METHOD 3535A

SOLID-PHASE EXTRACTION (SPE)

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

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

1.0 SCOPE AND APPLICATION

1.1 This method is a procedure for isolating target organic analytes from aqueous samples using solid-phase extraction (SPE) media. It describes conditions for extracting a variety of organic compounds from aqueous matrices that include groundwater, wastewater, and Toxicity Characteristic Leaching Procedure (TCLP, Method 1311) leachates. This method describes the use of disk extraction media for nine groups of analytes and the use of cartridge extraction media for two groups of analytes. Other solid-phase extraction media may be employed as described in Sec. 6.0. The extraction procedures are specific to the analytes of interest and vary by group of analytes and type of extraction media. The groups of analytes that have been evaluated thus far are listed below, along with the types of extraction media that have been evaluated and the determinative methods in which the corresponding performance data can be found.

Analyte Group	Extraction Media Type	Determinative Method
Phthalate esters	Disks	8061
Organochlorine pesticides	Disks	8081
Polychlorinated biphenyls (PCBs)	Disks	8082
Organophosphorus pesticides	Disks	8141
Nitroaromatics and nitramines	Disks and Cartridges	8330
Explosives*	Disks and Cartridges	8095
TCLP leachates containing organochlorine pesticides	Disks	8081
TCLP leachates containing semivolatiles	Disks	8270
TCLP leachates containing phenoxyacid herbicides	Disks	8321

* Includes the nitroaromatics, nitramines, and nitrate esters listed in Method 8095

1.2 This technique may also be applicable to other semivolatile or extractable compounds. It may also be used for the extraction of additional target analytes or may employ other solid-phase media and extraction solvents, provided that the analyst demonstrates adequate performance (e.g., recovery of 70 - 130%, or at levels that meet project-specific recovery criteria) using spiked sample matrices and an appropriate determinative method of the type included as an 8000 series method in this manual. The use of organic-free reagent water alone is not considered sufficient for conducting such performance studies; performance must be supported by data from actual sample matrices.

1.3 This method may not be appropriate for aqueous samples with high levels of suspended solids greater than 1%. However, if the particulate matter is not considered to be part of the sample composition based on specific project objectives and intended data usage, samples may be allowed to settle before measuring the aliquot to be extracted. If significant particulate matter is present and the total sample is of concern, then the sample should be treated as a multi-phase sample per Chapter Two.

1.4 This method also provides procedures for concentrating extracts and for solvent exchange.

1.5 Solid-phase extraction is called liquid-solid extraction (LSE) in some methods associated with the Safe Drinking Water Act.

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

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

1.7 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 Sample preparation procedures vary by analyte group. For the extraction of some analyte groups, the pH of the sample is adjusted to a specified value prior to extraction (see Sec. 11.2). Other groups do not need a pH adjustment.

2.2 Following any necessary pH adjustment, a measured volume of sample is extracted by passing it through the solid-phase extraction medium (disks or cartridges), which is held in an extraction device designed for vacuum filtration of the sample.

2.3 Target analytes are eluted from the solid-phase media using an appropriate solvent (see Secs. 11.7 and 11.8.7) which is collected in a receiving vessel. The resulting solvent extract is dried using sodium sulfate and concentrated, as needed.

2.4 As necessary for the specific analysis, the concentrated extract may be exchanged into a solvent compatible extract with subsequent cleanup procedures (see the 3600 series of methods) or determinative procedures (see the 8000 series of methods) for the measurement of the target analytes.

3.0 DEFINITIONS

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

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and refer to Chapter Four for general guidance on the cleaning of glassware. Also refer to Method 3500 for additional information regarding interferences and quality control procedures.

4.2 The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may dechlorinate and phthalate esters may hydrolyze. The rates of these reactions increase with increasing pH and reaction times.

4.3 Bonded-phase silica (e.g., C_{18}) will hydrolyze on prolonged exposure to aqueous samples with pH levels of less than 2 or greater than 9. Hydrolysis will increase at the extremes of this pH range and with longer contact times. Hydrolysis may reduce extraction efficiency or cause baseline irregularities. Styrene divinylbenzene (SDB) extraction disks should be considered when hydrolysis is a problem.

4.4 Phthalates are ubiquitous laboratory contaminants. All-glass extraction apparatus should be used for this method because phthalates are used as release agents when molding rigid plastic (e.g., PVC) and as plasticizers for flexible tubing. A method blank should be analyzed, demonstrating that there is no phthalate contamination of the sodium sulfate or other reagents listed in this method.

4.5 Sample particulates may clog the solid-phase media and result in extremely slow sample extractions. Use of an appropriate filter aid will result in shorter extractions without loss of method performance if clogging is a problem. Even when a filter aid is employed, this method may not be appropriate for aqueous samples with high levels of suspended solids (>1%), as the extraction efficiency may not be sufficient, given the small volumes of solvents employed and the short contact time.

5.0 SAFETY

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

5.2 When handling samples that contain explosives, carefully follow the concentration instructions of this method. Otherwise, THE EXPLOSIVES MAY DETONATE!

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented. The apparatus and materials described in this method are based on data provided to EPA for the extraction of eight groups of analytes using disk-type materials and for the extraction of one group of analytes using cartridge-type materials. Other solid-phase extraction media configurations may be employed, provided that method performance appropriate for the intended application has been demonstrated and documented. The procedures described in Sec. 11.0 need to be modified for the use of another SPE configuration. Consult the manufacturer's instructions regarding such modifications.

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

6.1 Solid-phase disk extraction system -- Empore™ manifold that holds three 90-mm filter standard apparatus or six 47-mm standard filter apparatus, or equivalent. Other manual, automatic, or robotic sample preparation systems designed for solid-phase media may be utilized for this method if adequate performance is achieved and all project quality control requirements are satisfied.

6.1.1 Manifold station -- Fisher Scientific 14-378-1B [3-place], 14-378-1A [6-place], or equivalent.

6.1.2 Standard filter apparatus -- Fisher Scientific 14-378-2A [47-mm], 14-378-2B [90-mm], or equivalent, consisting of a sample reservoir, clamp, fritted disk and filtration head equipped with drip tip.

6.1.3 Collection tube -- 60-mL. The collection tube should have an appropriate ID and length so that the drip tip of the standard filter apparatus can be positioned well into the neck of the tube to prevent splattering.

6.1.4 Filter flask -- 2-L equipped with a ground-glass receiver joint (optional). May be used to carry out individual disk extractions with the standard filter apparatus and collection vial in an all-glass system.

6.2 Solid-phase cartridge extraction system -- Visiprep solid-phase extraction manifold (Supelco) or equivalent system suitable for use with the extraction cartridges (see Sec. 6.4).

Consult the manufacturer's recommendations for the associated glassware and hardware necessary to perform sample extractions.

6.3 Solid-phase extraction disks -- Empore™, 47-mm, 90-mm, or equivalent. Disks are available in 47-mm and 90-mm diameters, composed of a variety of solid-phase materials. Other solid phases may be employed, provided that adequate performance is demonstrated for the analytes of interest. Guidance for selecting the specific disk is provided in Table 1.

6.3.1 C_{18} disks -- Empore™ disks, 47-mm diameter (3M product number 98-0503-0015-5), 90-mm diameter (3M product number 98-0503-0019-7), or equivalent.

6.3.2 C_{18} fast flow disks -- Empore™ disks, 47-mm diameter (3M product number 98-0503-0138-5), 90-mm diameter (3M product number 98-0503-0136-9), or equivalent. These disks may be a better choice for samples that are difficult to filter even with the use of a filter aid.

6.3.3 Styrene divinylbenzene (SDB-XC) disks -- Empore™ disks, 47-mm diameter (3M product number 98-0503-0067-6), 90-mm diameter (3M product number 98-0503-0068-4), or equivalent.

6.3.4 Styrene divinylbenzene reversed-phase sulfonated (SDB-RPS) disks -- Empore™ disks, 47-mm diameter (3M product number 98-0503-0110-4), 90-mm diameter (3M product number 98-0503-0111-2), or equivalent.

6.4 Solid-phase extraction cartridges -- Porapak® R SPE device, Waters Corporation, or equivalent. Other solid phases may be employed, provided that adequate performance is demonstrated for the analytes of interest.

6.5 Filtration aid (optional)

6.5.1 Filter Aid 400 -- (Fisher Scientific 14-378-3, or equivalent).

6.5.2 In-situ glass micro-fiber prefilter -- (Whatman GMF 150, 1-µm pore size, or equivalent).

6.6 Drying column -- 22-mm ID glass chromatographic column equipped with a PTFE stopcock (Kontes K-420530-0242, or equivalent).

NOTE: Fritted glass discs used to retain sodium sulfate in some columns may be difficult to decontaminate after contact with highly contaminated or viscous extracts. Columns suitable for this method use a small pad of glass wool to retain the drying agent.

6.7 Kuderna-Danish (K-D) apparatus

6.7.1 Concentrator tube -- 10-mL, graduated. A ground-glass stopper is used to prevent evaporation of extracts during short-term storage.

6.7.2 Evaporation flask -- 500-mL, or other size appropriate for the volumes of solvents to be concentrated. Attach to concentrator tube using springs or clamps.

6.7.3 Three-ball macro-Snyder column.

6.7.4 Two-ball micro-Snyder column (optional).

6.7.5 Springs -- ½-inch.

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

NOTE: This glassware is recommended for the purpose of solvent recovery during the concentration procedures (see Secs. 11.9 and 11.10) using the Kuderna-Danish evaporative concentrators. Incorporation of this apparatus may be required by Federal, State or local municipality regulations that govern air emissions of volatile organics. EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program. Solvent recovery is a means to conform with waste minimization and pollution prevention initiatives.

6.9 Boiling chips -- Solvent extracted, approximately 10/40 mesh (silicon carbide, or equivalent).

6.10 Water bath -- Heated, equipped with concentric ring cover, capable of temperature control to within ± 5 EC. The bath should be used in a hood.

6.11 Nitrogen evaporation apparatus (optional) -- N-Evap, 12- or 24-position (Organomation Model 112, or equivalent).

6.12 Vials, glass -- Sizes as appropriate, e.g., 2-mL or 10-mL, equipped with polytetrafluoroethylene (PTFE)-lined screw caps or crimp tops for storage of extracts.

6.13 pH indicator paper -- Wide pH range.

6.14 Vacuum system -- Capable of maintaining a vacuum of approximately 66 cm (26 inches) of mercury.

6.15 Graduated cylinders -- Sizes as appropriate.

6.16 Pipets -- disposable.

6.17 Disposable cartridge filters, 0.45 micron (Millex SR or equivalent).

7.0 REAGENTS AND STANDARDS

7.1 Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without decreasing the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

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

7.3 Sodium sulfate (granular, anhydrous), Na_2SO_4 -- Purify by heating at 400 EC for 4 hrs in a shallow tray, or by precleaning the sodium sulfate with methylene chloride.

7.4 Solutions for adjusting the pH of samples before extraction

7.4.1 Sulfuric acid solution (1:1 v/v), H_2SO_4 -- Slowly add 50 mL of concentrated H_2SO_4 (sp. gr. 1.84) to 50 mL of organic-free reagent water.

7.4.2 Sodium hydroxide solution (10N), NaOH -- Dissolve 40 g of NaOH in organic-free reagent water and dilute to 100 mL.

7.5 Extraction, washing, and exchange solvents

This method has been validated using a combination of the solvents recommended in Sec. 11.0. Other solvents may have applicability in solid-phase extraction, provided that acceptable performance that meets the project requirements can be demonstrated for the intended target analytes.

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

At a minimum, all solvents must be pesticide quality or equivalent. Solvents may be degassed prior to use.

7.5.1 Methylene chloride, CH_2Cl_2.

7.5.2 Hexane, C_6H_{14}.

7.5.3 Ethyl acetate, $CH_3COOCH_2CH_3$.

7.5.4 Acetonitrile, CH_3CN.

7.5.5 Methanol, CH_3OH.

7.5.6 Acetone, $(CH_3)_2CO$.

7.5.7 Methyl-*tert*-butyl ether (MTBE), $C_5H_{12}O$.

7.5.8 Isopropanol, $(CH_3)_2CHOH$.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

See Secs. 11.1 and 11.2 of this method. Also see the introductory material to Chapter Four, "Organic Analytes," Method 3500, and the specific determinative methods to be employed.

9.0 QUALITY CONTROL

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

9.2 Initial demonstration of proficiency

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

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

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

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

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

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

9.8 As noted earlier, use of any extraction technique, including solid-phase extraction, should be supported by data that demonstrate the performance of the specific solvent system and operating conditions for the analytes of interest, at the levels of interest, in the sample matrix.

10.0 CALIBRATION AND STANDARDIZATION

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

11.0 PROCEDURE

The procedures for solid-phase extraction are very similar for most organic analytes. The procedures for sample preparation (Sec. 11.1), pH adjustment (Sec. 11.2), setting up the extraction apparatus (Sec. 11.3), and information regarding extract concentration generally apply to all target analytes. The procedures for disk washing (Sec. 11.4), disk conditioning (Sec. 11.5), sample extraction (Sec. 11.6), and sample elution (Sec. 11.7) vary among the groups of analytes. Sec. 11.8 provides procedural information regarding use of the SPE cartridge technique for nitroaromatics, nitramines, and explosives. Sec. 11.9 provides procedural information regarding the K-D concentration technique and, if further concentration is necessary, Sec. 11.10 provides procedural information regarding both the micro-Snyder column technique and the nitrogen evaporation technique.

11.1 Sample preparation

Most of the specific procedures described in this method were developed for a nominal sample size of 1 L, because this sample size is usually employed for other extraction methods such as separatory funnel or continuous liquid-liquid extraction. This method also may be employed with a smaller sample size when overall analytical sensitivity is not a concern or when high levels of the target analytes are anticipated. However, such samples are best collected in an appropriately-sized container. For optimized analytical results, the entire sample must be used.

The extraction of aqueous samples presents several challenges that must be considered during sample preparation. First, if the specific project requirements indicate that the analytes of interest are associated with the particulate matter in the sample, the sample preparation procedures must ensure that any particulates in the original sample are included in the sample aliquot that is extracted. However, the efficiency of the extraction media may be affected when samples containing greater than 1% solids are fully extracted. For some applications, it may be desirable to quantitate only the soluble constituents based on the stated project objectives and the intended uses of the data. In these situations, samples containing particulates may be allowed to settle before measuring the aliquot to be extracted. Conversely, if significant particulate matter is present and the total constituent concentration is necessary, the sample phases may be spilt, with the aqueous phase extracted using this method and the solid phase extracted using an appropriate extraction technique based on the target analytes. The sample extracts then can be either analyzed separately or combined for a single analysis. Secondly, the majority of the organic analytes are hydrophobic and may preferentially adhere to the surfaces of the sample container. For this reason, most extraction methods have traditionally specified that, once the sample is transferred to the extraction apparatus, the sample container should be rinsed with solvent which is added to the apparatus. As a result, it is generally <u>not</u> appropriate to extract only part of the sample from a sample container, e.g., 250 mL from a 1-L sample bottle.

The appropriate sample volume may vary with the intended use of the results and, in general, is the volume necessary to provide the analytical sensitivity necessary to meet the objectives of the project (see Chapter Two). Under ideal conditions, the sample should be collected by completely filling the container. The sample should generally be collected without additional volume and with little or no headspace. Thus, a 1-L sample is collected in a 1-L container, a 250-mL sample is collected in a 250-mL container, not a 1-L container, etc.

<u>CAUTION</u>: The presence of light will cause photodegradation of several polyaromatic hydrocarbons. If this class of compounds includes target analytes, the samples

should be extracted away from light sources, and preferably in darker environments.

Any surrogates and matrix spiking compounds (if applicable) are added to the sample in the original container. The container is then recapped and shaken to mix the spiked analytes into the sample. For some groups of analytes, the pH of the sample needs to be adjusted to a designated value (see Table 1). When pH adjustment is necessary, it should be performed after the surrogates and matrix spiking compounds (if applicable) have been added and mixed with the sample. Otherwise, the recoveries of these compounds will have little relevance to those of the target analytes in the sample.

If this approach is not possible, then a sample aliquot may be transferred to a graduated cylinder and spiked. However, in such instances, the analyst must take great care to mix the sample well, by shaking, to ensure a homogeneous distribution of the particulate matter and must record the fact that the container was not rinsed.

NOTE: This method may not be appropriate for aqueous samples with greater than 1% solids, as such samples can be difficult to filter and the extraction efficiency may be reduced as a result of the small volumes of solvents employed and the short contact time. If the particulate load significantly slows or prevents filtration, it may be more appropriate to employ an alternative extraction procedure.

11.1.1 Mark the level of the sample on the outside of the sample container for later determination of the sample volume used. Shake the container for several minutes, with the cap tightly sealed, to ensure that any particulate matter is evenly distributed throughout the sample.

11.1.2 Prepare a method blank from a 1-L volume of organic-free reagent water, or a volume of reagent water similar to that being used for the samples (e.g., a 250-mL blank should be used when the sample size is 250 mL, etc.). The blank may be prepared in a graduated cylinder, beaker, or other suitable container. Chapter One provides guidelines regarding the frequency of method blank preparation.

11.1.3 Add any surrogate standards listed in the determinative method to the samples in their original containers and to the blank.

11.1.4 Shake the samples to mix the surrogates and allow the sample to stand for at least several minutes. This will permit the surrogates to dissolve in the sample and will also allow the particulate matter to settle after spiking, which will speed the filtration process.

11.1.5 Prepare matrix spikes by adding listed matrix spike standards to representative sample replicates in their original containers. Chapter One or the determinative method provide guidelines regarding the frequency of matrix spike preparation. For disk extractions, add 5.0 mL of methanol after spiking the samples. Mix the matrix spike samples as described in Sec.11.1.4 and allow to stand.

11.1.6 If cleanup procedures are to be employed that result in the loss of extract, adjust the amount of surrogate and spiking cocktail(s) accordingly. In the case of Method 3640, Gel Permeation Cleanup, it may be necessary to double the amount of standards to compensate for the loss of one half of the extract concentrate when loading the GPC column.

11.2 pH adjustment

Check the pH of the sample with wide-range pH paper and, if necessary, adjust the pH to the range listed below. If pH adjustment is needed, this step should be performed in the original sample container to ensure that analytes are not lost in precipitates or flocculated material. Any adjustment of the sample pH should take place after the surrogates and matrix spiking compounds are added, so that they are affected by the pH in the same manner as the target analytes.

CAUTION: Depending on the target analytes, dechlorination may be necessary at the time of sample collection. Any pH adjustment that is needed for extraction should always be performed after the dechlorination step.

NOTE: The efficiency of solid-phase extraction of acid herbicide compounds is greatly affected by pH. If acid herbicides are to be extracted from TCLP leachates or other samples, adjust the pH to 1.0 before extraction.

Analyte Group	Extraction pH
Phthalate esters	5 - 7
Organochlorine pesticides	5 - 9
Polychlorinated biphenyls (PCBs)	5 - 9
Organophosphorus pesticides	as received
Nitroaromatics and nitramines	as received
Explosives	as received
TCLP leachates containing organochlorine pesticides	as produced by TCLP
TCLP leachates containing semivolatiles	as produced by TCLP
TCLP leachates containing phenoxyacid herbicides	1.0

11.3 Setting up the extraction apparatus

11.3.1 Assemble a manifold for multiple disk extractions using 47-mm or 90-mm extraction disks. Use a filter flask equipped with the standard filter apparatus (Figure 1) for single extractions, using 47-mm or 90-mm extraction disks. The solid-phase disks that are generally appropriate for each group of analytes are listed below, and in Table 1.

Analyte Group	Disk Medium
Phthalate esters	C_{18}
Organochlorine pesticides	C_{18}
Polychlorinated biphenyls (PCBs)	C_{18}
Organophosphorus pesticides	SDB-RPS
Nitroaromatics and nitramines	SDB-RPS
Explosives	SDB-RPS
TCLP leachates containing organochlorine pesticides	SDB-XC
TCLP leachates containing semivolatiles	SDB-XC

Analyte Group	Disk Medium
TCLP leachates containing phenoxyacid herbicides	SDB-XC

Samples also may be extracted using an SPE cartridge for nitroaromatics, nitramines, and explosives. Assemble the cartridge apparatus according to the manufacturer's instructions, using Porapak R, or equivalent, SPE cartridges, and proceed to Sec. 11.8.

11.3.2 If samples contain significant quantities of particulates, the use of a filter aid or prefilter is advisable for disk extractions. Empore™ Filter Aid 400, Whatman GMF 150, or equivalent prefilters are recommended.

11.3.2.1 Pour about 40 g of Filter Aid 400 onto the surface of the disk after assembling the standard filter apparatus.

11.3.2.2 Alternatively, place the Whatman GMF 150 on top of the extraction disk prior to clamping the glass reservoir into the standard filter apparatus.

11.3.2.3 Do not add the filter aid if using the cartridge extraction procedure for nitroaromatics, nitramines, or explosives (Sec. 11.8).

11.4 Washing the extraction apparatus

Prior to use, the extraction disks must undergo two separate washing steps, usually with different solvents. The steps involved in washing the extraction apparatus before use depend on the analytes of interest and the sample matrix.

11.4.1 First washing step

The following table illustrates the solvents recommended for the first washing step.

Analyte Group	1st solvent wash volume
Phthalate esters	20 mL methylene chloride
Organochlorine pesticides	20 mL methylene chloride
Polychlorinated biphenyls (PCBs)	20 mL methylene chloride
Organophosphorus pesticides	5 mL acetone
Nitroaromatics and nitramines	5 mL acetonitrile
Explosives	5 mL acetone
TCLP leachates containing organochlorine pesticides	5 mL acetone
TCLP leachates containing semivolatiles	5 mL acetone
TCLP leachates containing phenoxyacid herbicides	5 mL acetonitrile

Wash the extraction apparatus and disk with the volume of the solvent listed above by rinsing the solvent down the sides of the glass reservoir. Pull a small amount of solvent through the disk with a vacuum. Turn off the vacuum and allow the disk to soak for about one minute. Pull the remaining solvent through the disk and allow the disk to dry.

11.4.1.1 When using a filtration aid, adjust the volume of all wash solvents so the entire filtration bed is submerged.

11.4.1.2 In subsequent conditioning steps, volumes should be adjusted so that a level of solvent is always maintained above the entire filter bed.

11.4.2 Second washing step

The following table illustrates the solvents recommended for the second washing step.

Analyte Group	2nd solvent wash volume
Phthalate esters	10 mL acetone
Organochlorine pesticides	10 mL acetone
Polychlorinated biphenyls (PCBs)	not needed
Organophosphorus pesticides	5 mL methanol
Nitroaromatics and nitramines	15 mL acetonitrile
Explosives	15 mL isopropanol
TCLP leachates containing organochlorine pesticides	5 mL ethyl acetate
TCLP leachates containing semivolatiles	5 mL ethyl acetate
TCLP leachates containing phenoxyacid herbicides	not needed

11.4.3 Third washing step

The third washing step only applies to explosives.

Analyte Group	3rd solvent wash volume
Explosives	15 mL methanol

11.5 Disk conditioning

The extraction disks are composed of hydrophobic materials which will not allow water to pass unless the disks are pre-wetted with a water-miscible solvent before use for sample extraction. This step is referred to as conditioning, and the solvent used is dependent on the analytes of interest. The following table illustrates the solvents recommended for specific groups of analytes.

CAUTION: Beginning with the conditioning step, it is CRITICAL that the disk NOT go dry until after the extraction steps are completed. Should a disk accidentally go dry during the conditioning steps, the conditioning steps for that disk MUST be repeated prior to adding the sample.

Analyte Group	Conditioning steps
Phthalate esters	20 mL methanol, soak 1 min, 20 mL reagent water

Analyte Group	Conditioning steps
Organochlorine pesticides	20 mL methanol, soak 1 min, 20 mL reagent water
Polychlorinated biphenyls (PCBs)	20 mL methanol, soak 1 min, 20 mL reagent water
Organophosphorus pesticides	5 mL methanol, soak 1 min, 20 mL reagent water
Nitroaromatics and nitramines	15 mL acetonitrile, soak 3 min 30 mL reagent water
Explosives	20 mL acetonitrile, soak 3 min 20 mL acetonitrile 50 mL reagent water 50 mL reagent water
TCLP leachates containing organochlorine pesticides	5 mL methanol soak 1 min, 15 mL reagent water
TCLP leachates containing semivolatiles	5 mL methanol soak 1 min, 15 mL reagent water
TCLP leachates containing phenoxyacid herbicides	5 mL methanol soak 1 min, 15 mL reagent water

11.5.1 Add the conditioning solvent to the extraction apparatus. Apply a vacuum until a few drops of solvent pass through the disk, ensuring that the disk is soaked with solvent. Turn off the vacuum and allow the disk to soak in the solvent for the time listed above.

11.5.2 When using a filtration aid, adjust the volume of conditioning solvents so that the entire filtration bed remains submerged until the extraction is completed.

11.5.3 Once the soaking time is over, apply the vacuum again, drawing all but a thin layer of solvent through the disk. Stop the vacuum just before the disk goes dry.

11.5.4 Add the volume of organic-free reagent water listed above and apply vacuum to draw the water through the disk. Stop the vacuum just before the disk goes dry, leaving 2-3 mm of water above the surface of the disk.

11.5.5 The disks used for explosives need two rinses with acetonitrile and two rinses with reagent water.

11.6 Sample extraction using SPE disks

11.6.1 After performing the washing and conditioning steps, pour the sample into the reservoir and, under full vacuum, filter it as quickly as the vacuum will allow (at least 10 min). Transfer as much of the measured volume of water as possible.

NOTE: With heavily particle-laden samples, allow the sediment in the sample to settle and decant as much liquid as is practical into the reservoir. Reduce the vacuum level to minimize pulling the particles into the disk structure. After most of the

aqueous portion of the sample has passed through the disk, swirl the portion of the sample containing sediment and add it to the reservoir. Use additional portions of organic-free reagent water to transfer any remaining particulates to the reservoir. Particulates must be transferred to the reservoir before all of the aqueous sample has passed through the disk. Alternatively, for some applications it may be desirable to quantitate only the soluble constituents based on the stated project objectives and the intended use of the data. In those situations, samples containing particulates may be allowed to settle with the intention of excluding the particulate matter from extraction.

11.6.2 After the sample has passed through the solid-phase media, dry the disk by maintaining vacuum for about 3 min. Method blanks and matrix spike aliquots (see Sec. 11.1) are handled in the same manner as the samples.

NOTE: Maintain the vacuum for 20 min when drying the disks used for the explosives, however, for other target analytes that may be sensitive to oxidation the drying time should be kept to a minimum.

11.7 Elution of the analytes from the disk

The choice of elution solvent is critical to the success of solid-phase extraction. The recommended elution solvents for each group of analytes are listed below.

Analyte Group	Sample elution steps
Phthalate esters	5 mL acetone, soak 15-20 sec. Rinse bottle with 15 mL acetonitrile and add to disk.
Organochlorine pesticides	5 mL acetone, soak 15-20 sec. Rinse bottle with 15 mL methylene chloride and add to disk.
Polychlorinated biphenyls (PCBs)	5 mL acetone, soak 15-20 sec. Rinse bottle with 20 mL acetonitrile and add to disk.
Organophosphorus pesticides	0.6 mL acetone, soak 1 min. Rinse bottle with 5 mL MTBE and add to disk. Repeat bottle rinse twice more.
Nitroaromatics and nitramines	5 mL acetonitrile, soak 3 min.
Explosives	4 mL acetonitrile, soak 3 min.
TCLP leachates containing organochlorine pesticides	Rinse bottle with 4 mL acetone and add to disk. Rinse glassware with 2 mL acetone and add to disk. Soak 1 min. Rinse bottle twice with 5 mL ethyl acetate and add to disk.
TCLP leachates containing semivolatiles	Rinse bottle with 4 mL acetone and add to disk. Rinse glassware with 2 mL acetone and add to disk. Soak 1 min. Rinse bottle twice with 5 mL ethyl acetate and add to disk.
TCLP leachates containing phenoxyacid herbicides	Rinse bottle with 5 mL acetonitrile and add to disk. Soak 1 min. Rinse bottle twice more with 5 mL acetonitrile and add to disk.

11.7.1 Remove the entire standard filter assembly (do not disassemble) from the manifold and insert a collection tube. The collection tube should have sufficient capacity

to hold all of the elution solvents. The drip tip of the filtration apparatus should be seated sufficiently below the neck of the collection tube to prevent analyte loss due to splattering when vacuum is applied. When using a filter flask for single extractions, empty the water from the flask before inserting the collection tube.

11.7.2 An initial elution with a water-miscible solvent, i.e., acetone or acetonitrile, improves the recovery of analytes trapped in water-filled pores of the sorbent. Use of a water-miscible solvent is particularly critical when methylene chloride is used as the second elution solvent. With the collection tube in place, add the volume of elution solvent listed above to the extraction apparatus. Allow the solvent to spread out evenly across the disk (or inert filter) then quickly turn the vacuum on and off to pull the first drops of solvent through the disk. Allow the disk to soak for the periods indicated above before proceeding to Sec. 11.7.3.

11.7.3 Rinse the sample bottle and/or glassware that held the sample with the second solvent listed above and transfer the solvent rinse to the extraction apparatus. As needed, use a disposable pipette to rinse the sides of the extraction apparatus with solvent from the bottle.

NOTE: These bottle rinsing steps may be omitted if the particulate matter in the bottom of the sample bottle is purposely being excluded from extraction due to the project requirements. However, the recommended solvent should still be added directly to the extraction apparatus.

11.7.4 Draw about half of the solvent through the disk and then release the vacuum. Allow the remaining elution solvent to soak the disk and particulates for about one minute before drawing the remaining solvent through the disk under vacuum. When using a filtration aid, adjust the volume of elution solvent so that the entire filtration bed is initially submerged.

11.7.5 Repeat the bottle rinsing step as listed in the table above, continuing to apply vacuum and collecting the solvent in the tube.

11.7.6 If the extract is turbid, filter through a Millex-SR filter unit, or equivalent

WARNING: Do NOT concentrate explosives any further. THE EXPLOSIVES MAY DETONATE!

11.8 Cartridge technique for nitroaromatics, nitramines, and explosives

Aqueous samples to be analyzed for nitroaromatics, nitramines, and explosives may also be extracted using the SPE cartridge technique described below. The same sample preparation considerations discussed in Sec. 11.1 also apply to this procedure.

Analyte Group	Washing steps
Nitroaromatics and nitramines	10 mL acetonitrile 30 mL reagent water
Explosives	30 mL acetonitrile 50 mL reagent water

11.8.1 After assembling the SPE cartridge in the extraction apparatus (see Sec. 11.3.1), wash the cartridge with the volume of acetonitrile listed above, using gravity flow. Do not allow the cartridge to go dry.

11.8.2 When only a thin layer of solvent remains above the sorbent bed in the cartridge, add the reagent water to the cartridge and allow it to flow through the sorbent bed under gravity flow. Stop the flow just before the cartridge goes dry.

11.8.3 Attach a connector to the top of the cartridge. The other end of the connector should be fitted with flexible PTFE tubing long enough to reach into the sample bottle or other container (e.g., a beaker) holding the sample.

11.8.4 Turn on the vacuum, and draw the sample through the cartridge at a rate of about 10 mL/min, until all of the sample has passed through the cartridge. As particulate matter plugs the cartridge and slows the flow, increase the vacuum to maintain a reasonable flow rate.

11.8.5 Follow the individual procedures below for nitroaromatics and nitramines or explosives.

11.8.5.1 Nitroaromatics and nitramines

Once all of the sample has been pulled through the cartridge, shut off the vacuum and add 5 mL of reagent water to the cartridge. Allow the reagent water to pass through the cartridge under gravity flow, if practical, or apply a vacuum to complete the process. Shut off the flow once the water has been drawn through the cartridge.

11.8.5.2 Explosives

Once all the sample has been drawn through a cartridge, draw air through the cartridge for 15 min in order to remove any excess water. Turn the vacuum off. Remove any drops of water that may be clinging to the cartridge tip.

11.8.6 Method blanks and matrix spike aliquots (see Sec. 11.1) are handled in the same manner as the samples.

11.8.7 Eluting the nitroaromatics and nitramines from the cartridge

Once the reagent water has passed through the column, place a collection tube under the cartridge. Add 5 mL of acetonitrile to the top of the cartridge and allow it to pass through the cartridge under gravity flow, collecting the solvent in the collection tube. Measure the actual volume (to the nearest 0.1 mL) of the solvent extract. If concentration of the extract is necessary, proceed to Sec. 11.9. Otherwise, store extracts in a freezer until analysis.

11.8.8 Eluting the explosives from the cartridge

Once the reagent water has passed through the column, place a collection tube under the cartridge. Add 4 mL (not 5 mL) of acetonitrile to the top of the cartridge and allow it to pass through the cartridge under gravity flow, collecting the solvent in the collection tube. Measure the actual volume (to the nearest 0.1 mL) of the solvent extract.

WARNING: Do NOT concentrate explosives any further. THE EXPLOSIVES MAY DETONATE!

Store extracts in a freezer until analysis.

11.9 K-D concentration technique

Where necessary to meet the sensitivity requirements of the particular application, sample extracts may be concentrated to the final volume necessary for the determinative method and specific application using the K-D technique or nitrogen evaporation.

WARNING: Do NOT concentrate explosives any further. THE EXPLOSIVES MAY DETONATE!

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

11.9.2 Dry the combined extracts in the collection tube (see Secs. 11.7.1 and 11.8.7) by passing them through a drying column containing about 10 g of anhydrous sodium sulfate. Collect the dried extract in the K-D concentrator. Use acidified sodium sulfate (see Method 8151) if acidic analytes are to be measured.

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

11.9.4 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Attach the solvent vapor recovery glassware (condenser and collection device, see Sec. 6.8) to the Snyder column of the K-D apparatus, following the manufacturer's instructions. Pre-wet the Snyder column by adding about 1 mL of methylene chloride (or other suitable solvent) to the top of the column. Place the K-D apparatus on a hot water bath (15 - 20 EC above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as necessary to complete the concentration in 10 - 20 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.

11.9.4.1 If a solvent exchange is needed (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent and a new boiling chip.

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

11.9.5 Remove the Snyder column. Rinse the K-D flask and the lower joints of the Snyder column into the concentrator tube with 1 - 2 mL of solvent. The extract may be further concentrated by using one of the techniques outlined in Sec. 11.10, or adjusted to a final volume of 5.0 - 10.0 mL using an appropriate solvent (see Table 1).

11.10 If further concentration is necessary, use either the micro-Snyder column technique (see Sec. 11.10.1) or the nitrogen evaporation technique (see Sec. 11.10.2).

WARNING: Do NOT concentrate explosives any further. THE EXPLOSIVES MAY DETONATE.

11.10.1 Micro-Snyder column technique

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

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

11.10.2 Nitrogen evaporation technique

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

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

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

CAUTION: When the volume of solvent is reduced below 1 mL, some semivolatile analytes such as cresols may be lost.

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

12.0 DATA ANALYSIS AND CALCULATIONS

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

13.0 METHOD PERFORMANCE

Refer to the appropriate determinative methods (e.g., those listed in Sec. 1.1) for any performance data examples and guidance related to solid-phase extraction. Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory 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

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6. M. E. Walsh and T. Ranney (1998), "Determination of Nitroaromatic, Nitramine, and nitrate ester explosives in water using SPE and GC-ECD: Comparison with HPLC," CRREL Report 98-2, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH, 1998.

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17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The following pages contain the table and figure referenced by this method.

TABLE 1
RECOMMENDED DISK EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative Method	Extraction pH	Disk Medium[a]	Elution Solvent	Exchange Solvent	Final Extract Volume for Analysis (mL)[b]
8061 (phthalate esters)	5-7	C_{18}	acetonitrile	hexane	10.0
8081 (organochlorine pesticides)	5-9	C_{18}	methylene chloride	hexane	10.0
8082 (PCBs)	5-9	C_{18}	methylene chloride	hexane	10.0
8141 (organophosphorus pesticides)	as received	SDB-RPS	MTBE	hexane	10.0
8330 (nitroaromatics and nitramines)	as received	SDB-RPS	acetonitrile	acetonitrile	10.0
8095 (explosives in water)	as received	SDB-RPS	acetonitrile	acetonitrile	5.0
TCLP pesticides (8081)	as produced by TCLP	SDB-XC	ethyl acetate	hexane	10.0
TCLP semivolatiles (8270)	as produced by TCLP	SDB-XC	ethyl acetate	methylene chloride	1.0
TCLP phenoxyacid herbicides (8321)	1.0	SDB-XC	acetonitrile	hexane	10.0

[a] SDB has a greater capacity than C_{18} and a greater affinity for more analytes but they may be more difficult to elute.

[b] For methods where the suggested final extract volume is 10.0 mL, the volume may be reduced to as low as 1.0 mL to achieve lower limits of quantitation. Other final extract volumes may be used, provided that the overall sensitivity meets project-specific needs.

FIGURE 1

EXAMPLE DISK EXTRACTION APPARATUS FOR SINGLE EXTRACTIONS