METHOD 3535A

SOLID-PHASE EXTRACTION (SPE)

1.0 SCOPE AND APPLICATION

1.1 This method describes a procedure for isolating target organic analytes from aqueous samples using solid-phase extraction (SPE) media. The method describes conditions for extracting a variety of organic compounds from aqueous matrices that include: groundwater, wastewater, and TCLP leachates. The 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. 4.0. 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 The 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, provided that the analyst demonstrates adequate performance (e.g., recovery of 70 - 130%, or project-specific recovery criteria) using spiked sample matrices and an appropriate determinative method of the type included in Chapter Four, Sec. 4.3. The use of organic-free reagent water alone is not considered sufficient for conducting such performance studies, and must be supported by data from actual sample matrices.

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

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

1.5 This method is restricted to use by or under the supervision of trained analysts. 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. Extraction of some groups requires that the pH of the sample be adjusted to a specified value prior to extraction (see Sec. 7.2). Other groups do not require 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. 7.7 and 7.8.7) 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 (Chapter Four, Sec. 4.2) or determinative procedures (Chapter Four, Sec. 4.3) for the measurement of the target analytes.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

3.2 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.

3.3 Bonded-phase silica (e.g., C_{18}) will hydrolyze on prolonged exposure to aqueous samples with pH 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.

3.4 Phthalates are a ubiquitous laboratory contaminant. 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, as described in Chapter One, should be analyzed, demonstrating that there is no phthalate contamination of the sodium sulfate or other reagents listed in this method.

3.5 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.

4.0 APPARATUS AND MATERIALS

The apparatus and materials described here 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 the laboratory demonstrates adequate performance for the analytes of interest. The use of other SPE configurations will require modifications to the procedures described in Sec. 7.0. Consult the manufacturer's instructions regarding such modifications.

4.1 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 quality control requirements are satisfied.

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

4.1.2 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 with drip tip.

4.1.3 Collection tube - 60-mL. The collection tube should be of 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.

4.1.4 Filter flask - 2-L 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.

4.2 Solid-phase cartridge extraction system - Visiprep solid-phase extraction manifold (Supelco) or equivalent system suitable for use with the extraction cartridges (see Sec. 4.4). Consult the manufacturer’s recommendations for the associated glassware and hardware necessary to perform sample extractions.

4.3 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.

4.3.1 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.

4.3.2 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.

4.3.3 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.

4.3.4 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.

4.4 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.

4.5 Filtration aid (optional)

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

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

4.6 Drying column - 22-mm ID glass chromatographic column 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.

4.7 Kuderna-Danish (K-D) apparatus

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

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

4.7.3 Three-ball macro-Snyder column.

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

4.7.5 Springs - ½-inch.

4.8 Solvent Vapor Recovery System - Kontes 545000-1006 or K-547300-0000, Ace Glass 6614-30, or equivalent.

NOTE: The glassware in Sec. 4.8 is recommended for the purpose of solvent recovery during the concentration procedures (see Secs. 7.9 and 7.10) using the 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.

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

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

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

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

4.13 pH indicator paper - Wide pH range.

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

4.15 Graduated cylinders - Sizes as appropriate.

4.16 Pipets - disposable.

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

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall 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.

5.2 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.

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

5.4 Solutions for adjusting the pH of samples before extraction.

5.4.1 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.

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

5.5 Extraction, washing, and exchange solvents - At a minimum, all solvents must be pesticide quality or equivalent.

5.5.1 Methylene chloride, CH_2Cl_2.

5.5.2 Hexane, C_6H_{14}.

5.5.3 Ethyl acetate, $CH_3COOCH_2CH_3$.

5.5.4 Acetonitrile, CH_3CN.

5.5.5 Methanol, CH_3OH.

5.5.6 Acetone, $(CH_3)_2CO$.

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

5.5.8 Isopropanol, $(CH_3)_2CHOH$.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to Chapter Four, Organic Analytes, Sec. 4.1, Method 3500, Sec. 7.1 of this method, and the specific determinative methods to be employed.

7.0 PROCEDURE

The procedures for solid-phase extraction are very similar for most organic analytes. Therefore, this section describes procedures for sample preparation, pH adjustment, preparation of the extraction apparatus, and extract concentration that apply to all target analytes. The procedures for disk washing, disk conditioning, sample extraction, and sample elution vary among the groups of analytes.

7.1 Sample preparation

Most of the specific procedures described in this method were developed for a nominal sample size of 1 L, as 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 smaller samples 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. The extraction of aqueous samples presents several challenges that must be considered during sample preparation. First, the analytes of interest are often associated with the particulate matter in the sample and sample preparation procedures must ensure that any particulates in the original sample are included in the sample aliquot that is extracted. 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 has been transferred to the extraction apparatus, the sample container be rinsed with solvent which is added to the apparatus. As a result, it is generally not 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.

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. The extraction of some groups of analytes also requires that the pH of the sample be adjusted to a specified 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.

7.1.1 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.

7.1.2 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. The frequency of method blank preparation is described in Chapter One.

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

7.1.4 For disk extractions, also add 5.0 mL of methanol to each sample in the original container. All samples, blanks, and QC samples should receive the same amount of methanol. (This step is not necessary for the cartridge extraction of nitroaromatics, nitramines, and explosives).

7.1.5 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 somewhat.

7.1.6 Prepare matrix spikes by adding listed matrix spike standards to representative sample replicates in their original containers . The frequency with which matrix spikes are prepared and analyzed is described in Chapter One or as part of the determinative method. For disk extractions, add 5.0 mL of methanol after spiking the samples. Mix the matrix spike samples as described in Sec.7.1.5 and allow to stand.

7.1.7 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.

7.2 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 required, 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.

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

7.3 Setting up the extraction apparatus

7.3.1 Assemble a manifold for multiple disk extractions using 47-mm or 90-mm extraction disks. Use a filter flask 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
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. 7.8.

7.3.2 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.

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

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

7.3.2.3 Do not add the filter aid if using the cartridge extraction procedure for nitroaromatics, nitramines, or explosives.

7.4 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.

7.4.1 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.

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

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

7.4.2 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 required
Organophosphorus pesticides	5 mL methanol

Analyte Group	2nd solvent wash volume
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 required

7.4.3 Third washing step

The third washing step only applies to explosives.

Analyte Group	3rd solvent wash volume
Explosives	15 mL methanol

7.5 Disk conditioning

The extraction disks are composed of hydrophobic materials which will not allow water to pass unless they are pre-wetted with a water-miscible solvent before being used 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.

NOTE: 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
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

7.5.1 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.

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

7.5.3 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.

7.5.4 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.

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

7.6 Sample extraction using SPE disks

7.6.1 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 minutes). 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. 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.

7.6.2 After the sample has passed through the solid-phase media, dry the disk by maintaining vacuum for about 3 minutes. Method blanks and matrix spike aliquots (see Sec. 7.1) are handled in the same manner as the samples.

NOTE: Maintain the vacuum for 20 minutes when drying the disks used for the explosives

7.7 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.

7.7.1 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.

7.7.2 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. 7.7.3.

7.7.3 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.

7.7.4 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.

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

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

7.7.7 Do NOT concentrate explosives any further. THEY MAY DETONATE!

7.8 Cartridge SPE 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. 7.1 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

7.8.1 After assembling the SPE cartridge in the extraction apparatus (see Sec. 7.3.1), wash the cartridge with the volume of acetonitrile listed above, using gravity flow. Do not allow the cartridge to go dry.

7.8.2 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.

7.8.3 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.

7.8.4 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.

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

7.8.5.1 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.

7.8.5.2 Explosives

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

7.8.6 Method blanks and matrix spike aliquots (see Sec. 7.1) are handled in the same manner as are the samples.

7.8.7 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. 7.9. Otherwise, store extracts in a freezer until analysis.

7.8.8 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.

7.8.8.1 Do NOT concentrate explosives any further. THEY MAY DETONATE!

7.8.8.2 Store extracts in a freezer until analysis.

7.9 K-D concentration technique

Where necessary to meet the sensitivity requirements, 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.

NOTE: Do NOT concentrate explosives any further. THEY MAY DETONATE!

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

7.9.2 Dry the combined extracts in the collection tube (see Secs. 7.7 and 7.8.7) 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.

7.9.3 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.

7.9.4 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. 4.6) to the Snyder column of the K-D apparatus, following the manufacturer's instructions. Pre-wet the Snyder column by adding about 1 mL of methylene chloride (or other suitable solvent) to the top of the column. Place the K-D apparatus on a hot water bath (15 - 20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as necessary to complete the concentration in 10 - 20 minutes. 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 minutes.

7.9.4.1 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.

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

7.9.5 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. 7.10, or adjusted to a final volume of 5.0 - 10.0 mL using an appropriate solvent (see Table 1).

7.10 If further concentration is necessary, use either the micro-Snyder column technique in Sec. 7.10.1 or the nitrogen evaporation technique in Sec. 7.10.2.

NOTE: Do NOT concentrate explosives any further, THEY MAY DETONATE.

7.10.1 Micro-Snyder column technique

7.10.1.1 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 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood.

7.10.1.2 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 minutes. 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.

7.10.2 Nitrogen evaporation technique

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

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

7.10.2.2 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.

7.11 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 with a PTFE-lined screw-cap, labeled appropriately, and stored in a refrigerator.

8.0 QUALITY CONTROL

8.1 Any method blanks or matrix spike samples should be subjected to exactly the same analytical procedures as those used for actual samples.

8.2 Refer to Chapter One for general quality control procedures and Method 3500 for specific QC procedures for extraction and sample preparation.

9.0 METHOD PERFORMANCE

Refer to the determinative methods listed in Sec. 1.1 for performance data related to solid-phase extraction.

10.0 REFERENCES

1. Lopez-Avila, V., Beckert, W., et. al., "Single Laboratory Evaluation of Method 8060 - Phthalate Esters", EPA/600/4-89/039.

2. Tomkins, B.A., Merriweather, R., et. al., "Determination of Eight Organochlorine Pesticides at Low Nanogram/Liter Concentrations in Groundwater Using Filter Disk Extraction and Gas Chromatography", *JAOAC International*, 75(6), pp. 1091-1099 (1992).

3. Markell, C., "3M Data Submission to EPA," letter to B. Lesnik, June 27, 1995.

4. Jenkins, T. F., Thorne, P. G., Myers, K. F., McCormick, E. F., Parker, D. E., and B. L. Escalon (1995), "Evaluation of Clean Solid Phases for Extraction of Nitroaromatics and Nitramines from Water," USACE Cold Regions Research and Engineering Laboratory, Special Report 95-22.

5. Walsh, M.E. and T. Ranney, "Determination of Nitroaromatic, Nitramine, and Nitrate Ester Explosives in Water Using Solid Phase Extraction and GC-ECD," *Proceedings of the 13th Annual Waste Testing and Quality Assurance Symposium*, July 6-9, 1997, Arlington, VA.

6. Walsh, M.E. 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.

7. Walsh, M.E. and T. Ranney, "Determination of Nitroaromatic, Nitramine, and Nitrate Ester Explosives in Water using Solid-phase Extraction and Gas Chromatography-electron Capture Detection: Comparison with High-performance Liquid Chromatography," *Journal of Chromatographic Science*, 36, pp. 406-416 (1998).

TABLE 1

RECOMMENDED DISK EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

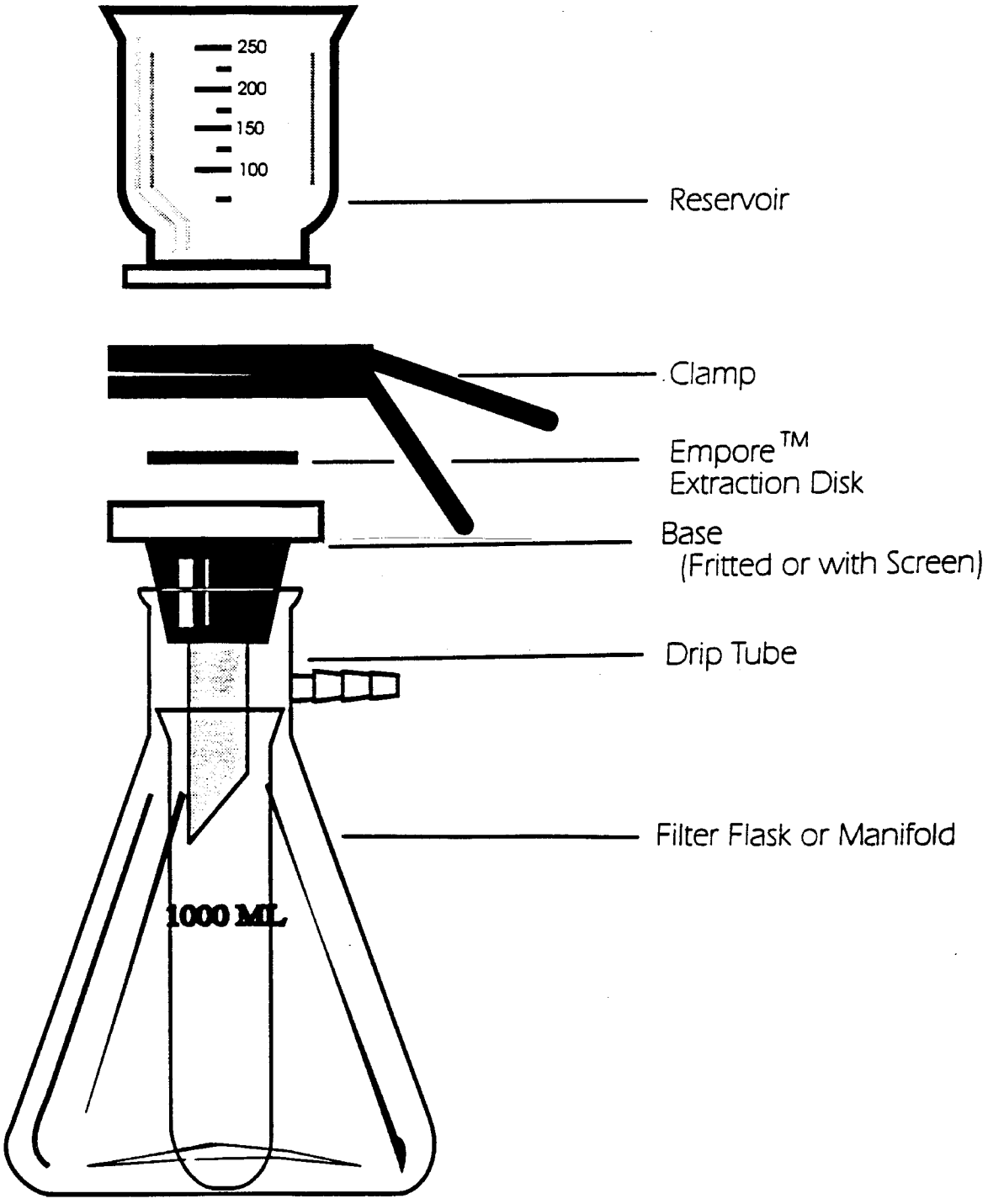
Determinative Method	Extraction pH	Disk Medium[a]	Elution Solvent	Exchange Solvent	Final Extract Volume for Analysis (mL)[b]
8061 (phthalate esters)	5-7	C_{18}	acetonitrile	hexane	10.0
8081 (organochlorine pesticides)	5-9	C_{18}	methylene chloride	hexane	10.0
8082 (PCBs)	5-9	C_{18}	methylene chloride	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.

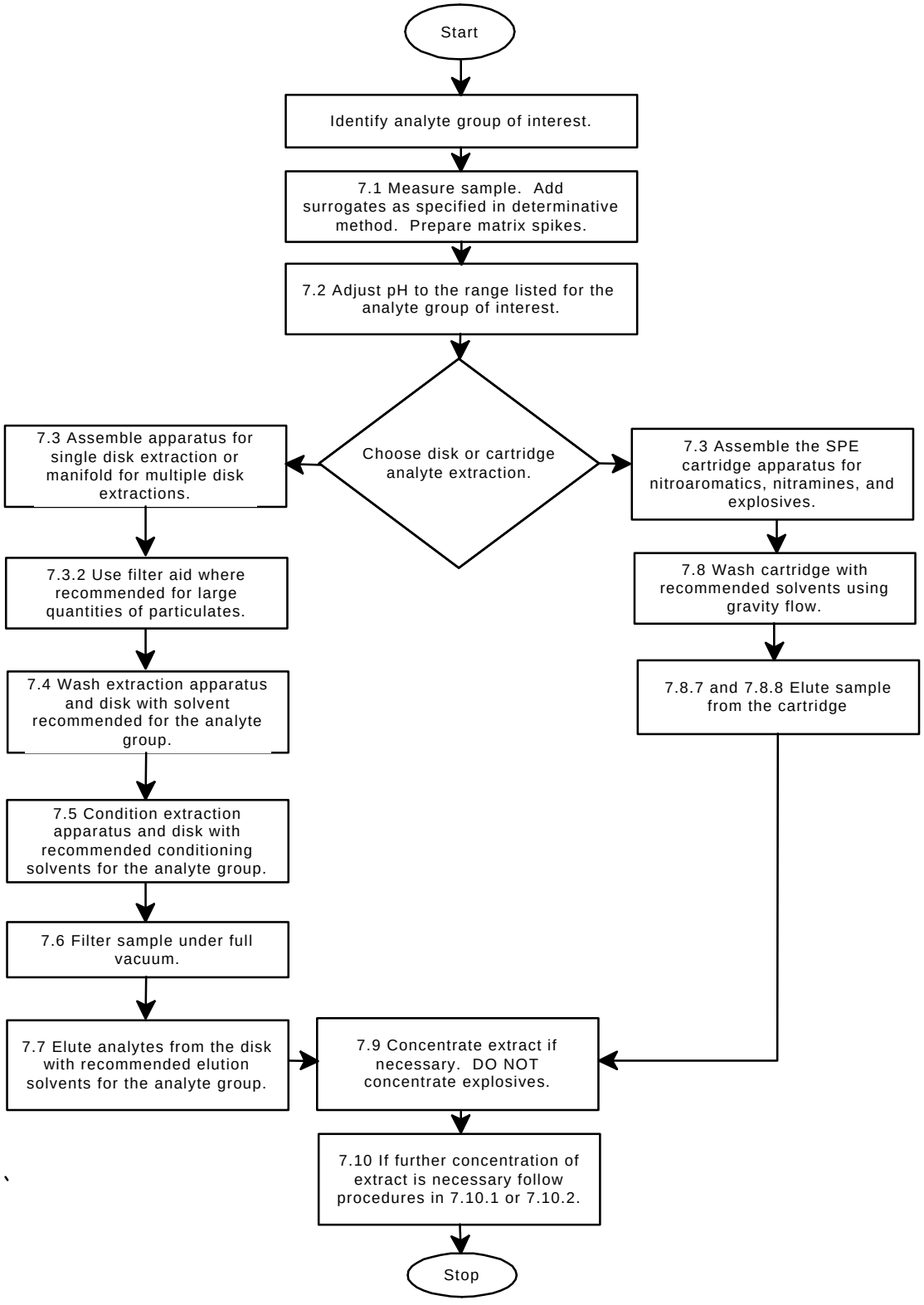
[b] For methods where the suggested final extract volume is 10.0 mL, the volume may be reduced to as low as 1.0 mL to achieve lower detection limits. Other final extract volumes may be used, provided that the overall sensitivity meets project-specific needs.

FIGURE 1

EXAMPLE DISK EXTRACTION APPARATUS FOR SINGLE EXTRACTIONS



Pre-release version - This method has NOT been released by OSW as part of Update IV



Pre-release version - This method has NOT been released by OSW as part of Update IV