METHOD 3500B

ORGANIC EXTRACTION AND SAMPLE PREPARATION

1.0 SCOPE AND APPLICATION

1.1 Method 3500 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. Cleanup and/or 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 and the analyte category.

SAMPLE EXTRACTION METHODS FOR SEMIVOLATILES AND NONVOLATILES

Method #	Matrix	Extraction Type	Analytes
3510	Aqueous	Separatory Funnel Liquid-Liquid Extraction	Semivolatile & Nonvolatile Organics
3520	Aqueous	Continuous Liquid-Liquid Extraction	Semivolatile & Nonvolatile Organics
3535	Aqueous	Solid-Phase Extraction (SPE)	Semivolatile & Nonvolatile Organics
3540	Solids	Soxhlet Extraction	Semivolatile & Nonvolatile Organics
3541	Solids	Automated Soxhlet Extraction	Semivolatiles & Nonvolatile Organics
3542	Air Sampling Train	Separatory Funnel & Soxhlet Extraction	Semivolatile Organics
3545	Solids	Pressurized Fluid Extraction (ASE) (Heat & Pressure)	Semivolatile & Nonvolatile Organics
3550	Solids	Ultrasonic Extraction	Semivolatile & Nonvolatile Organics
3560/ 3561	Solids	Supercritical Fluid Extraction (SFE)	Semivolatile Petroleum Hydrocarbons & Polynuclear Aromatic Hydrocarbons
3580	Non-aqueous Solvent Soluble Waste	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, 3560, and 3561 are techniques that utilize pressurized 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 allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in this procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to meet the data quality objectives or needs for the intended use of the data.

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 or heated pressurized fluid 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 the quality control requirements of the determinative methods are met (Method 8000, Sec. 8.0).

NOTE: Solvent recovery apparatus is recommended for use in methods that require the use of Kuderna-Danish 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. 7.0 for additional guidance to assist in selection of the appropriate method.

3.0 INTERFERENCES

3.1 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 for specific guidance on quality control procedures and to Chapter Four for guidance on the cleaning of glassware.

3.2 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.

3.3 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.

3.4 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.

4.0 APPARATUS AND MATERIALS

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

4.2 Solvent recovery apparatus is recommended for use in methods that require the use of Kuderna-Danish evaporative concentrators. Incorporation of this apparatus may be required by 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.

5.0 REAGENTS

5.1 Refer to the specific method of interest for a description of the solvents needed.

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

5.3 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.

5.3.1 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.

5.3.2 Stock standard solutions should be stored in polytetrafluoroethylene (PTFE)-sealed containers at 4°C or below. The solutions should be checked frequently for stability. Refer to the determinative method for holding times of the stock solutions.

5.4 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.

5.4.1 Recommended surrogates for certain analyte groups are listed in Table 1. For methods where no recommended surrogates are listed, the lab 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 a surrogate as long as historical data are available to ensure their absence at a given site. Normally one or more standards are added for each analyte group.

5.4.2 Prepare a surrogate spiking concentrate 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 into 1000 mL of a sample provides a concentration of 10 times the quantitation limit 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 recommended surrogates. The spiking volumes are normally listed in each extraction method. Where concentrations are not listed in a method, a concentration of 10 times the quantitation limit is recommended. If the surrogate quantitation limit is unknown, the average quantitation limit of method target analytes may be utilized to estimate a surrogate quantitation limit. As necessary or appropriate to meet project objectives, the surrogates listed in Table 1 may be modified by the laboratory. The concentration of the surrogate in the sample (or sample extract) should either be near the middle of the calibration range or approximately ten times the quantitation limit.

5.5 Matrix spike standards - The following are recommended matrix spike standard mixtures for a few analyte groups. 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. A few methods provide guidance on concentrations and the selection of compounds for matrix spikes (see Table 2).

5.5.1 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/neutrals	Acids
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	

5.5.2 Organochlorine pesticide matrix spiking solution - Prepare a spiking solution in acetone or methanol that contains the following pesticides in the concentrations listed for water and sediment/soil. The concentration should be five times higher for waste 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

5.5.3 For methods with no guidance, select five or more analytes (select all analytes for methods with five or less) from each analyte group for use in a spiking solution. Where matrix spike concentrations in the sample are not listed it should be at or below the regulatory concentration or action level, or 1 to 5 times higher than the background concentration, whichever, concentration would be larger.

5.5.4 Sec. 8.3.3 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. 5.5.1, 5.5.2, 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. 8.3.3.3) the concentration of the matrix spike compound in the sample (or sample extract) should be near the middle of the calibration range or approximately ten times the quantitation limit.

5.6 Laboratory control spike standard - Use the matrix spike standard prepared in Sec. 5.5 as the spike standard for the laboratory control sample (LCS). The LCS should be spiked at the same concentration as the matrix spike.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See Chapters Two and Four for guidance on sample collection.

7.0 PROCEDURE

7.1 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 required for sample preparation.

7.1.1 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.

7.1.1.1 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. 8.2. This demonstration applies to all SW-846 extraction methods, including those for which specific performance data are provided in a determinative method.

7.1.1.2 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, they should be conducted 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. 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.

7.1.1.3 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 either as good or better than that of the "reference" method, or adequate for project needs, that is, meeting the requirements of the QA Project Plan for a specific project.

7.1.1.4 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.

7.1.2 Each method has QC requirements 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.

7.2 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. Method

3520 should be used if an emulsion forms between the solvent-sample phases, which cannot be broken by mechanical techniques.

7.3 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, require no hands-on manipulation. However, they require more expensive glassware, use fairly large volumes of solvent and extraction time is rather lengthy (6 to 24 hours).

7.4 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 effects the extraction of 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 require some specialized pieces of equipment.

7.5 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, once loaded requires no hands-on manipulation, provides efficient extraction, but is rather lengthy (16 to 24 hours) 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.

7.6 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 in 2 hours, combines the concentration step within the same device but requires a rather expensive device.

7.7 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.

7.8 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 require the use of an expensive extraction device.

7.9 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, 3-minute extractions followed by filtration) but uses relatively large volumes of solvent, requires a somewhat expensive device and requires following the details of the method very closely to achieve acceptable extraction efficiency (proper tuning of the ultrasonic device is very critical). This technique is much less efficient than the other extraction techniques described in this section. This is most evident with very non-polar organic compounds (e.g., PCBs, etc.) that are normally strongly adsorbed to the soil matrix. EPA has not validated Method 3550 for the extraction of organophosphorus compounds from solid matrices. In addition, there are concerns that the ultrasonic energy may lead to breakdown of some organophosphorus compounds (see Reference 1). As a result, this extraction technique should not be used for organophosphorous compounds without extensive validation on real-world samples. Such studies should assess the precision, accuracy, ruggedness, and sensitivity of the technique relative to the appropriate regulatory limits or project-specific concentrations of interest.

7.10 Methods 3560 and 3561 - These methods are applicable to the extraction of total recoverable petroleum hydrocarbons and PAHs 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, may be automated, provides relatively rapid extraction, but, is currently limited to total recoverable petroleum hydrocarbons and PAHs. It also requires a rather expensive device and sample size is more limited. Research on SFE is currently focusing on optimizing supercritical fluid conditions to allow efficient extraction of a broader range of RCRA analytes in a broad range of environmental matrices.

7.11 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 soluble in 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.

7.12 Sample analysis - Following preparation of a sample by one of the methods described above, the sample is ready for further analysis. Samples prepared for semivolatile/nonvolatile analysis may, if necessary, undergo cleanup (See Method 3600) prior to application of a specific determinative method.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific guidance on quality control procedures. Each laboratory using SW-846 methods should maintain a formal quality assurance program. Each extraction batch of 20 or less samples should contain: a method blank; either a matrix spike/matrix spike duplicate or a matrix spike and duplicate samples; and a laboratory control sample, unless the determinative method provides other guidance.

8.2 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 should also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made.

8.2.1 The reference samples are prepared 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.

8.2.2 The procedure for preparation of the reference sample concentrate is dependent upon the method being evaluated. Guidance for reference sample concentrations for certain methods are listed below. In other cases, the determinative methods 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). Spike the reference sample at the concentration on which the method performance data are based. The spiking volume added to water should not exceed 1 mL/L so that the spiking solvent will not decrease extraction efficiency. If the method lacks performance data, prepare a reference standard concentrate at such a concentration that the spike will provide a concentration in the clean matrix that is 10 - 50 times the MDL for each analyte in that matrix.

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. 8.3.1 for information on selecting an appropriate spiking level.

8.2.3 To evaluate the performance of the total analytical process, the reference samples must be handled in exactly the same manner as actual samples. Therefore, 1 mL (unless the method specifies 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 sample), extracted as per the method. For matrices other than water or for determinative methods that specify 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 specified 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.

8.2.4 Preparation of reference samples

The following sections provide guidance on the QC reference sample concentrates for many SW-846 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. 8.3.3 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.

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

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

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

8.2.4.4 Method 8081 - Organochlorine pesticides: The QC reference sample concentrate should contain each single-component analyte at the following concentrations in acetone: 4,4'-DDD, 10 mg/L; 4,4'-DDT, 10 mg/L; endosulfan II, 10 mg/L; endosulfan sulfate, 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.

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

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

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

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

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

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

8.2.4.11 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.

8.2.4.12 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.

8.2.4.13 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.

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

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

8.2.5 Analyze at least four replicate aliquots of the well-mixed reference samples by the same procedures used to analyze actual samples (Sec. 7.0 of each of the methods). 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, Sec. 8.0.

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

8.2.6.1 Method 8275 - Thermal Extraction/Gas Chromatography/Mass Spectrometry (TE/GC/MS) for Semivolatile Organic Compounds.

8.2.6.2 Method 8280 - Polychlorinated Dibenzo-*p*-dioxins and Polychlorinated Dibenzofurans.

8.2.6.3 Method 8290 - Polychlorinated Dibenzo-*p*-dioxins and Polychlorinated Dibenzofurans.

8.2.6.4 Method 8318 - N-Methylcarbamates by High Performance Liquid Chromatography (HPLC).

8.2.6.5 Method 8321 - Solvent Extractable Nonvolatile Compounds by High Performance Liquid Chromatography/Thermospray/Mass Spectrometry (HPLC/TS/MS) or Ultraviolet (UV) Detection.

8.2.6.6 Method 8325 - Solvent Extractable Nonvolatiles by High Performance Liquid Chromatography/Particle Beam/Mass Spectrometry (HPLC/PB/MS).

8.2.6.7 Method 8330 - Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC).

8.2.6.8 Method 8331 - Tetrazene by Reverse Phase High Performance Liquid Chromatography (HPLC).

8.2.6.9 Method 8332 - Nitroglycerine by High Performance Liquid Chromatography (HPLC) or Thin-Layer Chromatography (TLC).

8.2.6.10 Method 8410 - Gas Chromatography/Fourier Transform Infrared (GC/FT-IR) Spectrometry for Semivolatile Organics.

8.2.6.11 Method 8430 - Bis(2-chloroethyl) ether and Hydrolysis Products by GC/FT-IR.

8.2.6.12 Method 8440 - Total Recoverable Petroleum Hydrocarbons (TRPH) by Infrared (IR) Spectrophotometry.

8.3 Sample Quality Control for Preparation and Analysis

8.3.1 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, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, the laboratories should use a matrix spike and matrix spike duplicate pair. See Sec. 5.5 for additional guidance on matrix spike preparation. Sec. 8.3.3 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.

8.3.2 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 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.

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

8.3.3.1 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.

8.3.3.2 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.

8.3.3.3 If the concentration of a specific analyte in a sample is not being checked against a limit specific to that analyte, then the spike should be at the same concentration as the reference sample (Sec. 8.2.4) or 20 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.

8.3.4 Analyze these QC samples (the LCS and the matrix spikes or the optional matrix duplicates) following the procedure (Sec. 7.0) of the selected determinative method. Calculate and evaluate the QC data as outlined in Sec. 8.0 of Method 8000.

8.3.5 Blanks - Use of method blanks and other blanks are necessary to track contamination of samples during the sampling and analysis processes. Refer to Chapter One for specific quality control procedures.

8.3.6 Surrogates - A surrogate is a compound that is chemically similar to the analyte group but not expected to occur in an environmental sample. Surrogate should be added to all samples when specified in the appropriate determinative method (See Table 1). See Sec. 5.4 for additional guidance on surrogates.

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

9.0 METHOD PERFORMANCE

9.1 The recovery of surrogates is used to monitor unusual matrix effects, sample processing problems, etc. The recovery of matrix spiking compounds, when compared to laboratory control sample (LCS) recoveries, indicates the presence or absence of unusual matrix effects.

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

10.0 REFERENCES

None required.

TABLE 1

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

Method Number	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
8070	Nitrosamines by GC	None listed**
8081	Organochlorine Pesticides by GC	2,4,5,6-Tetrachloro-m-xylene, and Decachlorobiphenyl
8082	Polychlorinated Biphenyls by GC	Decachlorobiphenyl
8091	Nitroaromatics by GC	2-Fluorobiphenyl
8100	PAHs by GC	2-Fluorobiphenyl, and 1-Fluoronaphthalene
8111	Haloethers by GC	None listed**
8121	Chlorinated Hydrocarbons by GC	α,2,6-Trichlorotoluene, 2,3,4,5,6-Pentachlorotoluene, and 1,4-Dichloronaphthalene
8131	Anilines by GC	None listed**
8141	Organophosphorus Pesticides by GC	None listed**
8151	Acid 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}
8275	Semivolatiles by TE/GC/MS	Not listed**
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
8318	Carbamates by HPLC	None listed**
8321	Nonvolatiles by HPLC/TS/MS or UV Detection	None listed**

Table 1 (continued)

Method Number	Technique	Suggested Surrogates*
8325	Nonvolatiles by HPLC/PB/MS or UV/Vis	Benzidine-d_8, Caffeine-$^{15}N_2$, 3,3'-Dichlorobenzidine-d_6, Bis-(perfluorophenyl)-phenylphosphine oxide
8330	Explosives by HPLC	None listed**
8331	Tetrazene by HPLC	None listed**
8332	Nitroglycerine by HPLC or TLC	None listed**
8410	GC/FT-IR for Semivolatiles	None listed**
8430	Bis(2-chloroethyl) ether and Hydrolysis Products by GC/FT-IR	None listed**
8440	Total Recoverable Petroleum Hydrocarbons by IR	None listed**

* Suggested water concentration = 10 times the quantitation limit or near the mid-point of the calibration curve. See Sec. 5.4.2.

** Surrogate compounds selected should be similar in analytical behavior to the analytes of interest, but which are not expected to be present in the sample matrix or extract.

GC = Gas Chromatography
HR = High Resolution
LR = Low Resolution
IR = Infrared
TS = Thermospray
PB = Particle Beam
MS = Mass Spectrometry
HPLC = High Performance Liquid Chromatography
PCDD = Polychlorinated Dibenzo-*p*-dioxins
PCDF = Polychlorinated Dibenzofurans
FT-IR = Fourier Transform Infrared Detector
UV = Ultraviolet
TLC = Thin-Layer Chromatography
TE = Thermal Extraction