

## METHOD 3550A

### ULTRASONIC EXTRACTION

See DISCLAIMER-1. See manufacturer's specifications for operational settings.

#### 1.0 SCOPE AND APPLICATION

1.1 Method 3550 is a procedure for extracting nonvolatile and semi-volatile organic compounds from solids such as soils, sludges, and wastes. The ultrasonic process ensures intimate contact of the sample matrix with the extraction solvent.

1.2 The method is divided into two sections, based on the expected concentration of organics in the sample. The low concentration method (individual organic components of  $\leq 20$  mg/kg) uses a larger sample size and a more rigorous extraction procedure (lower concentrations are more difficult to extract). The medium/high concentration method (individual organic components of  $> 20$  mg/kg) is much simpler and therefore faster.

1.3 It is highly recommended that the extracts be cleaned up prior to analysis. See Chapter Four (Cleanup), Sec. 4.2.2, for applicable methods.

#### 2.0 SUMMARY OF METHOD

2.1 Low concentration method - A 30 g sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. This is solvent extracted three times using ultrasonic extraction. The extract is separated from the sample by vacuum filtration or centrifugation. The extract is ready for cleanup and/or analysis following concentration.

2.2 Medium/high concentration method - A 2 g sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. This is solvent extracted once using ultrasonic extraction. A portion of the extract is removed for cleanup and/or analysis.

#### 3.0 INTERFERENCES

3.1 Refer to Method 3500.

#### 4.0 APPARATUS AND MATERIALS

4.1 Apparatus for grinding dry waste samples.

4.2 Ultrasonic preparation - A horn type device equipped with a titanium tip, or a device that will give equivalent performance, shall be used.

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

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

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

4.4 Apparatus for determining percent dry weight.

4.4.1 Oven - Drying.

4.4.2 Desiccator.

4.4.3 Crucibles - Porcelain or disposable aluminum.

4.5 Pasteur glass pipets - 1 mL, disposable.

4.6 Beakers - 400 mL.

4.7 Vacuum or pressure filtration apparatus.

4.7.1 Buchner funnel.

4.7.2 Filter paper - Whatman No. 41 or equivalent.

4.8 Kuderna-Danish (K-D) apparatus.

4.8.1 Concentrator tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.8.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.8.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.8.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.8.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

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 ( $\pm 5^{\circ}\text{C}$ ). The bath should be used in a hood.

4.11 Balance - Top loading, capable of accurately weighing to the nearest 0.01 g.

4.12 Vials - 2 mL, for GC autosampler, with Teflon lined screw caps or crimp tops.

4.13 Glass scintillation vials - 20 mL, with Teflon lined screw caps.

4.14 Spatula - Stainless steel or Teflon.

4.15 Drying column - 20 mm ID Pyrex chromatographic column with Pyrex glass wool at bottom.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.16 Syringe - 5 mL.

## 5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise specified, it is intended that all inorganic 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 lessening the accuracy of the determination.

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

5.3 Sodium sulfate (granular, anhydrous),  $\text{Na}_2\text{SO}_4$ . Purify by heating at  $400^{\circ}\text{C}$  for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.4 Extraction solvents.

5.4.1 Low concentration soil/sediment and aqueous sludge samples shall be extracted using a solvent system that gives optimum, reproducible recovery for the matrix/analyte combination to be measured. Suitable solvent choices are given in Table 1.

5.4.2 Methylene chloride:Acetone,  $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{COCH}_3$  (1:1, v:v). Pesticide quality or equivalent.

5.4.3 Methylene chloride,  $\text{CH}_2\text{Cl}_2$ . Pesticide quality or equivalent.

5.4.4 Hexane,  $\text{C}_6\text{H}_{14}$ . Pesticide quality or equivalent.

5.5 Exchange solvents.

5.5.1 Hexane,  $\text{C}_6\text{H}_{14}$ . Pesticide quality or equivalent.

5.5.2 2-Propanol,  $(\text{CH}_3)_2\text{CHOH}$ . Pesticide quality or equivalent.

5.5.3 Cyclohexane,  $\text{C}_6\text{H}_{12}$ . Pesticide quality or equivalent.

5.5.4 Acetonitrile,  $\text{CH}_3\text{CN}$ . Pesticide quality or equivalent.

5.5.5 Methanol,  $\text{CH}_3\text{OH}$ . Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this Chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Sample handling

7.1.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.1.1.2 Determine the dry weight of the sample (Sec. 7.2) remaining after decanting. Measurement of soil pH may be required.

7.1.2 Waste samples - Samples consisting of multiphases must be prepared by the phase separation method in Chapter Two before extraction. This procedure is for solids only.

7.1.3 Dry waste samples amenable to grinding - Grind or otherwise subdivide the waste so that it either passes through a 1 mm sieve or can be extruded through a 1 mm hole. Introduce sufficient sample into the grinder to yield at least 100 g after grinding.

7.1.4 Gummy, fibrous or oily materials not amenable to grinding should be cut, shredded, or otherwise broken up to allow mixing, and maximum exposure of the sample surfaces for extraction. The professional judgment of the analyst is required for handling of these difficult matrices.

7.2 Determination of percent dry weight - In certain cases, sample results are desired based on a dry weight basis. When such data are desired, or required, a portion of sample for this determination should be weighed out at the same time as the portion used for analytical determination.

**WARNING:** The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from drying a heavily contaminated hazardous waste sample.

However, samples known or suspected to contain significant concentrations of toxic, flammable, or explosive constituents should not be overdried because of concerns for personal safety. Laboratory discretion is advised. It may be prudent to delay overdrying of the weighed-out portion until other analytical results are available.

7.2.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

7.3 Extraction method for samples expected to contain low concentrations of organics and pesticides ( $\leq 20$  mg/kg):

7.3.1 The following step should be performed rapidly to avoid loss of the more volatile extractables. Weigh approximately 30 g of sample into a 400 mL beaker. Record the weigh to the nearest 0.1 g. Nonporous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture must be mixed with 60 g of anhydrous sodium sulfate, using a spatula. If required, more sodium sulfate may be added. After addition of sodium sulfate, the sample should be free flowing. Add 1 mL of surrogate standards to all samples, spikes, standards, and blanks (see Method 3500 for details on the surrogate standard solution and the matrix spike solution). For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 100 ng/ $\mu$ L of each base/neutral analyte and 200 ng/ $\mu$ L of each acid analyte in the extract to be analyzed (assuming a 1  $\mu$ L injection). If Method 3640, Gel-Permeation Cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half of the extract is lost due to loading of the GPC column. Immediately add 100 mL of 1:1 methylene chloride:acetone.

7.3.2 Place the bottom surface of the tip of the #207 3/4 in. disrupter horn about 1/2 in. below the surface of the solvent, but above the sediment layer.

7.3.3 Extract ultrasonically for 3 minutes, with output control knob set at 10 (full power) and with mode switch on Pulse (pulsing energy

rather than continuous energy) and percent-duty cycle knob set at 50% (energy on 50% of time and off 50% of time). Do not use microtip probe.

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

7.3.5 Repeat the extraction two or more times with two additional 100 mL portions of solvent. Decant off the solvent after each ultrasonic extraction. On the final ultrasonic extraction, pour the entire sample into the Buchner funnel and rinse with extraction solvent. Apply a vacuum to the filtration flask, and collect the solvent extract. Continue filtration until all visible solvent is removed from the funnel, but do not attempt to completely dry the sample, as the continued application of a vacuum may result in the loss of some analytes. Alternatively, if centrifugation is used in Sec. 7.3.4, transfer the entire sample to the centrifuge bottle. Centrifuge at low speed, and then decant the solvent from the bottle.

7.3.6 Assemble a Kuderna-Danish (K-D) concentrator (if necessary) by attaching a 10 mL concentrator tube to a 500 mL evaporator flask. Transfer filtered extract to a 500 mL evaporator flask and proceed to the next section.

7.3.7 Add one to two clean boiling chips to the evaporation flask, and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (80-90 °C) 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 required, to complete the concentration in 10-15 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.3.8 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent and a new boiling chip, and re-attach the Snyder column. Concentrate the extract as described in Sec. 7.3.10, raising the temperature of the water bath, if necessary, to maintain proper distillation. When the apparent volume again reaches 1-2 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

7.3.9 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Sec. 7.3.10 or adjusted to 10.0 mL with the solvent last used.

7.3.10 If further concentration is indicated in Table 1, either micro Snyder column technique (Sec. 7.3.10.1) or nitrogen blow down technique (Sec. 7.3.10.2) is used to adjust the extract to the final volume required.

#### 7.3.10.1 Micro Snyder Column Technique

7.3.10.1.1 Add a clean boiling chip and attach a two ball micro Snyder column to the concentrator tube. Prewet the column by adding approximately 0.5 mL of methylene chloride or exchange solvent through the top. Place the apparatus in the hot water bath. Adjust the vertical position and the water temperature, as required, 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. When the liquid reaches an apparent volume of approximately 0.5 mL, remove the apparatus from the water bath and allow to drain and cool for at least 10 minutes. Remove the micro Snyder column and rinse its lower joint with approximately 0.2 mL of appropriate solvent and add to the concentrator tube. Adjust the final volume to the volume required for cleanup or for the determinative method (see Table 1).

#### 7.3.10.2 Nitrogen Blowdown Technique

7.3.10.2.1 Place the concentrator tube in a warm water bath (approximately 35 °C) and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: Do not use plasticized tubing between the carbon trap and the sample.

7.3.10.2.2 The internal wall of the tube must be rinsed down several times with the appropriate solvent during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry.

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatiles may be lost.

7.4 If analysis of the extract will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer than 2 days, it should be transferred to a vial with a Teflon lined cap and labeled appropriately.

7.5 Extraction method for samples expected to contain high concentrations of organics (> 20 mg/kg):

7.5.1 Transfer approximately 2 g (record weight to the nearest 0.1 g) of sample to a 20 mL vial. Wipe the mouth of the vial with a tissue to remove any sample material. Record the exact weight of sample taken. Cap the vial before proceeding with the next sample to avoid any cross contamination.

7.5.2 Add 2 g of anhydrous sodium sulfate to sample in the 20 mL vial and mix well.

7.5.3 Surrogate standards are added to all samples, spikes, and blanks (see Method 3500 for details on the surrogate standard solution and on the matrix spike solution). Add 1.0 mL of surrogate spiking solution to sample mixture. For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 100 ng/ $\mu$ L of each base/neutral analyte and 200 ng/ $\mu$ L of each acid analyte in the extract to be analyzed (assuming a 1  $\mu$ L injection). If Method 3640, Gel-Permeation Cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

7.5.4 Immediately add whatever volume of solvent is necessary to bring the final volume to 10.0 mL considering the added volume of surrogates and matrix spikes. Disrupt the sample with the 1/8 in. tapered microtip ultrasonic probe for 2 minutes at output control setting 5 and with mode switch on pulse and percent duty cycle at 50%. Extraction solvents are:

1. For nonpolar compounds (i.e., organochlorine pesticides and PCBs), use hexane or appropriate solvent.
2. For extractable priority pollutants, use methylene chloride.

7.5.5 Loosely pack disposable Pasteur pipets with 2 to 3 cm Pyrex glass wool plugs. Filter the extract through the glass wool and collect 5.0 mL in a concentrator tube if further concentration is required. Follow Sec. 7.3.10 for details on concentration. Normally, the 5.0 mL extract is concentrated to approximately 1.0 mL or less.

7.5.6 The extract is ready for cleanup or analysis, depending on the extent of interfering co-extractives.

## 8.0 QUALITY CONTROL

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



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

## 9.0 METHOD PERFORMANCE

9.1 Refer to the determinative method for performance data.

## 10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.
2. U.S. EPA, Interlaboratory Comparison Study: Methods for Volatile and Semi-Volatile Compounds, Environmental Monitoring Systems Laboratory, Office of Research and Development, Las Vegas, NV, EPA 600/4-84-027, 1984.
3. Christopher S. Hein, Paul J. Marsden, Arthur S. Shurtleff, "Evaluation of Methods 3540 (Soxhlet) and 3550 (Sonication) for Evaluation of Appendix IX Analytes from Solid Samples", S-CUBED, Report for EPA Contract 68-03-33-75, Work Assignment No. 03, Document No. SSS-R-88-9436, October 1988.

TABLE 1.  
EFFICIENCY OF EXTRACTION SOLVENT SYSTEMS<sup>a</sup>

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

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

<sup>b</sup> Chemical Abstracts Service Registry Number

<sup>c</sup> Compound Type: A = Acid, B = Base, N = neutral

<sup>d</sup> A = Methylene chloride  
 B = Methylene chloride/Acetone (1/1)  
 C = Hexane/Acetone (1/1)  
 D = Methyl t-butyl ether  
 E = Methyl t-butyl ether/Methanol (2/1)

TABLE 2.  
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

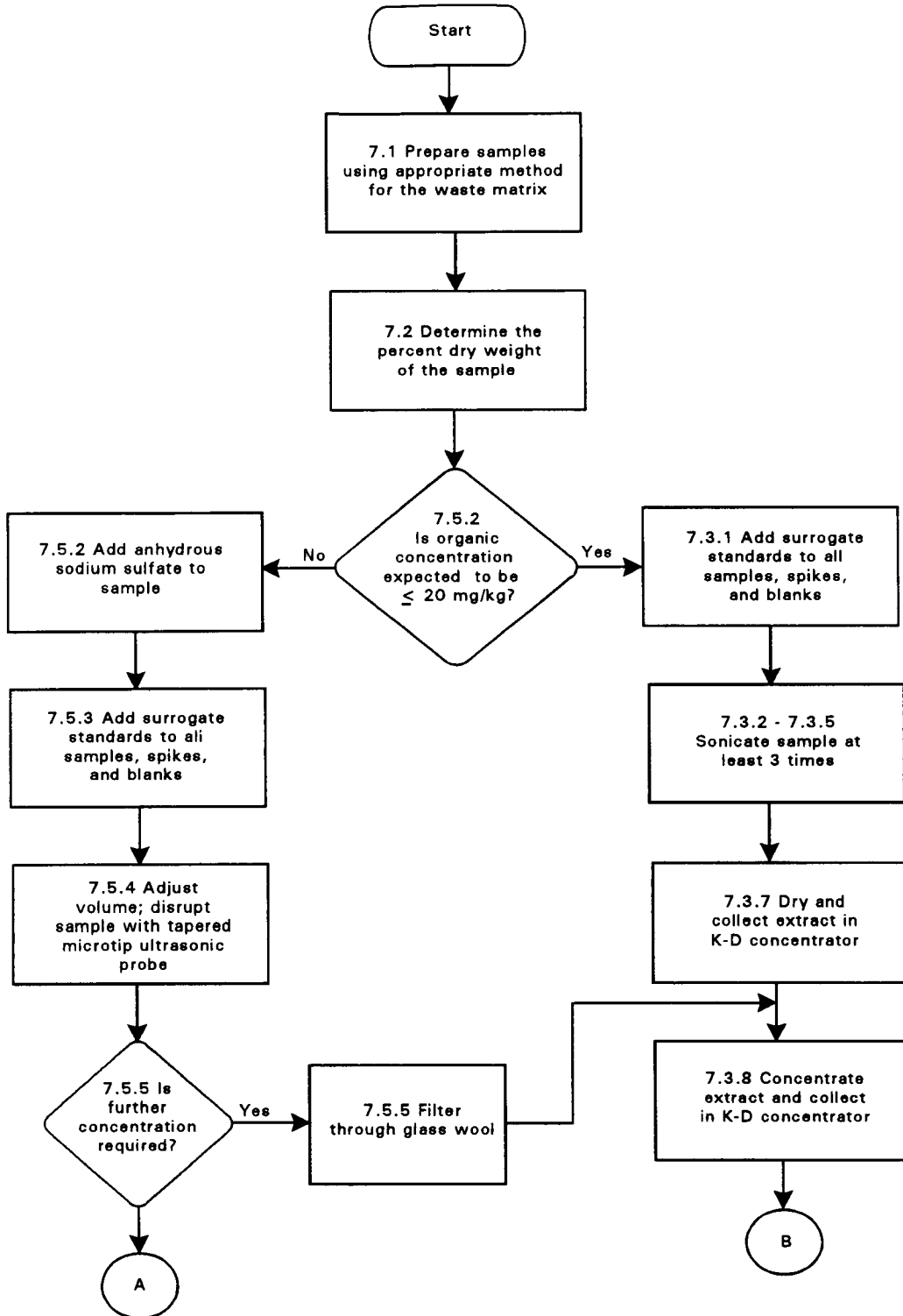
Determinative method	Extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040 <sup>a</sup>	as received	2-propanol	hexane	1.0	1.0, 10.0 <sup>b</sup>
8060	as received	hexane	hexane	2.0	10.0
8061	as received	hexane	hexane	2.0	10.0
8070	as received	methanol	methylene chloride	2.0	10.0
8080	as received	hexane	hexane	10.0	10.0
8081	as received	hexane	hexane	10.0	10.0
8090	as received	hexane	hexane	2.0	1.0
8100	as received	none	cyclohexane	2.0	1.0
8110	as received	hexane	hexane	2.0	10.0
8120	as received	hexane	hexane	2.0	1.0
8121	as received	hexane	hexane	2.0	1.0
8250 <sup>a,c</sup>	as received	none	--	--	1.0
8270 <sup>c</sup>	as received	none	--	--	1.0
8310	as received	acetonitrile	--	--	1.0
8321	as received	methanol	--	--	1.0
8410	as received	methylene chloride	methylene chloride	10.0	0.0 (dry)

<sup>a</sup> To obtain separate acid and base/neutral extracts, Method 3650 should be performed following concentration of the extract to 10.0 mL.

<sup>b</sup> Phenols may be analyzed, by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optical derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.

<sup>c</sup> The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

METHOD 3550A  
ULTRASONIC EXTRACTION



METHOD 3550A  
continued

