METHOD 3500C

ORGANIC EXTRACTION AND SAMPLE PREPARATION

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 provides general guidance on the selection of methods used in the quantitative extraction (or dilution) of samples for analysis by one of the semivolatile or nonvolatile determinative methods. Procedures for the cleanup and analysis of the resultant extracts are described in Chapter Two, as well as in Method 3600 (cleanup) and Method 8000 (analysis).

1.2 The following table lists the extraction methods, the matrix types, the techniques, and the analyte categories.

Method	Matrix Types	Extraction Technique	Analytes
3510	Aqueous	Separatory Funnel Liquid-Liquid Extraction	Semivolatile and Nonvolatile Organics
3520	Aqueous	Continuous Liquid-Liquid Extraction	Semivolatile and Nonvolatile Organics
3535	Aqueous	Solid-phase Extraction (SPE)	Semivolatile and Nonvolatile Organics
3540	Solids	Soxhlet Extraction	Semivolatile and Nonvolatile Organics
3541	Solids	Automated Soxhlet Extraction	Semivolatile and Nonvolatile Organics
3542	Air Sampling Train	Separatory Funnel & Soxhlet Extraction	Semivolatile Organics
3545	Solids	Pressurized Fluid Extraction (PFE)	Semivolatile and Nonvolatile Organics
3546	Solids	Microwave Extraction	Semivolatile and Nonvolatile Organics
3550	Solids	Ultrasonic Extraction	Semivolatile and Nonvolatile Organics
3560	Solids	Supercritical Fluid Extraction (SFE)	Semivolatile Petroleum Hydrocarbons
3561	Solids	Supercritical Fluid Extraction (SFE)	Polynuclear Aromatic Hydrocarbons
3562	Solids	Supercritical Fluid Extraction (SFE)	Polychlorinated Biphenyls and Organochlorine Pesticides

Method	Matrix Types	Extraction Technique	Analytes
3580	Non-aqueous Solvent-soluble Wastes	Solvent Dilution	Semivolatile & Nonvolatile Organics

1.3 Method 3580 may be used for the solvent dilution of non-aqueous semivolatile and nonvolatile organic samples prior to cleanup and/or analysis.

1.4 Methods 3545, 3546, 3560, 3561, and 3562 are techniques that utilize pressurized fluid or solvent extraction to reduce the amount of solvent needed to extract target analytes and reduce the extraction time when compared to more traditional techniques such as Soxhlet extraction.

1.5 Prior to employing this method, analysts are advised to 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 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 A sample of a known volume or weight is extracted with solvent or diluted with solvent. Method choices for aqueous samples include liquid-liquid extraction by separatory funnel or by continuous extractor and solid-phase extraction (SPE). Method choices for soil/sediment and solid waste samples include standard solvent extraction methods utilizing either Soxhlet, automated Soxhlet, or ultrasonic extraction. Solids may also be extracted using pressurized extraction techniques such as supercritical fluid extraction, pressurized fluid extraction, or microwave extraction.

2.2 The resultant extract is dried and concentrated in a Kuderna-Danish (K-D) apparatus. Other concentration devices or techniques may be used in place of the Kuderna-Danish concentrator if they give acceptable results for the intended application.

NOTE: Solvent recovery apparatus is recommended for use in methods that use Kuderna-Danish or other evaporative concentrators. EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program.

2.3 See Sec. 11.0 for additional guidance to assist in selection of the appropriate method.

3.0 DEFINITIONS

See Chapter One for definitions that may be relevant to this analytical procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All 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 guidance on the cleaning of glassware.

4.2 Interferences coextracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be necessary. Refer to Method 3600 for guidance on cleanup procedures.

4.3 Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

4.4 Soap residue (e.g. sodium dodecyl sulfate), which results in a basic pH on glassware surfaces, may cause degradation of certain analytes. Specifically, Aldrin, Heptachlor, and most organophosphorus pesticides will degrade in this situation. This problem is especially pronounced with glassware that may be difficult to rinse (e.g., 500-mL K-D flask). These items should be hand-rinsed very carefully to avoid this problem.

5.0 SAFETY

This method does not address all safety issues associated with its use. For additional information, refer to the specific method of interest for guidance on 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

6.1 Refer to the specific method of interest for a description of the apparatus and materials needed.

6.2 Solvent recovery apparatus 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.

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 Refer to the specific method of interest as listed in Sec. 1.2 for a description of the solvents needed.

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

7.4 Stock standards for spiking solutions -- Stock solutions may be prepared from pure standard materials or purchased as certified solutions. The stock solutions used for the calibration standards are acceptable (dilutions must be made in a water-miscible solvent) except for the quality control check sample stock concentrate which must be prepared independently to serve as a check on the accuracy of the calibration solution.

7.4.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure compound. Dissolve the compound in a water-miscible solvent (i.e., methanol, acetone, 2-propanol, etc.) and dilute to volume in a 10-mL volumetric flask. If compound purity is 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard solution. Commercially-prepared stock standard solutions can be used at any concentration if they are certified by the manufacturer or by an independent source.

7.4.2 Stock standard solutions should be stored in polytetrafluoroethylene (PTFE)-sealed containers at $\leq$6 °C or below. The solutions should be checked frequently for stability. Refer to the determinative method for holding times of the stock solutions.

7.5 Surrogate standards -- A surrogate (i.e., a compound that is chemically similar to the analyte group but is not expected to occur in an environmental sample) should be added to each sample, blank, laboratory control sample (LCS), and matrix spike sample just prior to extraction or processing. The recovery of the surrogate standard is used to monitor for unusual matrix effects, gross sample processing errors, etc. Surrogate recovery is evaluated for acceptance by determining whether the measured concentration falls within the acceptance limits for a particular project or laboratory SOP. If multiple surrogates are used, all should meet the laboratory or project-specific QC acceptance criteria for recovery. See the note in Sec. 9.3.1 for important information regarding spiking samples.

7.5.1 Surrogates for certain analyte groups are listed in Table 1. These surrogates are *only* recommendations. Other surrogates may be used by the analyst, based on knowledge of the samples, similarities to the target analytes, their use as surrogates in other methods for similar analytes, etc. For example, Method 8085 may be employed for the analysis of a wide range of pesticide compounds, many of which are also included in other 8000 series methods. Therefore, surrogates from those other methods may also be useful as surrogates in Method 8085.

For methods where no recommended surrogates are listed, the analyst is free to select compounds that fall within the definition provided above. Even compounds that are on the method target analyte list may be used as surrogates as long as historical data are available to ensure their absence at the given sample collection site. Normally one or more surrogates are added for each analyte group.

7.5.2 Prepare a surrogate spiking solution by mixing stock standards prepared above and diluting with a water-miscible solvent. Commercially-prepared spiking solutions are acceptable. The concentration for semivolatile/nonvolatile organic and pesticide analyses should be such that a 1-mL aliquot spiked into 1000 mL of an aqueous sample provides a concentration of 10 times the quantitation limit of a target analyte that is chemically similar to the surrogate, or near the mid-point of the calibration curve. Where volumes of less than 1000 mL are extracted, adjust the volume of surrogate standard proportionately. For matrices other than water, 1 mL of surrogate standard is still the normal spiking volume. However, if gel permeation chromatography will be used for sample cleanup, 2 mL should be added to the sample. See Table 1 for suggested surrogates. The spiking volumes are normally listed in each extraction method. As necessary or appropriate to meet project objectives, the surrogates listed in Table 1 may be modified by the laboratory.

7.6 Matrix spike standards -- Secs. 7.6.1 and 7.6.2 contain recommended matrix spike standard mixtures for two analyte groups. The recommendations are based on the historical use of these compounds in various EPA methods. However, as noted above, these are only recommendations. Prepare a matrix spike concentrate by mixing stock standards prepared above and diluting with a water-miscible solvent. Commercially-prepared spiking solutions are acceptable. The matrix spike standards should be independent of the calibration standard, but do not need to be obtained from a second source. See the note in Sec. 9.3.1 for important information regarding spiking samples.

NOTE: The recommended matrix spike compounds in Secs. 7.6.1 and 7.6.2 are considered a minimum recommendation. If these compounds are not target analytes for a specific project, or if other compounds are known to be of greater concern at a given site, then other matrix spike compounds should be employed. The choice of compounds to be spiked should represent the analytes of interest for the specific project, i.e., those analytes reasonably expected to be present. It is generally good laboratory practice to include all expected target analytes in matrix spike standards. For some projects, it may be necessary to develop matrix spike data for all the target analytes for the project. Analysts may need to consult the project plan for specific information.

7.6.1 Base/neutral and acid matrix spiking solution -- Prepare a spiking solution in methanol that contains each of the following base/neutral compounds at 100 mg/L and the acid compounds at 200 mg/L for water and sediment/soil samples. The concentration of these compounds should be five times higher for waste samples.

Base/neutral compounds	Acid compounds
1,2,4-Trichlorobenzene	Pentachlorophenol
Acenaphthene	Phenol
2,4-Dinitrotoluene	2-Chlorophenol
Pyrene	4-Chloro-3-methylphenol
N-Nitroso-di-*n*-propylamine	4-Nitrophenol
1,4-Dichlorobenzene	

7.6.2 Organochlorine pesticide matrix spiking solution -- For water and sediment/soil samples, prepare a spiking solution in acetone or methanol that contains the following pesticides at the concentrations listed below. The concentrations should be five times higher for waste samples. The concentrations listed below are in the spiking solution, not the samples.

Pesticide	Concentration (mg/L)
Lindane	0.2
Heptachlor	0.2
Aldrin	0.2
Dieldrin	0.5
Endrin	0.5
4,4'-DDT	0.5

7.6.3 For methods with no guidance, select five or more analytes (select all analytes for methods with five analytes or less) from each analyte group for use in a spiking solution.

7.6.4 Sec. 9.3.3 provides guidance on determining the concentration of the matrix spike compounds in the sample. As necessary or appropriate to meet project objectives, the matrix spiking compounds listed in Secs. 7.6.1 and 7.6.2, and/or the concentrations listed in the spiking solutions may be modified by the laboratory. When the concentration of an analyte is not being checked against a regulatory limit or action level (see Sec. 9.3.3.3) the concentration of the matrix spike compound in the sample (or sample extract) should be at the same concentration as the reference sample (see Sec. 9.2.4), near the middle of the calibration range, or approximately 10 times the quantitation limit.

7.7 Laboratory control spike standard -- Use the matrix spike standard prepared in Sec. 7.6 as the spiking standard for the laboratory control sample (LCS). The LCS is spiked with the same analytes and at the same concentrations as the matrix spike, when appropriate. See the note in Sec. 9.3.1 for important information regarding spiking samples.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

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

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 reference matrix. This will include a combination of the sample extraction method (usually a 3500 series method for extractable organics) and the determinative method (an 8000 series method). The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made.

9.2.1 Prepare the reference samples from a spiking solution containing each analyte of interest. The reference sample concentrate (spiking solution) may be prepared from pure standard materials, or purchased as certified solutions. If prepared by the laboratory, the reference sample concentrate should be made using stock standards prepared independently from those used for calibration.

9.2.2 The procedure for preparation of the reference sample concentrate is dependent upon the method being evaluated. Guidance for reference sample concentrations for certain methods is listed in Sec. 9.2.4. In other cases, the determinative methods may contain guidance on preparing the reference sample concentrate and the reference sample. If no guidance is provided, prepare a reference sample concentrate in methanol (or other water-miscible solvent). The spiking volume added to water should not exceed 1 mL/L so that the spiking solvent will not decrease extraction efficiency. A similar spiking volume is typically used for solid matrices, but smaller volumes of more concentrated spiking solutions may also be employed. In the absence of any other guidance, consult Sec. 9.3.3 and prepare the spiking solution accordingly.

The concentration of target analytes in the reference sample may be adjusted to more accurately reflect the concentrations that will be analyzed by the laboratory. If the concentration of an analyte is being evaluated relative to a regulatory limit or action level, see Sec. 9.3.3 for information on selecting an appropriate spiking level.

9.2.3 To evaluate the performance of the total analytical process, the reference samples must be handled in exactly the same manner as actual samples. Therefore, for aqueous samples, 1 mL (unless the method, or SOP, utilizes a different volume) of the reference sample concentrate is spiked into each of four (minimum number of replicates) 1-L aliquots of organic-free reagent water (now called the reference samples), and extracted as per the method. For matrices other than water or for determinative methods that use a different volume of water, add 1.0 mL of the reference sample concentrate to at least four replicates of the volume or weight of sample stated in the method. Use a clean matrix for spiking purposes (one that does not have any target or interference compounds), e.g., organic-free reagent water for the water matrix, or sand or soil (free of organic interferences) for the solid matrix. See the note in Sec. 9.3.1 for important information regarding spiking samples.

NOTE: For those methods, or SOPs, that include a choice of extraction solvents or solvent systems, the initial demonstration must be completed for each solvent system that the laboratory intends to employ.

9.2.4 Preparation of reference samples for specific determinative methods

The following sections provide guidance on the QC reference sample concentrates for many determinative methods. The concentration of the target analytes in the QC reference sample for the methods listed below may need to be adjusted to more accurately reflect the concentrations of interest in different samples or projects. If the concentration of an analyte is being evaluated relative to a regulatory limit or action level, see Sec. 9.3.3 for information on selecting an appropriate spiking level. In addition, the analyst may vary the concentration of the spiking solution and the volume of solution spiked into the sample. However, because of concerns about the effects of the spiking solution solvent on the sample, the total volume spiked into a sample should generally be held to no more than 1 mL. For any determinative method not listed below, the analyst should consult Sec. 9.3.3 and is free to choose analytes and spiking concentrations appropriate for the intended application. See the note in Sec. 9.3.1 for important information regarding spiking samples.

NOTE: All of the concentrations listed below refer to the concentration of the spiking solution itself, not the concentration of the spiked sample.

9.2.4.1 Method 8041, Phenols -- The QC reference sample concentrate should contain each analyte at 100 mg/L in 2-propanol.

9.2.4.2 Method 8061, Phthalate esters -- The QC reference sample concentrate should contain the following analytes at the indicated concentrations in acetone: Butyl benzyl phthalate at 10 mg/L; bis(2-ethylhexyl)phthalate at 50 mg/L; di-*n*-octyl phthalate at 50 mg/L; and any other phthalate at 25 mg/L.

9.2.4.3 Method 8070, Nitrosamines -- The QC reference sample concentrate should contain each analyte at 20 mg/L in isooctane.

9.2.4.4 Method 8081, Organochlorine pesticides -- The QC reference sample concentrate should contain each single-component analyte at the following indicated concentrations in acetone: 4,4'-DDD at 10 mg/L; 4,4'-DDT at 10 mg/L; endosulfan II at 10 mg/L; endosulfan sulfate at 10 mg/L; and any other single-component pesticide at 2 mg/L. If the method is only to be used to analyze chlordane or toxaphene, the QC reference sample concentrate should contain the most representative multicomponent parameter at a concentration of 50 mg/L in acetone.

9.2.4.5 Method 8082, PCBs -- The QC reference sample concentrate should contain the most representative multicomponent parameter at a concentration of 50 mg/L in acetone.

9.2.4.6 Method 8091, Nitroaromatics and cyclic ketones -- The QC reference sample concentrate should contain each analyte at the following indicated concentrations in acetone: Each dinitrotoluene at 20 mg/L; and isophorone and nitrobenzene at 100 mg/L.

9.2.4.7 Method 8095, Explosives by GC -- The QC reference sample concentrate should contain the following analytes at the indicated concentrations: 1,3-DNB, 2,6-DNT, 2,4-DNT, 1,3,5-TNB, 2,4,6-TNT, RDX, 4-Am-DNT, 2-Am-DNT, tetryl, and DNA at 0.2 µg/L; NB, 3-NT, 2-NT, 4-NT, NG, and PETN at 1.0 µg/L; and HMX at 2.0 µg/L.

9.2.4.8 Method 8100, Polynuclear aromatic hydrocarbons (PAHs) -- The QC reference sample concentrate should contain each analyte at the following indicated concentrations in acetonitrile -- Naphthalene at 100 mg/L; acenaphthylene at 100 mg/L; acenaphthene at 100 mg/L; fluorene at 100 mg/L; phenanthrene at 100 mg/L; anthracene at 100 mg/L; benzo(k)fluoranthene at 5 mg/L; and any other PAH at 10 mg/L.

9.2.4.9 Method 8111, Haloethers -- The QC reference sample concentrate should contain each analyte at a concentration of 20 mg/L in isooctane.

9.2.4.10 Method 8121, Chlorinated hydrocarbons -- The QC reference sample concentrate should contain each analyte at the following indicated concentrations in acetone: Hexachloro-substituted hydrocarbons at 10 mg/L; and any other chlorinated hydrocarbon at 100 mg/L.

9.2.4.11 Method 8131, Aniline and selected derivatives -- The QC reference sample concentrate should contain each analyte in acetone at a concentration 1,000 times more concentrated than the selected spike concentration.

9.2.4.12 Method 8141, Organophosphorus compounds -- The QC reference sample concentrate should contain each analyte in acetone at a concentration 1,000 times more concentrated than the selected spike concentration.

9.2.4.13 Method 8151, Chlorinated herbicides -- The QC reference sample concentrate should contain each analyte in acetone at a concentration 1,000 times more concentrated than the selected spike concentration.

9.2.4.14 Method 8260, Volatile organics -- The QC reference sample concentrate should contain each analyte in methanol at a concentration of 10 mg/L. This concentrate is spiked into 100 mL of organic-free reagent water, producing enough reference sample for four aliquots of up to 25 mL each.

9.2.4.15 Method 8270, Semivolatile organics -- The QC reference sample concentrate should contain each analyte in acetone at a concentration of 100 mg/L.

9.2.4.16 Method 8310, Polynuclear aromatic hydrocarbons (PAHs) -- The QC reference sample concentrate should contain each analyte at the following concentrations in acetonitrile: naphthalene at 100 mg/L; acenaphthylene at 100 mg/L; acenaphthene at 100 mg/L; fluorene at 100 mg/L; phenanthrene at 100 mg/L; anthracene at 100 mg/L; benzo(k)fluoranthene at 5 mg/L; and any other PAH at 10 mg/L.

9.2.5 Analyze at least four replicate aliquots of the well-mixed reference samples by the same procedures used to analyze actual samples. This will include a combination of the sample preparation method (usually a 3500 series method for extractable organics) and the determinative method (an 8000 series method). Follow the guidance on data calculation and interpretation presented in Method 8000.

9.2.6 The following methods contain specific extraction and sample preparation criteria applicable only to that method. Refer to these individual methods for extraction and preparation procedures needed prior to instrumental analysis, and for information on the preparation of QC reference samples.

9.2.6.1 Method 8085 – Compound-independent elemental quantitation of pesticides by gas chromatography with atomic emission detection (GC/AED)

9.2.6.2 Method 8275 -- Semivolatile organic compounds using thermal extraction/gas chromatography/mass spectrometry (TE/GC/MS).

9.2.6.3 Method 8280 -- Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans by high resolution gas chromatography/low resolution mass spectrometry (HRGC/LRMS).

9.2.6.4 Method 8290 -- Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans by high resolution gas chromatography/high resolution mass spectrometry (HRGC/LRMS).

9.2.6.5 Method 8318 -- *N*-Methylcarbamates by high performance liquid chromatography (HPLC).

9.2.6.6 Method 8321 -- Solvent extractable nonvolatile compounds by high performance liquid chromatography/thermospray/mass spectrometry (HPLC/TS/MS) or ultraviolet (UV) detection.

9.2.6.7 Method 8325 -- Solvent extractable nonvolatiles by high performance liquid chromatography/particle beam/mass spectrometry (HPLC/PB/MS).

9.2.6.8 Method 8330 -- Nitroaromatics and nitramines by high performance liquid chromatography (HPLC).

9.2.6.9 Method 8331 -- Tetrazene by reverse phase high performance liquid chromatography (HPLC).

9.2.6.10 Method 8332 -- Nitroglycerine by high performance liquid chromatography (HPLC) or thin-layer chromatography (TLC).

9.2.6.11 Method 8410 -- Semivolatile organics by gas chromatography/Fourier transform infrared (GC/FT-IR) spectrometry.

9.2.6.12 Method 8430 -- Bis(2-chloroethyl) ether and hydrolysis products by GC/FT-IR.

9.2.6.13 Method 8440 -- Total recoverable petroleum hydrocarbons by infrared spectrophotometry.

9.3 Sample quality control for preparation and analysis

9.3.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair per analytical batch. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, then laboratories should use a matrix spike and matrix spike duplicate pair. The consideration as to which sample for a given batch is selected for QC analyses should be decided during the project planning process and documented in an approved sampling and analysis plan. The actual sample selected for QC analyses should be representative of the entire matrix composition for a given extraction batch, since data quality assumptions will likely be applied to all batch samples based on compliance to the stated data quality objectives and meeting the recommended precision and accuracy criteria. Therefore, it is inappropriate to combine dissimilar matrices in a single sample preparatory batch and expect to use a single set of QC samples. See Sec. 7.6 for additional guidance on matrix spike preparation. Sec. 9.3.3 provides guidance on establishing the concentration of the matrix spike compounds in the sample chosen for spiking.

The choice of analytes to be spiked should reflect the analytes of interest for the specific project. Thus, if only a subset of the list of target analytes provided in a determinative method are of interest (e.g., Method 8270 is used for the analysis of only PAHs), then these would be the analytes of interest for the project. In the absence of project-specific analytes of interest, it is suggested that the laboratory periodically change the analytes that are spiked with the goal of obtaining matrix spike data for most, if not all, of the analytes in a given determinative method. As noted in Sec. 7.6, the recommended matrix spike compounds in Secs 7.6.1 and 7.6.2 are considered a minimum recommendation. If these compounds are not target analytes for a specific project, or if other compounds are known to be of greater concern at a given site, then other matrix spike compounds should be employed.

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, or PRIOR TO making further adjustment to the pH of an aqueous sample, such as in a base/neutral extraction at pH>11. 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. As each 3500 series extraction procedure is revised, the order of the procedural steps will be made consistent with this note. However, until such time as all those methods are revised, the instructions in this note SUPERSEDE those in each extraction method.

9.3.2 A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume: e.g., organic-free reagent water for the water

matrix or sand or soil (free of organic interferences) for the solid matrix. The LCS is spiked with the same analytes at the same concentrations as the matrix spike, when appropriate. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

9.3.3 The concentration of the matrix spike sample and/or the LCS should be determined as described in the following sections.

9.3.3.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory limit or action level, the spike should be at or below the regulatory limit or action level, or 1 - 5 times the background concentration (if historical data are available), whichever concentration is higher.

9.3.3.2 If historical data are not available, it is suggested that an uncontaminated sample of the same matrix from the site be submitted for matrix spiking purposes to ensure that high concentrations of target analytes and/or interferences will not prevent calculation of recoveries.

9.3.3.3 If the concentration of a specific analyte in a sample is not being checked against a limit specific to that analyte, then the concentration of the matrix spike should be at the same concentration as the reference sample (Sec. 9.2.4), near the middle of calibration range, or approximately 10 times the quantitation limit in the matrix of interest. It is again suggested that a background sample of the same matrix from the site be submitted as a sample for matrix spiking purposes.

9.3.4 Analyze these QC samples (the LCS and the matrix spikes or the optional matrix duplicates) following the procedures in the determinative method. Calculate and evaluate the QC data as outlined in Method 8000.

9.3.5 Blanks -- The preparation and analysis of method blanks and other blanks are necessary to track potential contamination of samples during the extraction and analysis processes. Refer to Chapter One for specific quality control procedures.

9.3.6 Surrogates -- A surrogate is a compound that is chemically similar to the analyte group but not expected to occur in an environmental sample. Surrogates should be added to all samples when included in the appropriate determinative method (see Table 1 for the suggested surrogates for some determinative methods). See Sec. 7.5 for additional guidance on surrogates. See the note in Sec. 9.3.1 for important information regarding spiking samples.

9.4 The laboratory must also have procedures for documenting the effect of the matrix on method performance. Refer to Chapter One and Method 8000 for specific guidance on developing method performance data.

10.0 CALIBRATION AND STANDARDIZATION

There are no calibration or standardization steps directly associated with this method.

11.0 PROCEDURE

11.1 Water, soil/sediment, sludge, and waste samples requiring analysis for semivolatile and nonvolatile organic compounds (within this broad category are special subsets of analytes, i.e., the different groups of pesticides, explosives, PCBs, etc.) must undergo solvent extraction prior to analysis. This manual contains method choices that are dependent on the matrix, the physical properties of the analytes, the sophistication and cost of equipment available to a given laboratory, and the turn-around time needed for sample preparation.

Many of the extraction methods include choices of extraction solvents or solvent systems that may be employed. The choice of extraction solvent may 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 a given extraction method, the analyst *must* demonstrate adequate performance for the analytes of interest. At a minimum, such a demonstration will encompass the initial demonstration of proficiency described in Sec. 9.2, 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.

11.1.1 The laboratory should be responsible for ensuring that the method chosen for sample extraction will provide acceptable extraction efficiency for the target analytes in a given matrix. There are several approaches that may be employed to ensure the appropriateness of the extraction method.

11.1.1.1 Prior to employing any extraction procedure on samples submitted for regulatory compliance monitoring purposes, the laboratory should complete the initial demonstration of proficiency described in Sec. 9.2. This demonstration applies to all extraction methods, including those for which specific performance data are provided in a determinative method.

11.1.1.2 In addition, when a new or different extraction technique is to be applied to samples, the laboratory should also demonstrate that their application of the technique provides acceptable performance in the matrix of interest for the analytes of interest. One approach to demonstrating extraction method performance is to make a direct comparison between the chosen method and either Method 3520 (continuous liquid-liquid extraction of aqueous samples) or Method 3540 (Soxhlet extraction of solid samples), as these methods have the broadest applicability to environmental matrices.

When direct comparisons are performed, the preferred approach is to conduct the comparisons using either standard reference materials derived from real-world matrices or samples from a given site that can be reasonably expected to contain the analytes of interest at the concentrations of interest. Because of concerns with the incorporation of spiking materials into samples, the use of samples spiked by the laboratory is generally a less useful comparison relative to either real-world contaminated samples or standard reference materials, and thus should generally only be employed when neither of these latter materials are available. Analyze at least four portions of a well-homogenized sample by the extraction method of interest and either Method 3520 or Method 3540, depending on the matrix.

11.1.1.3 When direct comparisons between methods are conducted, the laboratory may use statistical tests such as an F-test to determine if the results

are comparable between the methods. The laboratory may employ the method of interest provided that the demonstrated performance can be shown to be adequate for project needs, that is, meeting the requirements of the QA Project Plan for a specific project or the QC acceptance criteria for a laboratory SOP.

11.1.1.4 Whatever approaches are taken to ensure the adequacy of the extraction procedure for the matrix of interest, it is the responsibility of the laboratory to document the results and maintain records of such demonstrations.

11.1.2 Each method usually contains QC procedures that normally include the addition of surrogates to each analytical sample and QC sample as well as the inclusion of a matrix spike/matrix spike duplicate (or matrix spike and duplicate sample), a laboratory control sample, and a method blank in each sample extraction batch. As defined in Chapter One, a "batch" consists of up to 20 environmental samples processed as a unit. In the case of samples that must undergo extraction prior to analysis, each group of 20 samples extracted together by the same method constitutes an extraction batch.

The decision of whether to prepare and analyze a matrix spike/matrix spike duplicate pair or a matrix spike and a duplicate sample should be based on knowledge of the samples in the extraction batch. If the samples are expected to contain the analytes of interest, then the analysis of a duplicate sample may yield data on the precision of the analytical process and the analysis of the matrix spike will yield data on the accuracy of the process. In contrast, when the samples are not known or expected to contain the analytes of interest, then the batch should include a matrix spike/matrix spike duplicate pair to ensure that both accuracy and precision data will be generated within the extraction batch. The consideration as to which sample for a given batch is selected for QC analyses should be decided during the project planning process and documented in an approved sampling and analysis plan. The actual sample selected for QC analyses should be representative of the entire matrix composition for a given extraction batch, since data quality assumptions will likely be applied to all batch samples based on compliance to the stated data quality objectives and meeting the recommended precision and accuracy criteria. Therefore, it is inappropriate to combine dissimilar matrices in a single sample preparatory batch and expect to use a single set of QC samples. See the note in Sec. 9.3.1 for important information regarding spiking samples.

11.2 Method 3510 -- Applicable to the extraction and concentration of water-insoluble and slightly water-soluble organics from aqueous samples. A measured volume of sample is solvent extracted using a separatory funnel. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis. Separatory funnel extraction utilizes relatively inexpensive glassware and is fairly rapid (three, 2-minute extractions followed by filtration) but is labor intensive, uses fairly large volumes of solvent and is subject to emulsion problems. It can result in poor recovery for the more water soluble analytes, e.g. phenols. Method 3520 should be used if an emulsion forms between the solvent-sample phases which cannot be broken by mechanical techniques or if water soluble compounds are analytes of concern.

11.3 Method 3520 -- Applicable to the extraction and concentration of water-insoluble and slightly water-soluble organics from aqueous samples. A measured volume of sample is extracted with an organic solvent in a continuous liquid-liquid extractor. The solvent must have a density greater than that of the sample. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis. Continuous extractors are excellent for samples with particulates (of up to 1% solids) that cause emulsions, provide more efficient

extraction of analytes that are more difficult to extract and, once loaded, do not need hands-on manipulation. However, continuous extractors need more expensive glassware, use fairly large volumes of solvent and have a rather lengthy extraction time (6 to 24 hrs).

11.4 Method 3535 -- Applicable to the extraction and concentration of water-insoluble and slightly water-soluble organics from aqueous samples. A measured volume of water is pumped through an appropriate medium (e.g., disk or cartridge) containing a solid phase that extracts the organics from water. A small volume of extraction solvent is passed through the medium to elute the compounds of interest. The eluant is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis. Appropriate solid-phase extraction media allow extraction of water containing particulates, are relatively fast, and use small volumes of solvent. However, they do involve the use of some specialized equipment. In addition, for successful use of this technique, the analyst needs to follow the details of the method very closely. Proper preparation of the extraction medium is critical to the success of this technique.

11.5 Method 3540 -- This method is applicable to the extraction of nonvolatile and semivolatile organic compounds from solids such as soils, relatively dry sludges, and solid wastes. A solid sample is mixed with anhydrous sodium sulfate, placed into an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. The extract is concentrated and, if necessary, exchanged into a solvent compatible with further analysis. Soxhlet extraction uses relatively inexpensive glassware and, once loaded; does not need hands-on manipulation; provides efficient extraction but is rather lengthy (16 to 24 hrs) and uses fairly large volumes of solvent. It is considered a rugged extraction method because there are very few variables that can adversely affect extraction efficiency.

11.6 Method 3541 -- This method utilizes a modified Soxhlet extractor and is applicable to the extraction of semivolatile/nonvolatile organic compounds from solids such as soils, relatively dry sludges, and solid wastes. A solid sample is mixed with anhydrous sodium sulfate, placed into an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in an automated Soxhlet extractor. This device allows the extraction thimble to be lowered into the boiling liquid for the first hour and then extracted in the normal thimble position for one additional hour. The automated Soxhlet allows equivalent extraction efficiency to Method 3540 in 2 hrs, combines the concentration step within the same device but needs a rather expensive device.

11.7 Method 3542 -- This method is applicable to the extraction of semivolatile organic compounds from the Method 0010 air sampling train. The solid trapping material (i.e., glass or quartz fiber filter and porous polymeric adsorbent resin) are extracted using Soxhlet extraction and the condensate and impinger fluid are extracted using separatory funnel extraction.

11.8 Method 3545 -- This method is applicable to the extraction of nonvolatile/semivolatile organic compounds from solids such as soils, relatively dry sludges, and solid wastes. A solid sample is mixed with anhydrous sodium sulfate, placed into an extraction cell and extracted under pressure with small volumes of solvent. The extract is concentrated and, if necessary, exchanged into a solvent compatible with further analysis. The method is rapid and efficient, in that it uses small volumes of solvent, but does involve the use of an expensive extraction device.

11.9 Method 3546 -- This method is applicable to the extraction of nonvolatile and semivolatile organic compounds from solid samples such as soils, relatively dry sludges, and solid wastes, using microwave energy to produce elevated temperature and pressure conditions

in a closed vessel containing the sample and organic solvent(s). The method is applicable to solid samples only with small particle sizes. If practical, 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. Following extraction, the extract is concentrated and, if necessary, exchanged into a solvent compatible with further analysis. The method is rapid and efficient, in that it uses small volumes of solvent, but does involve the use of an expensive extraction device.

11.10 Method 3550 -- This method is applicable to the extraction of nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes using the technique of ultrasonic extraction. Two procedures are detailed depending upon the expected concentration of organics in the sample; a low concentration and a high concentration method. In both, a known weight of sample is mixed with anhydrous sodium sulfate and solvent extracted using ultrasonic extraction. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis. Ultrasonic extraction is fairly rapid (three, three-minute extractions, followed by filtration) but uses relatively large volumes of solvent, and does involve a somewhat expensive device. However, extraction efficiency is generally lower than that obtained using the Soxhlet-type techniques.

NOTE: Because the extraction time is relatively short compared to other techniques described here, the extraction efficiency of this technique is greatly influenced by the choice of the extraction solvent or solvent system and proper maintenance of the extraction devices. This is particularly true when attempting to extract very hydrophobic compounds from wet samples. For successful use of this technique, the analyst needs to follow the details of the method very closely. The proper choice of an extraction solvent and proper tuning and maintenance of the ultrasonic device are critical.

11.11 Methods 3560, 3561, and 3562 -- These methods are applicable to the extraction of total recoverable petroleum hydrocarbons, PAHs, polychlorinated biphenyls, and organochlorine pesticides from solids such as soils, sludges, and wastes using the technique of supercritical fluid extraction (SFE). SFE normally uses CO_2 (which may contain very small volumes of solvent modifiers). Therefore, there is no solvent waste for disposal, the method may be automated, and it provides relatively rapid extraction. However, it is currently limited to a small number of analyte categories. It also involves a rather expensive device and sample size is somewhat limited.

11.12 Method 3580 -- This method describes the technique of solvent dilution of non-aqueous waste samples. It is designed for wastes that may contain organic chemicals at a level greater than 20,000 mg/kg and that are miscible with the dilution solvent. When using this method, the analyst must use caution in the addition of surrogate compounds, so as not to dilute out the surrogate response when diluting the sample.

11.13 Sample analysis -- Following preparation of a sample by one of the methods described above, the sample is ready for further analysis. Samples prepared for analysis of various semivolatile/nonvolatile compounds may, if necessary, undergo cleanup prior to application of a specific determinative method. The specific cleanup procedure used will depend on the nature of the sample to be analyzed and the data quality objectives for the measurements. General guidance for sample cleanup is provided in Method 3600.

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 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 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 a particular 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 The recovery of surrogates is used to monitor unusual matrix effects, sample processing problems, etc.

13.3 Generally speaking, the matrix spike results are intended to be used to indicate the presence or absence of unusual matrix effects, and not to evaluate laboratory performance. Thus, when problems are noted with the recovery of the matrix spiking compounds, those results are compared to laboratory control sample (LCS) recoveries to determine if the laboratory was able to achieve acceptable recovery in a clean matrix. See Method 8000 for more information on the evaluation of matrix spike and LCS results.

13.4 The performance of each 3500 series method will be dictated by the overall performance of the sample preparation in combination with the cleanup method and/or the analytical determinative method.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity 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

No references.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The following page contains the table referenced by this method.

TABLE 1

SUGGESTED SURROGATES FOR SW-846 CHROMATOGRAPHIC METHODS
FOR SEMIVOLATILE AND NONVOLATILE COMPOUNDS

Method	Technique	Suggested Surrogates*
8041	Phenols by GC	2-Fluorophenol, and 2,4,6-tribromophenol
8061	Phthalate esters by GC	Diphenyl phthalate, diphenyl isophthalate, and dibenzyl phthalate
8081	Organochlorine pesticides by GC	2,4,5,6-Tetrachloro-*m*-xylene, and decachlorobiphenyl
8082	Polychlorinated biphenyls by GC	Decachlorobiphenyl
8085	Pesticides by GC/AED	1,3-dimethyl-2-nitrobenzene, dibromo-octafluorobiphenyl, tetrachloro-*m*-xylene, decachlorobiphenyl, and triphenylphosphate.
8091	Nitroaromatics by GC	2-Fluorobiphenyl
8095	Explosives by GC	2,5-Dinitrotoluene and 3,4-dinitrotoluene
8100	PAHs by GC	2-Fluorobiphenyl, and 1-fluoronaphthalene
8121	Chlorinated hydrocarbons by GC	α,2,6-Trichlorotoluene, 2,3,4,5,6-pentachlorotoluene, and 1,4-dichloronaphthalene
8151	Chlorinated herbicides by GC	2,4-Dichlorophenylacetic acid
8270	Semivolatiles by GC/MS	Phenol-d_6, 2-fluorophenol, 2,4,6-tribromophenol, nitro-benzene-d_5, 2-fluorobiphenyl, and *p*-terphenyl-d_{14}
8280	PCDDs and PCDFs by HRGC/LRMS	Internal standards added at time of extraction. No surrogates.
8290	PCDDs and PCDFs by HRGC/HRMS	Internal standards added at time of extraction. No surrogates.
8310	PAHs by HPLC	Decafluorobiphenyl
8325	Nonvolatiles by HPLC/PB/MS or UV/Vis	Benzidine-d_8, caffeine-$^{15}N_2$, 3,3'-dichlorobenzidine-d_6, and bis-(perfluorophenyl)-phenylphosphine oxide

* Suggested surrogate concentration in the sample is 10 times the quantitation limit, or near the mid-point of the calibration curve. See Sec. 7.5.2.

Consult Sec. 7.5 regarding the choice of surrogates for any method not listed here.

GC	Gas Chromatography	HPLC	High Performance Liquid Chromatography
HR	High Resolution	PCDD	Polychlorinated Dibenzo-*p*-dioxins
LR	Low Resolution	PCDF	Polychlorinated Dibenzofurans
PB	Particle Beam	UV/Vis	Ultraviolet/Visible Spectrometry
MS	Mass Spectrometry	AED	Atomic Emission Detector