

METHOD 3550C

ULTRASONIC EXTRACTION

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 a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes. The ultrasonic process ensures intimate contact of the sample matrix with the extraction solvent.

1.2 This method is divided into two procedures, based on the expected concentration of organic compounds. The low concentration procedure (Sec. 11.3) is for individual organic components expected at less than or equal to 20 mg/kg and uses the larger sample size and three serial extractions (lower concentrations are more difficult to extract). The medium/high concentration procedure (Sec. 11.4) is for individual organic components expected at greater than 20 mg/kg and uses the smaller sample and a single extraction.

1.3 It is highly recommended that the extracts be subject to some form of cleanup (e.g., using a method from the 3600 series) prior to analysis.

1.4 Because of the limited contact time between the solvent and the sample, ultrasonic extraction may not be as rigorous as other extraction methods for soils/solids. Therefore, it is **critical** that the method (including the manufacturer's instructions) be followed explicitly, in order to achieve the maximum extraction efficiency. See Sec. 11.0 for a discussion of the critical aspects of the extraction procedure. **Consult the manufacturer's instructions regarding specific operational settings.**

1.5 This method describes at least three extraction solvent systems that may be employed for different groups of analytes (see Sec. 7.4). Other solvent systems may be employed, provided that adequate performance can be demonstrated for the analytes 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. As a result of concerns about the efficiency of ultrasonic extraction, particularly at concentrations near or below about 10 µg/kg, it is imperative that the analyst demonstrate the performance of the specific solvent system and operating conditions for the analytes of interest and the concentrations of interest. This demonstration applies to any solvent system that is employed, *including* those specifically listed in this method. 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.

1.6 EPA notes that there are limited published data on the efficiency of ultrasonic extraction with regard to organophosphorus pesticides at low part-per-billion (ppb) concentrations and below. As a result, use of this method for these compounds in particular should be supported by performance data such as those discussed above and in Method 3500.

1.7 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.

1.8 Use of this method is restricted to use by, or under the supervision of, appropriately experienced and trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method. As noted above, such demonstrations are specific to the analytes of interest and the solvent system used, as well as to the procedures for low and medium/high concentration samples.

2.0 SUMMARY OF METHOD

2.1 Low concentration procedure -- The sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. The mixture is extracted with solvent three times, using ultrasonic extraction. The extract is separated from the sample by vacuum filtration or centrifugation. The extract is ready for final concentration, cleanup, and/or analysis.

2.2 Medium/high concentration procedure -- The sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. This is extracted with solvent once, using ultrasonic extraction. A portion of the extract is collected for cleanup and/or analysis.

3.0 DEFINITIONS

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

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 Interferences are usually specific to the analytes of interest. Therefore, refer to Method 3500 and the appropriate determinative methods for specific guidance on extraction interferences.

5.0 SAFETY

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.

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 Apparatus for grinding dry waste samples.

6.2 Ultrasonic preparation -- A horn-type device equipped with a titanium tip, or a device that will give appropriate performance, must be used.

6.2.1 Ultrasonic disrupter -- The disrupter must have a minimum power wattage of 300 watts, with pulsing capability. A device designed to reduce the cavitation sound is recommended. Follow the manufacturers instructions for preparing the disrupter for extraction of samples with low and medium/high concentrations.

6.2.2 Use a 3/4-inch horn for the low concentration method procedure and a 1/8-inch tapered microtip attached to a 1/2-inch horn for the medium/high concentration method procedure.

6.3 Sonobox -- Recommended with the above disrupters for decreasing cavitation sound (Heat Systems - Ultrasonics, Inc., Model 432B or equivalent).

6.4 Apparatus for determining percent dry weight

6.4.1 Drying oven -- Capable of maintaining 105 °C.

6.4.2 Desiccator.

6.4.3 Crucibles -- Porcelain or disposable aluminum.

- 6.5 Pasteur pipets -- 1-mL, glass, disposable.
- 6.7 Vacuum or pressure filtration apparatus
 - 6.7.1 Buchner funnel
 - 6.7.2 Filter paper -- Whatman No. 41 or equivalent.
- 6.8 Kuderna-Danish (K-D) apparatus
 - 6.8.1 Concentrator tube -- 10-mL, graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.
 - 6.8.2 Evaporation flask -- 500-mL (Kontes K-570001-500 or equivalent). Attach the flask to the concentrator tube with springs, clamps, or equivalent.
 - 6.8.3 Snyder column -- Three-ball macro (Kontes K-503000-0121 or equivalent).
 - 6.8.4 Snyder column -- Two-ball micro (Kontes K-569001-0219 or equivalent).
 - 6.8.5 Springs -- 1/2-inch (Kontes K-662750 or equivalent).

6.9 Solvent vapor recovery system (Kontes K-545000-1006 or K-547300-0000, Ace Glass 6614-30, or equivalent).

NOTE: This glassware is recommended for the purpose of solvent recovery during the concentration procedures requiring the use of Kuderna-Danish evaporative concentrators. Incorporation of this apparatus may be required by Federal, State or local municipality regulations that govern air emissions of volatile organics. EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program. Solvent recovery is a means to conform with waste minimization and pollution prevention initiatives.

- 6.10 Boiling chips -- Solvent-extracted, approximately 10/40 mesh (silicon carbide or equivalent).
- 6.11 Water bath -- Heated, with a concentric ring cover, capable of temperature control to ± 5 °C. The bath should be used in a hood.
- 6.12 Balance -- Top-loading, capable of accurately weighing to the nearest 0.01 g.
- 6.13 Vials -- 2-mL, for GC autosampler, equipped with polytetrafluoroethylene (PTFE)-lined screw caps or crimp tops.
- 6.14 Glass scintillation vials -- 20-mL, equipped with PTFE-lined screw caps.
- 6.15 Spatula -- Stainless steel or PTFE.
- 6.16 Drying column -- 20-mm ID borosilicate glass chromatographic column with glass wool at the bottom.

NOTE: Columns with fritted glass discs are difficult to decontaminate after they have been used to dry highly-contaminated extracts. Columns without frits may be purchased.

Use a small pad of glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of the elution solvent prior to packing the column with adsorbent.

6.17 Nitrogen evaporation apparatus (optional) -- N-Evap, 12- or 24-position (Organomation Model 112, 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 Sodium sulfate (granular, anhydrous), Na_2SO_4 . Purify by heating at 400 °C for 4 hrs in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank should be analyzed, demonstrating that there is no interference from the sodium sulfate.

7.4 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 of 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 like methylene chloride may be used for polar analytes. The polarity of acetone may also help extract polar analytes in mixed solvent systems.

Table 1 provides example recovery data for selected semivolatile organic compounds extracted from an NIST SRM using various extraction solvent systems. The following sections provide guidance on the choice of solvents for various classes of analytes.

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

7.4.1 Semivolatile organics may be extracted with acetone/hexane (1:1, v/v $\text{CH}_3\text{COCH}_3/\text{C}_6\text{H}_{14}$), or acetone/methylene chloride (1:1, v/v $\text{CH}_3\text{COCH}_3/\text{CH}_2\text{Cl}_2$).

7.4.2 Organochlorine pesticides may be extracted with acetone/hexane (1:1, v/v $\text{CH}_3\text{COCH}_3/\text{C}_6\text{H}_{14}$), or acetone/methylene chloride (1:1, v/v $\text{CH}_3\text{COCH}_3/\text{CH}_2\text{Cl}_2$).

7.4.3 PCBs may be extracted with acetone/hexane (1:1, v/v $\text{CH}_3\text{COCH}_3/\text{C}_6\text{H}_{14}$), acetone/methylene chloride (1:1, v/v $\text{CH}_3\text{COCH}_3/\text{CH}_2\text{Cl}_2$) or hexane (C_6H_{14}).

7.4.4 Other solvent systems may be employed, provided that the analyst can demonstrate adequate performance for the analytes of interest, at the concentrations of interest, in the sample matrix (see Method 3500).

7.5 Exchange solvents -- With the use of some determinative methods, the extraction solvent will need to be exchanged to a solvent compatible with the instrumentation used in that determinative method. Refer to the determinative method to be used for selection of the appropriate exchange solvent. All solvents must be pesticide quality or equivalent. Examples of exchange solvents are given below.

7.5.1 Hexane, C_6H_{14}

7.5.2 2-Propanol, $(\text{CH}_3)_2\text{CHOH}$

7.5.3 Cyclohexane, C_6H_{12}

7.5.4 Acetonitrile, CH_3CN

7.5.5 Methanol, CH_3OH

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 additional 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 extracted 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 ultrasonic 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, in the sample matrix.

10.0 CALIBRATION AND STANDARDIZATION

There are no calibration or standardization steps directly associated with this sample extraction procedure.

11.0 PROCEDURE

As noted in Sec. 1.4, ultrasonic extraction may not be as rigorous a method as other extraction methods for soils/solids. Therefore, it is critical that this method be followed explicitly (including the manufacturer's instructions) to achieve the maximum extraction efficiency. At a minimum, for successful use of this technique:

- The extraction device must have a minimum of 300 watts of power and be equipped with appropriate size disrupter horns (see Sec. 6.2).
- The horn must be properly maintained, including tuning according to the manufacturer's instructions prior to use, and inspection of the horn tip for excessive wear.

- The sample must be properly prepared by thoroughly mixing it with sodium sulfate, so that it forms a free-flowing powder prior to the addition of the solvent.
- The extraction horns used for the low concentration and high concentration protocols (Secs. 11.3 and 11.4, respectively) are not interchangeable. Results indicate that the use of the 3/4-inch horn is inappropriate for the high concentration procedure, particularly for extraction of very non-polar organic compounds such as PCBs, which are strongly adsorbed to the soil matrix.
- For low concentration samples, three extractions are performed with the appropriate solvent, the extraction is performed in the designated pulse mode, and the horn tip is positioned just below the surface of the solvent, yet above the sample. The same approach is used for high concentration samples, except that only one extraction may be needed.
- Very active mixing of the sample and the solvent must occur when the ultrasonic pulse is activated. The analyst must observe such mixing at some point during the extraction process.

11.1 Sample handling

11.1.1 Sediment/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.

11.1.2 Waste samples -- Samples consisting of multiple phases must be prepared before extraction by the phase separation procedure described in Chapter Two. This extraction procedure is for solids only.

11.1.3 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 10 g after grinding.

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

11.1.4 Gummy, fibrous, or oily materials not amenable to grinding -- Cut, shred, or otherwise reduce in size these materials to allow mixing and maximum exposure of the sample surfaces for the extraction.

11.2 Determination of percent dry weight -- When sample results are to be calculated on a dry weight basis, a separate portion of sample 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.

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

Calculate the percent 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 Low concentration extraction procedure

This procedure applies to solid samples that are expected to contain less than or equal to 20 mg/kg of organic analytes.

NOTE: Add the surrogates and matrix spiking compounds to the sample aliquot prior to mixing the sample with the sodium sulfate drying agent. Spiking the sample first increases the contact time of the spiked compounds and the actual sample matrix. It should also lead to better mixing of the spiking solution with the sample when the sodium sulfate and sample are mixed to the point of free-flowing.

11.3.1 The following steps should be performed rapidly to avoid loss of the more volatile extractables.

11.3.1.1 Weigh approximately 30 g of sample into a 400-mL beaker. Record the weight to the nearest 0.1 g.

11.3.1.2 For the sample in each batch selected for spiking, add 1.0 mL of the matrix spiking solution. Consult Method 3500 for guidance on the appropriate choice of matrix spiking compounds and concentrations. Also see the note in Sec. 11.3.

11.3.1.3 Add 1.0 mL of the surrogate standard solution to all samples, spiked samples, QC samples, and blanks. Consult Method 3500 for guidance on the appropriate choice of surrogate compounds and concentrations. Also see the note in Sec. 11.3.

11.3.1.4 If gel permeation cleanup (see Method 3640) is to be employed, the analyst should either add twice the volume of the surrogate spiking solution (and matrix spiking solution, where applicable), or concentrate the final extract to half the normal volume, to compensate for the half of the extract that is lost due to loading of the GPC column. Also see the note in Sec. 11.3.

11.3.1.5 Nonporous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture must be mixed with 60 g of anhydrous sodium sulfate, using a spatula. If needed, more sodium sulfate may be added. After addition of sodium sulfate, the sample should be free flowing. Also see the note in Sec. 11.3.

11.3.1.6 Immediately add 100 mL of the extraction solvent or solvent mixture (see Sec. 7.4 and Table 2 for information on the choice of solvents).

11.3.2 Place the bottom surface of the tip of the 3/4-inch disrupter horn about 1/2-inch below the surface of the solvent, but above the sediment layer.

NOTE: Be sure that the horn is properly tuned according to the manufacturer's instructions.

11.3.3 Extract the sample ultrasonically for 3 min, with output control knob set at 10 (full power) or at the manufacturer's recommended power setting, the mode switch on Pulse (pulsing energy rather than continuous energy), and the percent-duty cycle knob set at 50% (energy on 50% of time and off 50% of time). Do **not** use the microtip probe.

11.3.4 Decant the extract and filter it through Whatman No. 41 filter paper (or equivalent) in a Buchner funnel that is attached to a clean 500-mL filtration flask. Alternatively, decant the extract into a centrifuge bottle and centrifuge at low speed to remove particles.

11.3.5 Repeat the extraction two more times with two additional 100-mL portions of clean solvent. Decant off the solvent after each ultrasonic extraction. After the final ultrasonic extraction, pour the entire sample into the Buchner funnel, rinse the beaker with extraction solvent, and add the rinse to the funnel. Apply a vacuum to the filtration flask, and collect the solvent extract. Continue filtration until all visible solvent is removed from the funnel, but do not attempt to completely dry the sample, as the continued application of a vacuum may result in the loss of some analytes. Alternatively, if centrifugation is used in Sec. 11.3.4, transfer the entire sample to the centrifuge bottle. Centrifuge at low speed, and then decant the solvent from the bottle.

11.3.6 If necessary, concentrate the extract prior to analysis following the procedure in Sec. 11.5. Otherwise, proceed to Sec. 11.7.

11.4 Medium/high concentration extraction procedure

This procedure applies to solid samples that are expected to contain more than 20 mg/kg of organic analytes.

11.4.1 Transfer approximately 2 g of sample to a 20-mL vial. Wipe the mouth of the vial with a tissue to remove any sample material. Cap the vial before proceeding with the next sample to avoid any cross-contamination. Record the weight to the nearest 0.1 g.

11.4.2 For the sample in each batch selected for spiking, add 1.0 mL of the matrix spiking solution. Consult Method 3500 for guidance on the appropriate choice of matrix spiking compounds and concentrations. Also see the note in Sec. 11.3.

11.4.3 Add 1.0 mL of surrogate spiking solution to all samples, spiked samples, QC samples, and blanks. Consult Method 3500 for guidance on the appropriate choice of matrix spiking compounds and concentrations. Also see the note in Sec. 11.3.

11.4.4 If gel permeation cleanup (see Method 3640) is to be employed, the analyst should either add twice the volume of the surrogate spiking solution (and matrix spiking solution, where applicable), or concentrate the final extract to half the normal volume, to compensate for the half of the extract that is lost due to loading of the GPC column.

11.4.5 Nonporous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture must be mixed with 2 g of anhydrous sodium sulfate, using a spatula. If needed, more sodium sulfate may be added. After addition of sodium sulfate, the sample should be free flowing (see the note in Sec. 11.3).

11.4.6 Immediately add whatever volume of solvent is necessary to bring the final volume to 10.0 mL, considering the added volume of surrogates and matrix spikes (see Sec. 7.4 and Table 2 for information on the choice of solvents).

11.4.7 Extract the sample with the 1/8-inch tapered microtip ultrasonic probe for 2 min at output control setting 5 and with mode switch on pulse and percent duty cycle at 50%.

11.4.8 Loosely pack a disposable Pasteur pipette with 2 to 3 cm of glass wool. Filter the sample extract through the glass wool and collect the extract in a suitable container. The entire 10 mL of extraction solvent cannot be recovered from the sample. Therefore, the analyst should collect a volume appropriate for the sensitivity of the determinative method to be used. For instance, for methods that do not need the extract to be concentrated further (e.g., Method 8081 typically employs a final extract volume of 10 mL), the extract may be collected in a scintillation vial or other sealable container. For extracts that will need further concentration, it is advisable to collect a standard volume for all such samples in order to simplify the calculation of the final sample results. For instance, collect 5.0 mL of extract in a clean concentrator tube. This volume represents exactly half of the total volume of the original sample extract. As necessary, account for the "loss" of half of the extract in the final sample calculations, or concentrate the final extract to one-half the nominal final volume (e.g., 0.5 mL vs. 1.0 mL) to compensate for the loss.

11.4.9 If necessary, concentrate the extract prior to analysis following the procedure in Sec. 11.5 or Sec. 11.6. Otherwise, proceed to Sec. 11.7.

11.5 K-D concentration technique

Where necessary to meet the sensitivity criteria, sample extracts from either the low concentration or medium/high concentration extraction procedure may be concentrated to the final volume necessary for the determinative method and specific application to be used, using either the K-D technique or nitrogen evaporation.

11.5.1 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to an appropriately sized evaporation flask.

11.5.2 Dry the extract by passing it through a drying column containing about 10 g of anhydrous sodium sulfate. Collect the dried extract in the K-D concentrator.

11.5.3 Rinse the collection tube and drying column into the K-D flask with an additional 20-mL portion of solvent in order to achieve a quantitative transfer.

11.5.4 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Attach the solvent vapor recovery glassware (condenser and collection device, see Sec. 6.9) to the Snyder column of the K-D apparatus, following the manufacturer's instructions. Pre-wet the Snyder column by adding about 1 mL of methylene chloride (or other suitable solvent) to the top of the column. Place the K-D apparatus on a hot water bath (15 - 20 °C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as needed to complete the concentration in 10 - 20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.

CAUTION: Do **not** let the extract go to dryness, as this will result in severe loss of some analytes. Organophosphorus pesticides are particularly susceptible to such losses.

11.5.4.1 If a solvent exchange is necessary (as indicated in Table 2 or the appropriate determinative method), momentarily remove the Snyder column, add 50 mL of the exchange solvent and a new boiling chip.

11.5.4.2 Reattach the Snyder column. Concentrate the extract, raising the temperature of the water bath, if necessary, to maintain a proper distillation rate.

11.5.5 Remove the Snyder column. Rinse the K-D flask and the lower joints of the Snyder column into the concentrator tube with 1 - 2 mL of solvent. The extract may be further concentrated by using one of the techniques outlined in Sec. 11.6, or adjusted to a final volume of 5.0 - 10.0 mL using an appropriate solvent (see Table 2 or the appropriate determinative method). If sulfur crystals are present, proceed to Method 3660 for cleanup.

11.6 If further concentration is necessary, use either the micro-Snyder column technique (see Sec. 11.6.1) or nitrogen evaporation technique (see Sec. 11.6.2).

11.6.1 Micro-Snyder column technique

11.6.1.1 Add a fresh clean boiling chip to the concentrator tube and attach a two-ball micro-Snyder column directly to the concentrator tube. Attach the solvent vapor recovery glassware (condenser and collection device) to the micro-Snyder column of the K-D apparatus, following the manufacturer's instructions. Pre-wet the Snyder column by adding 0.5 mL of methylene chloride or the exchange solvent to the top of the column. Place the micro-concentration apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as necessary, to complete the concentration in 5 - 10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood.

11.6.1.2 When the apparent volume of liquid reaches 0.5 mL, remove the apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Snyder column and rinse its lower joints into the concentrator tube with 0.2 mL of solvent. Adjust the final extract volume to 1.0 - 2.0 mL.

CAUTION: Do **not** let the extract go to dryness, as this will result in severe loss of some analytes. Organophosphorus pesticides are particularly susceptible to such losses.

11.6.2 Nitrogen evaporation technique

11.6.2.1 Place the concentrator tube in a warm bath (30 °C) and evaporate the solvent volume to 0.5 mL using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: New plastic tubing must not be used between the carbon trap and the sample, since it may introduce phthalate interferences.

11.6.2.2 Rinse down the internal wall of the concentrator tube several times with solvent during the concentration. During evaporation, position the concentrator tube to avoid condensing water into the extract. Under normal procedures, the extract must not be allowed to become dry.

CAUTION: Do **not** let the extract go to dryness, as this will result in severe loss of some analytes. Organophosphorus pesticides are particularly susceptible to such losses.

11.7 The extract may now be subjected to cleanup procedures or analyzed for the target analytes using the appropriate determinative technique(s). If further handling of the extract will not be performed immediately, stopper the concentrator tube and store in a refrigerator. If the extract will be stored longer than 2 days, it should be transferred to a vial equipped with a PTFE-lined screw-cap, and labeled appropriately.

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

Refer to the appropriate determinative methods 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 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. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

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 operation. 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. U.S. EPA, "Interlaboratory Comparison Study: Methods for Volatile and Semi-Volatile Compounds," Environmental Monitoring Systems Laboratory, Office of Research and Development, Las Vegas, NV, EPA 600/4-84-027, 1984.
2. C. S. Hein, P. J. Marsden, A. S. Shurtleff, "Evaluation of Methods 3540 (Soxhlet) and 3550 (Sonication) for Evaluation of Appendix IX Analytes from Solid Samples," S-CUBED, Report for EPA Contract 68-03-33-75, Work Assignment No. 03, Document No. SSS-R-88-9436, October, 1988.

17.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

The following pages contain the tables referenced by this method.

TABLE 1

EXAMPLE EFFICIENCIES OF VARIOUS EXTRACTION SOLVENT SYSTEMS FOR SELECTED COMPOUNDS^a

| Compound | CAS No. ^b | ABN ^c | Solvent System ^d | | | | | | | | | |
|-------------------------------|----------------------|------------------|-----------------------------|------|------|-----|-------|-----|------|------|------|-----|
| | | | A | | B | | C | | D | | E | |
| | | | %R | SD | %R | SD | %R | SD | %R | SD | %R | SD |
| 4-Bromophenyl phenyl ether | 101-55-3 | N | 64.2 | 6.5 | 56.4 | 0.5 | 86.7 | 1.9 | 84.5 | 0.4 | 73.4 | 1.0 |
| 4-Chloro-3-methylphenol | 59-50-7 | A | 66.7 | 6.4 | 74.3 | 2.8 | 97.4 | 3.4 | 89.4 | 3.8 | 84.1 | 1.6 |
| Bis(2-chloroethoxy)methane | 111-91-1 | N | 71.2 | 4.5 | 58.3 | 5.4 | 69.3 | 2.4 | 74.8 | 4.3 | 37.5 | 5.8 |
| Bis(2-chloroethyl) ether | 111-44-4 | N | 42.0 | 4.8 | 17.2 | 3.1 | 41.2 | 8.4 | 61.3 | 11.7 | 4.8 | 1.0 |
| 2-Chloronaphthalene | 91-58-7 | N | 86.4 | 8.8 | 78.9 | 3.2 | 100.8 | 3.2 | 83.0 | 4.6 | 57.0 | 2.2 |
| 4-Chlorophenyl phenyl ether | 7005-72-3 | N | 68.2 | 8.1 | 63.0 | 2.5 | 96.6 | 2.5 | 80.7 | 1.0 | 67.8 | 1.0 |
| 1,2-Dichlorobenzene | 95-50-1 | N | 33.3 | 4.5 | 15.8 | 2.0 | 27.8 | 6.5 | 53.2 | 10.1 | 2.0 | 1.2 |
| 1,3-Dichlorobenzene | 541-73-1 | N | 29.3 | 4.8 | 12.7 | 1.7 | 20.5 | 6.2 | 46.8 | 10.5 | 0.6 | 0.6 |
| Diethyl phthalate | 84-66-2 | N | 24.8 | 1.6 | 23.3 | 0.3 | 121.1 | 3.3 | 99.0 | 4.5 | 94.8 | 2.9 |
| 4,6-Dinitro- <i>o</i> -cresol | 534-52-1 | A | 66.1 | 8.0 | 63.8 | 2.5 | 74.2 | 3.5 | 55.2 | 5.6 | 63.4 | 2.0 |
| 2,4-Dinitrotoluene | 121-14-2 | N | 68.9 | 1.6 | 65.6 | 4.9 | 85.6 | 1.7 | 68.4 | 3.0 | 64.9 | 2.3 |
| 2,6-Dinitrotoluene | 606-20-2 | N | 70.0 | 7.6 | 68.3 | 0.7 | 88.3 | 4.0 | 65.2 | 2.0 | 59.8 | 0.8 |
| Heptachlor epoxide | 1024-57-3 | N | 65.5 | 7.8 | 58.7 | 1.0 | 86.7 | 1.0 | 84.8 | 2.5 | 77.0 | 0.7 |
| Hexachlorobenzene | 118-74-1 | N | 62.1 | 8.8 | 56.5 | 1.2 | 95.8 | 2.5 | 89.3 | 1.2 | 78.1 | 4.4 |
| Hexachlorobutadiene | 87-68-3 | N | 55.8 | 8.3 | 41.0 | 2.7 | 63.4 | 4.1 | 76.9 | 8.4 | 12.5 | 4.6 |
| Hexachlorocyclopentadiene | 77-47-4 | N | 26.8 | 3.3 | 19.3 | 1.8 | 35.5 | 6.5 | 46.6 | 4.7 | 9.2 | 1.7 |
| Hexachloroethane | 67-72-1 | N | 28.4 | 3.8 | 15.5 | 1.6 | 31.1 | 7.4 | 57.9 | 10.4 | 1.4 | 1.2 |
| 5-Nitro- <i>o</i> -toluidine | 99-55-8 | B | 52.6 | 26.7 | 64.6 | 4.7 | 74.7 | 4.7 | 27.9 | 4.0 | 34.0 | 4.0 |
| Nitrobenzene | 98-95-3 | N | 59.8 | 7.0 | 38.7 | 5.5 | 46.9 | 6.3 | 60.6 | 6.3 | 13.6 | 3.2 |
| Phenol | 108-95-2 | A | 51.6 | 2.4 | 52.0 | 3.3 | 65.6 | 3.4 | 65.5 | 2.1 | 50.0 | 8.1 |
| 1,2,4-Trichlorobenzene | 120-82-1 | N | 66.7 | 5.5 | 49.9 | 4.0 | 73.4 | 3.6 | 84.0 | 7.0 | 20.0 | 3.2 |

Footnotes appear on the following page.

TABLE 1
FOOTNOTES

^a Percent recovery of analytes spiked at 200 mg/kg into NIST sediment SRM 1645

^b Chemical Abstracts Service Registry Number

^c Compound Type: A = Acid, B = Base, N = neutral

^d Solvent system A = Methylene chloride
Solvent system B = Methylene chloride/acetone (1/1)
Solvent system C = Hexane/acetone (1/1)
Solvent system D = Methyl t-butyl ether
Solvent system E = Methyl t-butyl ether/methanol (2/1)

%R = Percent recovery

SD = Standard deviation of the recoveries

All data are taken from Reference 2.

TABLE 2

SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

| Determinative Method | Recommended Solvent for Analysis | Recommended Solvent for Cleanup | Extract Volume Recommended for Cleanup (mL) | Recommended Final Extract Volume for Analysis (mL) ^a |
|----------------------|----------------------------------|---------------------------------|---|---|
| 8041 | 2-propanol | hexane | 1.0 | 1.0, 0.5 ^b |
| 8061 | hexane | hexane | 2.0 | 10.0 |
| 8070 | methanol | methylene chloride | 2.0 | 10.0 |
| 8081 | hexane | hexane | 10.0 | 10.0 |
| 8082 | hexane | hexane | 10.0 | 10.0 |
| 8085 | isooctane | hexane | 10.0 | NS |
| 8091 | hexane | hexane | 2.0 | 1.0 |
| 8100 | none | cyclohexane | 2.0 | 1.0 |
| 8111 | hexane | hexane | 2.0 | 10.0 |
| 8121 | hexane | hexane | 2.0 | 1.0 |
| 8141 | hexane | hexane | 10.0 | 10.0 |
| 8270 ^c | none | - | - | 1.0 |
| 8310 | acetonitrile | - | - | 1.0 |
| 8321 | methanol | - | - | 1.0 |
| 8325 | methanol | - | - | 1.0 |
| 8410 | methylene chloride | methylene chloride | 10.0 | 0.0 (dry) |

^a These volumes are only recommendations. The final extract volume should be established based on the sensitivity necessary for the intended application. For methods where the recommended final extract volume is 10.0 mL, the volume may be reduced to as low as 1.0 mL to achieve lower limits of quantitation.

^b Phenols may be analyzed by Method 8041, using a 1.0-mL 2-propanol extract by GC/FID. Method 8041 also contains an optional derivatization procedure for phenols which results in a 0.5-mL hexane extract to be analyzed by GC/ECD.

^c The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the available cleanup procedures, if necessary.

NS = Not specified. The final extract volume should be established based on the sensitivity necessary for the intended application.