1999.

17.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

There are no tables or figures associated with this method.