METHOD 3540A

SOXHLET EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 Method 3540 is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes. The Soxhlet extraction process ensures intimate contact of the sample matrix with the extraction solvent.

1.2 This method is applicable to the isolation and concentration of water insoluble and slightly water soluble organics in preparation for a variety of chromatographic procedures.

2.0 SUMMARY OF METHOD

2.1 The solid sample is mixed with anhydrous sodium sulfate, placed in an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. The extract is then dried, concentrated, and, as necessary, exchanged into a solvent compatible with the cleanup or determinative step being employed.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Soxhlet extractor - 40 mm ID, with 500 mL round bottom flask.

4.2 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.

4.3 Kuderna-Danish (K-D) apparatus

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

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

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

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

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

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

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

4.6 Vials - Glass, 2 mL capacity, with Teflon lined screw or crimp top.

4.7 Glass or paper thimble or glass wool - Contaminant free.

4.8 Heating mantle - Rheostat controlled.

4.9 Disposable glass pasteur pipet and bulb.

4.10 Apparatus for determining percent dry weight.

4.10.1 Oven - Drying.

4.10.2 Desiccator.

4.10.3 Crucibles - Porcelain or disposable aluminum.

4.11 Apparatus for grinding

4.12 Analytical balance - 0.0001 g.

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 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), 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. 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 Soil/sediment and aqueous sludge samples shall be extracted using either of the following solvent systems:

5.4.1.1 Toluene/Methanol (10:1) (v/v), $C_6H_5CH_3/CH_3OH$. Pesticide quality or equivalent.

5.4.1.2 Acetone/Hexane (1:1) (v/v), $CH_3COCH_3/CH_3(CH_2)_4CH_3$. Pesticide quality or equivalent.

5.4.2 Other samples shall be extracted using the following:

5.4.2.1 Methylene chloride, CH_2Cl_2. Pesticide quality or equivalent.

5.5 Exchange solvents

5.5.1 Hexane, C_6H_{14}. Pesticide quality or equivalent.

5.5.2 2-Propanol, $(CH_3)_2CHOH$. Pesticide quality or equivalent.

5.5.3 Cyclohexane, C_6H_{12}. Pesticide quality or equivalent.

5.5.4 Acetonitrile, CH_3CN. Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analysis, Section 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.

7.1.2 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 grinding apparatus to yield at least 10 g after grinding.

7.2 Determination of sample % dry weight - In certain cases, sample results are desired based on dry weight basis. When such data is desired, 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 a heavily contaminated hazardous waste sample.

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 Blend 10 g of the solid sample with 10 g of anhydrous sodium sulfate and place in an extraction thimble. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the Soxhlet extractor is an acceptable alternative for the thimble. Add 1.0 mL of the surrogate standard spiking solution onto the sample (see Method 3500 for details on the surrogate standard and matrix spiking solutions). 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/μL of each base/neutral analyte and 200 ng/μL of each acid analyte in the extract to be analyzed (assuming a 1 μL injection). If Method 3640, Gel Permeation Chromatography 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.

7.4 Place approximately 300 mL of the extraction solvent (Section 5.4) into a 500 mL round bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract the sample for 16-24 hours at 4-6 cycles/hr.

7.5 Allow the extract to cool after the extraction is complete.

7.6 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporation flask.

7.7 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Wash the extractor flask and sodium sulfate column with 100 to 125 mL of extraction solvent to complete the quantitative transfer.

7.8 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride 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 required, 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 1-2 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

5.4 Extraction solvents

5.4.1 Soil/sediment and aqueous sludge samples shall be extracted using either of the following solvent systems:

5.4.1.1 Toluene/Methanol (10:1) (v/v), $C_6H_5CH_3/CH_3OH$. Pesticide quality or equivalent.

5.4.1.2 Acetone/Hexane (1:1) (v/v), $CH_3COCH_3/CH_3(CH_2)_4CH_3$. Pesticide quality or equivalent.

5.4.2 Other samples shall be extracted using the following:

5.4.2.1 Methylene chloride, CH_2Cl_2. Pesticide quality or equivalent.

5.5 Exchange solvents

5.5.1 Hexane, C_6H_{14}. Pesticide quality or equivalent.

5.5.2 2-Propanol, $(CH_3)_2CHOH$. Pesticide quality or equivalent.

5.5.3 Cyclohexane, C_6H_{12}. Pesticide quality or equivalent.

5.5.4 Acetonitrile, CH_3CN. Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analysis, Section 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.

7.1.2 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 grinding apparatus to yield at least 10 g after grinding.

7.2 Determination of sample % dry weight - In certain cases, sample results are desired based on dry weight basis. When such data is desired, 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 a heavily contaminated hazardous waste sample.

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 Blend 10 g of the solid sample with 10 g of anhydrous sodium sulfate and place in an extraction thimble. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the Soxhlet extractor is an acceptable alternative for the thimble. Add 1.0 mL of the surrogate standard spiking solution onto the sample (see Method 3500 for details on the surrogate standard and matrix spiking solutions). 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/μL of each base/neutral analyte and 200 ng/μL of each acid analyte in the extract to be analyzed (assuming a 1 μL injection). If Method 3640, Gel Permeation Chromatography 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.

7.4 Place approximately 300 mL of the extraction solvent (Section 5.4) into a 500 mL round bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract the sample for 16-24 hours at 4-6 cycles/hr.

7.5 Allow the extract to cool after the extraction is complete.

7.6 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporation flask.

7.7 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Wash the extractor flask and sodium sulfate column with 100 to 125 mL of extraction solvent to complete the quantitative transfer.

7.8 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride 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 required, 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 1-2 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.9 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add approximately 50 mL of the exchange solvent and a new boiling chip, and reattach the Snyder column. Concentrate the extract as described in Section 7.8, 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 from the water batch and allow it to drain and cool for at least 10 minutes.

7.10 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 techniques described in Section 7.11 or adjusted to 10.0 mL with the solvent last used.

7.11 If further concentration is indicated in Table 1, either micro Snyder column technique (7.11.1) or nitrogen blowdown technique (7.11.2) is used to adjust the extract to the final volume required.

7.11.1 Micro Snyder Column Technique

7.11.1.1 Add another one or two clean boiling chips to the concentrator tube and attach a two ball micro Snyder column. Prewet the column by adding about 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D 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 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 apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints with about 0.2 mL of solvent and add to the concentrator tube. Adjust the final volume to 1.0-2.0 mL, as indicated in Table 1, with solvent.

7.11.2 Nitrogen Blowdown Technique

7.11.2.1 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.

7.11.2.2 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, semivolatile analytes may be lost.

7.12 The extracts obtained may now be analyzed for the target analytes using the appropriate organic technique(s) (see Section 4.3 of this Chapter). If analysis 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 Teflon lined screw cap or crimp top, and labeled appropriately.

8.0 QUALITY CONTROL

8.1 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 methods 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.

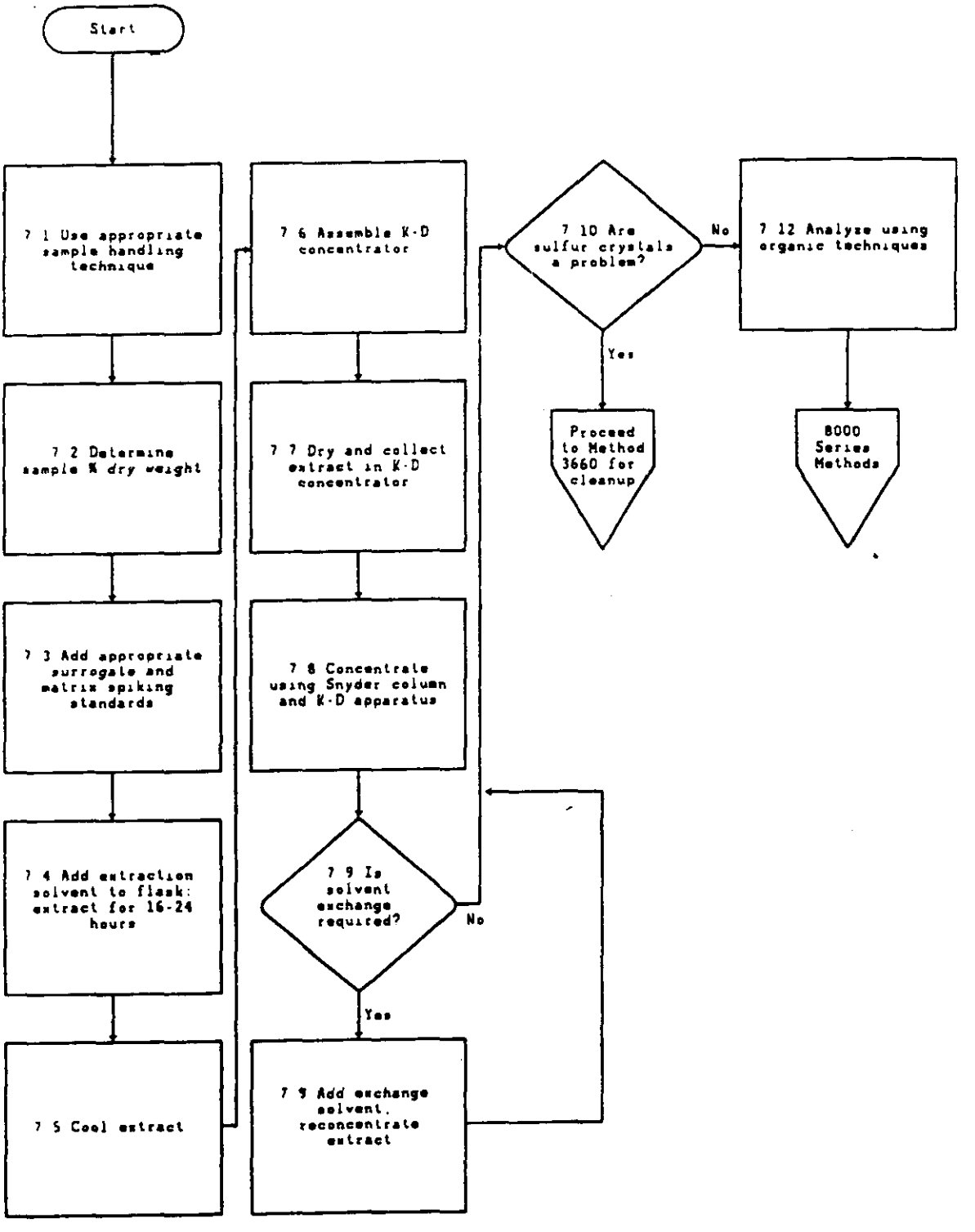
TABLE 1.
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

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[a]	as received	2-propanol	hexane	1.0	1.0, 10.0[b]
8060	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
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
8140	as received	hexane	hexane	10.0	10.0
8141	as received	hexane	hexane	10.0	10.0
8250[a,c]	as received	none	--	--	1.0
8270[c]	as received	none	--	--	1.0
8310	as received	acetonitrile	--	--	1.0

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

[b] 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.

[c] 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.


Start
7 1 Use appropriate sample handling technique
7 2 Determine sample % dry weight
7 3 Add appropriate surrogate and matrix spiking standards
7 4 Add extraction solvent to flask: extract for 16-24 hours
7 5 Cool extract
7 6 Assemble K-D concentrator
7 7 Dry and collect extract in K-D concentrator
7 8 Concentrate using Snyder column and K-D apparatus
7 9 Is solvent exchange required?
No
Yes
7 9 Add exchange solvent, reconcentrate extract
7 10 Are sulfur crystals a problem?
No
Yes
Proceed to Method 3660 for cleanup
7 12 Analyze using organic techniques
8000 Series Methods

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 semivolatile 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) 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. A portion of the extract is removed for cleanup and/or analysis.

2.2 Medium/high concentration method - A 2 g sample is mixed with anhydrous sodium sulfate to form a free flowing powder. This mixture 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.

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 ultrasonic extractor equipped with a titanium tip should be used. The following ultrasonic extractor, or an equivalent brand and model, is recommended.

Ultrasonic Disrupter - Heat Systems - Ultrasonics, Inc., Model W-385 (475 watt) ultrasonic extractor or equivalent (power wattage must be a minimum of 375 with pulsing capability) and No. 200 1/2" Tapped Disrupter Horn, plus No. 207 3/4" Tapped Disrupter Horn, and No. 419 1/8" Standard Tapered microtip probe.

4.3 Sonabox - 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 (± 5°C). The batch 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), 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. 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 Methylene chloride:Acetone, CH_2Cl_2:CH_3COCH_3 (1:1, v:v). Pesticide quality or equivalent.

5.4.2 Methylene chloride, CH_2Cl_2. Pesticide quality or equivalent.

5.4.3 Hexane, C_6H_{14}. Pesticide quality or equivalent.

5.5 Exchange solvents.

5.5.1 Hexane, C_6H_{14}. Pesticide quality or equivalent.

5.5.2 2-Propanol, $(CH_3)_2CHOH$. Pesticide quality or equivalent.

5.5.3 Cyclohexane, C_6H_{12}. Pesticide quality or equivalent.

5.5.4 Acetonitrile, CH_3CN. Pesticide quality or equivalent.

5.5.5 Methanol, CH_3OH. Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this Chapter, Organic Analytes, Section 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 (Section 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.

7.2 Determination of percent dry weight - In certain cases, sample results are desired based on a dry weight basis. When such data is 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.

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/μL of each base/neutral analyte and 200 ng/μL of each acid analyte in the extract to be analyzed (assuming a 1 μL 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 and filter extracts through Whatman No. 41 filter paper using vacuum filtration or centrifuge, and decant extraction solvent.

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.

7.3.6 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporator flask.

7.3.7 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in the K-D concentrator. Wash the extractor flask and sodium sulfate column with 100-125 mL of extraction solvent to complete the quantitative transfer.

7.3.8 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.

7.3.9 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 Section 7.3.8, 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.

7.3.10 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 Section 7.3.11 or adjusted to 10.0 mL with the solvent last used.

7.3.11 If further concentration is indicated in Table 1, either micro Snyder column technique (Section 7.3.11.1) or nitrogen blow down technique (Section 7.3.11.2) is used to adjust the extract to the final volume required.

7.3.11.1 Micro Snyder Column Technique

7.3.11.1.1 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).

7.3.11.2 Nitrogen Blowdown Technique

7.3.11.2.1 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.

7.3.11.2.2 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, semivolatile analytes 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 2.0 mL of surrogate spiking solution to sample mixture. For the sample in each analytical batch selected for spiking, add 2.0 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 200 ng/μL of each base/neutral analyte and 400 ng/μL of each acid analyte in the extract to be analyzed (assuming a 1 μL 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. Nonpolar compounds (i.e., organochlorine pesticides and PCBs), hexane or appropriate solvent.

2. Extractable priority pollutants, 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 Section 7.3.11 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 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 form Solid Samples", S-CUBED, Report for EPA Contract 68-03-33-75, Work Assignment No. 03, Document No. SSS-R-88-9436, October 1988.

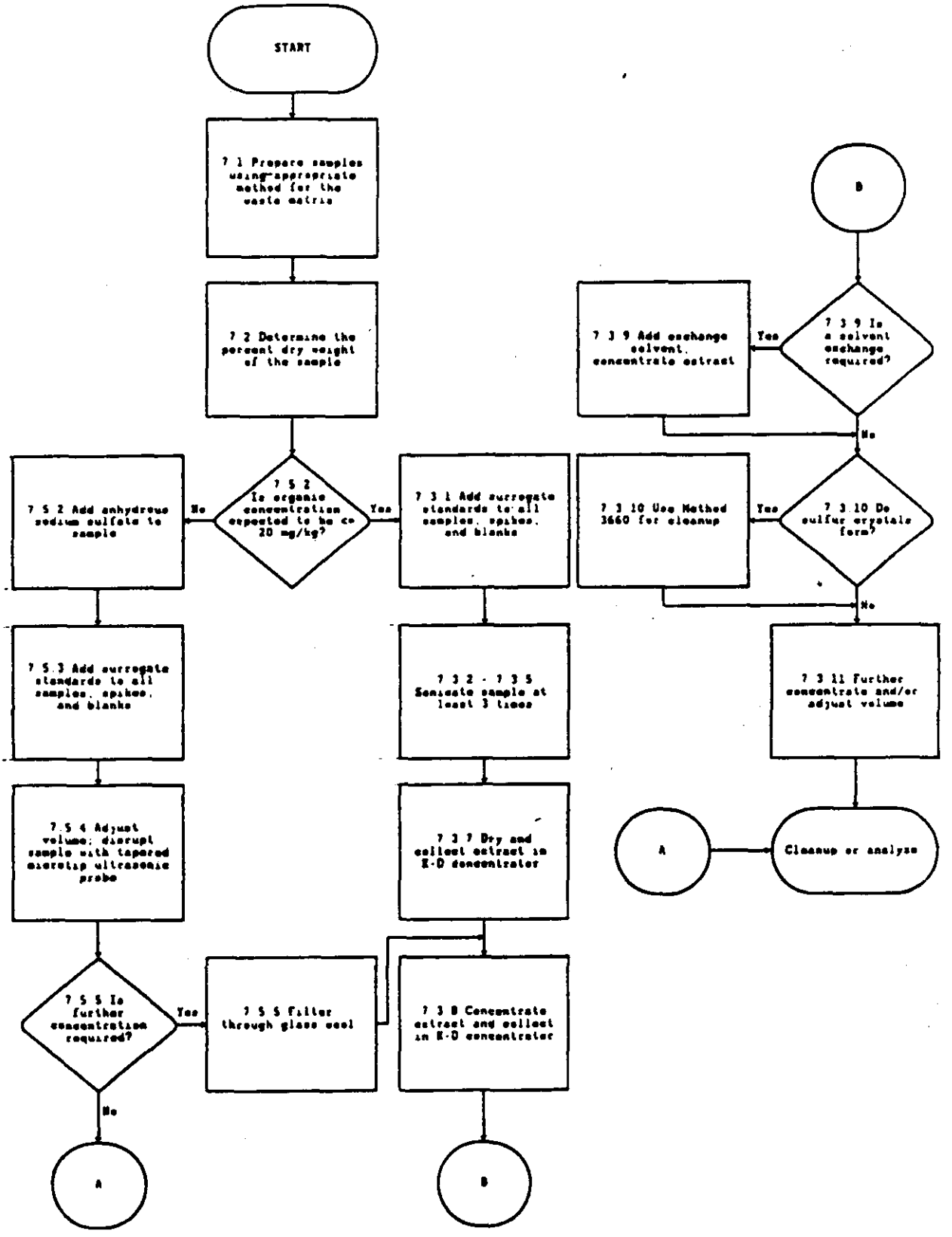
TABLE 1.
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

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[a]	as received	2-propanol	hexane	1.0	1.0, 10.0[b]
8060	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
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
8140	as received	hexane	hexane	10.0	10.0
8141	as received	hexane	hexane	10.0	10.0
8250[a,c]	as received	none	--	--	1.0
8270[c]	as received	none	--	--	1.0
8310	as received	acetonitrile	--	--	1.0

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

[b] 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.

[c] 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.


START
7.1 Prepare samples using appropriate method for the waste matrix
7.2 Determine the percent dry weight of the sample
7.5.2 Is organic concentration expected to be <= 20 mg/kg?
No
Yes
7.5.2 Add anhydrous sodium sulfate to sample
7.5.3 Add surrogate standards to all samples, spikes, and blanks
7.5.4 Adjust volume; disrupt sample with tapered microtip ultrasonic probe
7.5.5 Is further concentration required?
Yes
7.5.5 Filter through glass wool
No
A
7.3.1 Add surrogate standards to all samples, spikes, and blanks
7.3.2 - 7.3.5 Sonicate sample at least 3 times
7.3.7 Dry and collect extract in K-D concentrator
7.3.8 Concentrate extract and collect in K-D concentrator
B
B
7.3.9 Is a solvent exchange required?
Yes
7.3.9 Add exchange solvent, concentrate extract
No
7.3.10 Do sulfur crystals form?
Yes
7.3.10 Use Method 3660 for cleanup
No
7.3.11 Further concentrate and/or adjust volume
A
Cleanup or analyze

METHOD 3610A

ALUMINA COLUMN CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Scope: Alumina is a highly porous and granular form of aluminum oxide. It is available in three pH ranges (basic, neutral, and acidic) for use in column chromatography. It is used to separate analytes from interfering compounds of a different chemical polarity.

1.2 General Applications (Gordon and Ford):

1.2.1 Basic (B) pH (9-10): USES: Basic and neutral compounds stable to alkali, alcohols, hydrocarbons, steroids, alkaloids, natural pigments. DISADVANTAGES: Can cause polymerization, condensation, and dehydration reactions; cannot use acetone or ethyl acetate as eluants.

1.2.2 Neutral (N): USES: Aldehydes, ketones, quinones, esters, lactones, glycoside. DISADVANTAGES: Considerably less active than the basic form.

1.2.3 Acidic (A) pH (4-5): USES: Acidic pigments (natural and synthetic), strong acids (that otherwise chemisorb to neutral and basic alumina).

1.2.4 Activity grades: Acidic, basic, or neutral alumina can be prepared in various activity grades (I to V), according to the Brockmann scale, by addition of water to Grade 1 (prepared by heating at 400-450°C until no more water is lost). The Brockmann scale (Gordon and Ford, p. 374) is reproduced below:

Water added (wt. %):	0	3	6	10	15
Activity grade:	I	II	III	IV	V
RF (p-aminoazobenzene):	0.0	0.13	0.25	0.45	0.55

1.3 Specific applications: This method includes guidance for cleanup of sample extracts containing phthalate esters and nitrosamines. For alumina column cleanup of petroleum wastes, see Method 3611, Alumina Column Cleanup of Petroleum Wastes.

2.0 SUMMARY OF METHOD

2.1 The column is packed with the required amount of adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution of the analytes is effected with a suitable solvent(s), leaving the interfering compounds on the column. The eluate is then concentrated.

3.0 INTERFERENCES

3.1 A reagent blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the *method detection limit before this method is performed on actual samples.*

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

4.0 APPARATUS AND MATERIALS

4.1 Chromatography column: 300 mm x 10 mm ID, with Pyrex glass wool at bottom and a Teflon stopcock.

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.

4.2 Beakers: 500 mL.

4.3 Reagent bottle: 500 mL.

4.4 Muffle furnace.

4.5 Kuderna-Danish (K-D) apparatus:

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

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

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

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

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

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

4.7 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.8 Vials: Glass, 2 mL capacity, with Teflon lined screw caps or crimp tops.

4.9 Erlenmeyer flasks: 50 and 250 mL

5.0 REAGENTS

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

5.2 Sodium sulfate: 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. 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.

5.3 Eluting solvents:

5.3.1 Diethyl Ether, $C_2H_5OC_2H_5$. Pesticide quality or equivalent. Must be free of peroxides as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

5.3.2 Methanol, CH_3OH - Pesticide quality or equivalent.

5.3.3 Pentane, $CH_3(CH_2)_3CH_3$ - Pesticide quality or equivalent.

5.3.4 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.3.5 Methylene chloride, CH_2Cl_2 - Pesticide quality or equivalent.

5.4 Alumina:

5.4.1 For cleanup of phthalate extracts: Alumina-Neutral, activity Super I, W200 series (ICN Life Sciences Group, No. 404583). To prepare for use, place 100 g of alumina into a 500 mL beaker and heat for approximately 16 hr at 400°C. After heating, transfer to a 500 mL reagent bottle. Tightly seal and cool to room temperature. When cool, add 3 mL of organic-free reagent water. Mix thoroughly by shaking or rolling for 10 min and let it stand for at least 2 hr. Keep the bottle sealed tightly.

5.4.2 For cleanup of nitrosamine extracts: Alumina-Basic, activity Super I, W200 series (ICN Life Sciences Group, No. 404571, or equivalent). To prepare for use, place 100 g of alumina into a 500 mL reagent bottle and add 2 mL of organic-free reagent water. Mix the alumina preparation thoroughly by shaking or rolling for 10 min and let it stand for at least 2 hr. The preparation should be homogeneous before use. Keep the bottle sealed tightly to ensure proper activity.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Phthalate esters:

7.1.1 Reduce the sample extract volume to 2 mL prior to cleanup. The extract solvent must be hexane.

7.1.2 Place approximately 10 g of alumina into a 10 mm ID chromatographic column. Tap the column to settle the alumina and add 1-2 cm of anhydrous sodium sulfate to the top.

7.1.3 Pre-elute the column with 40 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2 mL sample extract onto the column using an additional 2 mL of hexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 35 mL of hexane and continue the elution of the column. Discard this hexane eluate.

7.1.4 Next, elute the column with 140 mL of 20% ethyl ether in hexane (v/v) into a 500 mL K-D flask equipped with a 10 mL concentrator tube. Concentrate the collected fraction using the Kuderna-Danish technique. No solvent exchange is necessary. Adjust the volume of the cleaned up extract to whatever volume is required (10.0 mL for Method 8060) and analyze. Compounds that elute in this fraction are as follows:

Bis(2-ethylhexyl) phthalate
Butyl benzyl phthalate
Di-n-butyl phthalate
Diethyl phthalate
Dimethyl phthalate
Di-n-octyl phthalate.

7.2 Nitrosamines:

7.2.1 Reduce the sample extract to 2 mL prior to cleanup.

7.2.2 Diphenylamine, if present in the original sample extract, must be separated from the nitrosamines if N-nitrosodiphenylamine is to be determined by this method.

7.2.3 Place approximately 12 g of the alumina preparation into a 10 mm ID chromatographic column. Tap the column to settle the alumina and add 1-2 cm of anhydrous sodium sulfate to the top.

7.2.4 Pre-elute the column with 10 mL of ethyl ether/pentane (3:7)(v/v). Discard the eluate (about 2 mL) and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2 mL sample extract onto the column using an additional 2 mL of pentane to complete the transfer.

7.2.5 Just prior to exposure of the sodium sulfate layer to the air, add 70 mL of ethyl ether/pentane (3:7)(v/v). Discard the first 10 mL of eluate. Collect the remainder of the eluate in a 500 mL K-D flask equipped

with a 10 mL concentrator tube. This fraction contains N-nitroso-di-n-propylamine.

7.2.6 Next, elute the column with 60 mL of ethyl ether/pentane (1:1)(v/v), collecting the eluate in a second 500 mL K-D flask equipped with a 10 mL concentrator tube. Add 15 mL of methanol to the K-D flask. This fraction will contain N-nitrosodimethylamine, most of the N-nitroso-di-n-propylamine, and any diphenylamine that is present.

7.2.7 Concentrate both fractions using the Kuderna-Danish Technique, using pentane to prewet the Snyder column. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of pentane. Adjust the final volume to whatever is required in the appropriate determinative method (Section 4.3 of this chapter). Analyze the fractions.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

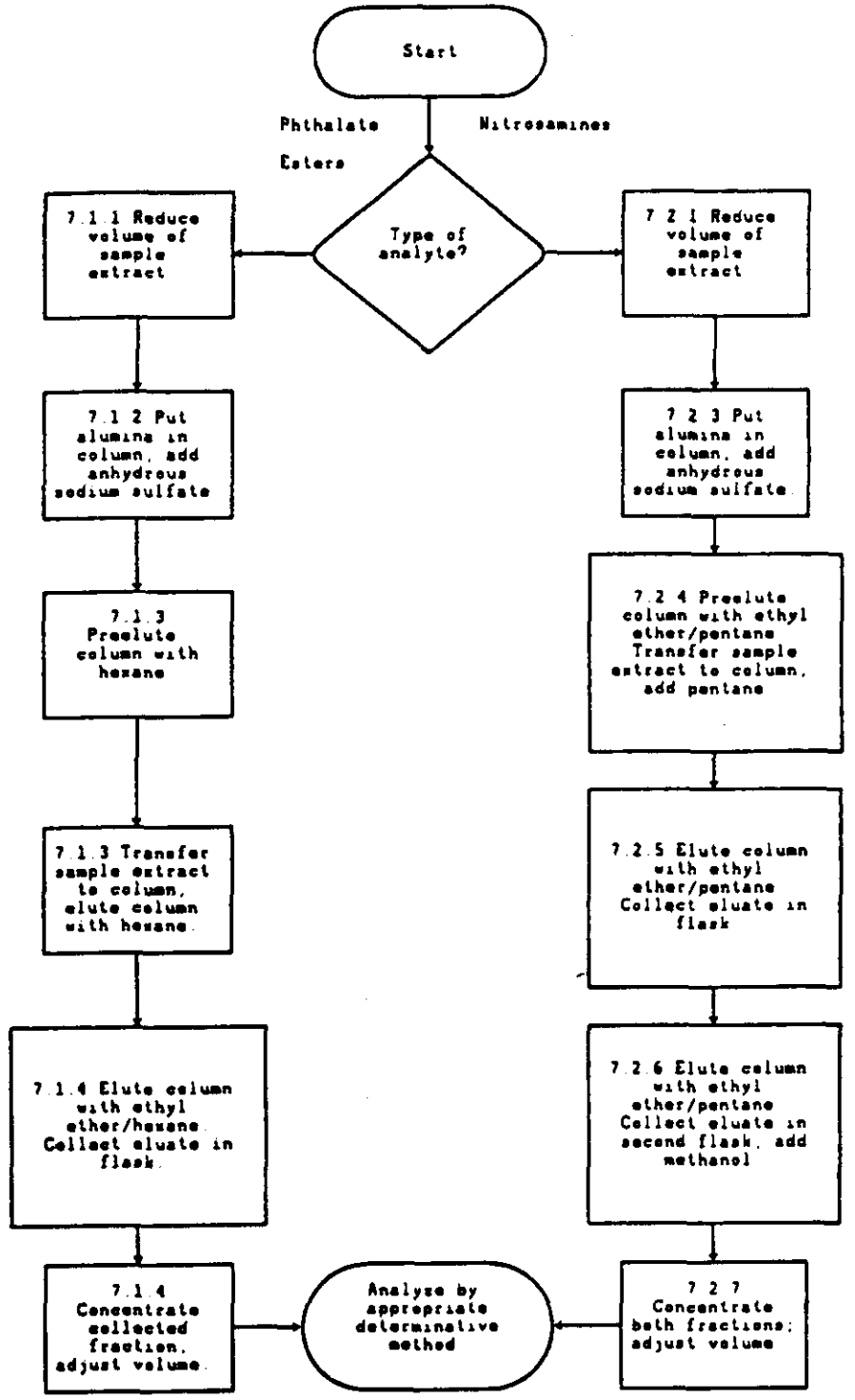
8.2 For sample extracts that are cleaned up using this method, the associated quality control samples must also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 Performance data are not available.

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.


Start
Phthalate Esters
Nitrosamines
Type of analyte?
7.1.1 Reduce volume of sample extract
7.1.2 Put alumina in column, add anhydrous sodium sulfate
7.1.3 Preelute column with hexane
7.1.3 Transfer sample extract to column, elute column with hexane.
7.1.4 Elute column with ethyl ether/hexane. Collect eluate in flask.
7.1.4 Concentrate collected fraction, adjust volume.
7.2.1 Reduce volume of sample extract
7.2.3 Put alumina in column, add anhydrous sodium sulfate.
7.2.4 Preelute column with ethyl ether/pentane. Transfer sample extract to column, add pentane.
7.2.5 Elute column with ethyl ether/pentane. Collect eluate in flask.
7.2.6 Elute column with ethyl ether/pentane. Collect eluate in second flask, add methanol.
7.2.7 Concentrate both fractions; adjust volume.
Analyze by appropriate determinative method

METHOD 3611A

ALUMINA COLUMN CLEANUP AND SEPARATION OF PETROLEUM WASTES

1.0 SCOPE AND APPLICATION

1.1 Method 3611 was formerly Method 3570 in the Second Edition of this manual.

1.2 Specific application: This method includes guidance for separation of petroleum wastes into aliphatic, aromatic, and polar fractions.

2.0 SUMMARY OF METHOD

2.1 The column is packed with the required amount of adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution of the analytes is effected with a suitable solvent(s), leaving the interfering compounds on the column. The eluate is then concentrated.

3.0 INTERFERENCES

3.1 A reagent blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

3.3 Caution must be taken to prevent overloading of the chromatographic column. As the column loading for any of these types of wastes approaches 0.300 g of extractable organics, separation recoveries will suffer. If overloading is suspected, an aliquot of the base-neutral extract prior to cleanup may be weighed and then evaporated to dryness. A gravimetric determination on the aliquot will indicate the weight of extractable organics in the sample.

4.0 APPARATUS AND MATERIALS

4.1 Chromatography column: 300 mm x 10 mm ID, with Pyrex glass wool at bottom and a Teflon stopcock.

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.

4.2 Beakers: 500 mL.

4.3 Reagent bottle: 500 mL.

4.4 Muffle furnace.

4.5 Kuderna-Danish (K-D) apparatus:

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

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

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

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

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

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

4.7 Water bath: Heated with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.8 Erlenmeyer flasks: 50 and 250 mL.

5.0 REAGENTS

5.1 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. 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.

5.2 Eluting solvents:

5.2.1 Methanol, CH_3OH - Pesticide quality or equivalent.

5.2.2 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.2.3 Methylene chloride, CH_2Cl_2 - Pesticide quality or equivalent.

5.3 Alumina: Neutral 80-325 MCB chromatographic grade or equivalent. Dry alumina overnight at 130°C prior to use.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 It is suggested that Method 3650, Acid-Base Partition Cleanup, be performed on the sample extract prior to alumina cleanup.

7.2 Place approximately 10 g of alumina into a chromatographic column, tap to settle the alumina, and add 1 cm of anhydrous sodium sulfate to the top.

7.3 Pre-elute the column with 50 mL of hexane. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 1 mL sample extract onto the column using an additional 1 mL of hexane to complete the transfer. To avoid overloading the column, it is suggested that no more than 0.300 g of extractable organics be placed on the column (see Section 3.3).

7.4 Just prior to exposure of the sodium sulfate to the air, elute the column with a total of 15 mL of hexane. If the extract is in 1 mL of hexane, and if 1 mL of hexane was used as a rinse, then 13 mL of additional hexane should be used. Collect the effluent in a 50 mL flask and label this fraction "base/neutral aliphatics." Adjust the flow rate to 2 mL/min.

7.5 Elute the column with 100 mL of methylene chloride and collect the effluent in a 250 mL flask. Label this fraction "base/neutral aromatics."

7.6 Elute the column with 100 mL of methanol and collect the effluent in a 250 mL flask. Label this fraction "base/neutral polars."

7.7 Concentrate the extracts by the standard K-D technique to the volume (1-10 mL) required in the appropriate determinative method (Chapter Four). Analyze the fractions containing the analytes of interest.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

8.3 For sample extracts that are cleaned up using this method, the associated quality control samples must also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 The precision and accuracy of the method will depend upon the overall performance of the sample preparation and analysis.

9.2 Rag oil is an emulsion consisting of crude oil, water, and soil particles. It has a density greater than crude oil and less than water. This material forms a layer between the crude oil and water when the crude oil is allowed to gravity separate at the refinery. A rag oil sample was analyzed by

a number of laboratories according to the procedure outlined in this method. The results of these analyses for selected components in the rag oil are presented in Table 1. Reconstructed ion chromatograms from the GC/MS analyses are included as Figures 1 and 2.

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.

Table 1.
RESULTS OF ANALYSIS FOR SELECTED COMPONENTS IN RAG OIL

Analyte	Mean Conc. (mg/Kg)[a]	Standard Deviation	%RSD[b]
Naphthalene	216	42	19
Fluorene	140	66	47
Phenanthrene	614	296	18
2-Methylnaphthalene	673	120	18
Dibenzothiophene	1084	286	26
Methylphenanthrene	2908	2014	69
Methyldibenzothiophene	2200	1017	46
	Average Surrogate Recovery		
Nitrobenzene-d_5	58.6	11	
Terphenyl-d_{14}	83.0	2.6	
Phenol-d_6	80.5	27.6	
Naphthalene-d_8	64.5	5.0	

[a] Based on five determinations from three laboratories.

[b] Percent Relative Standard Deviation.

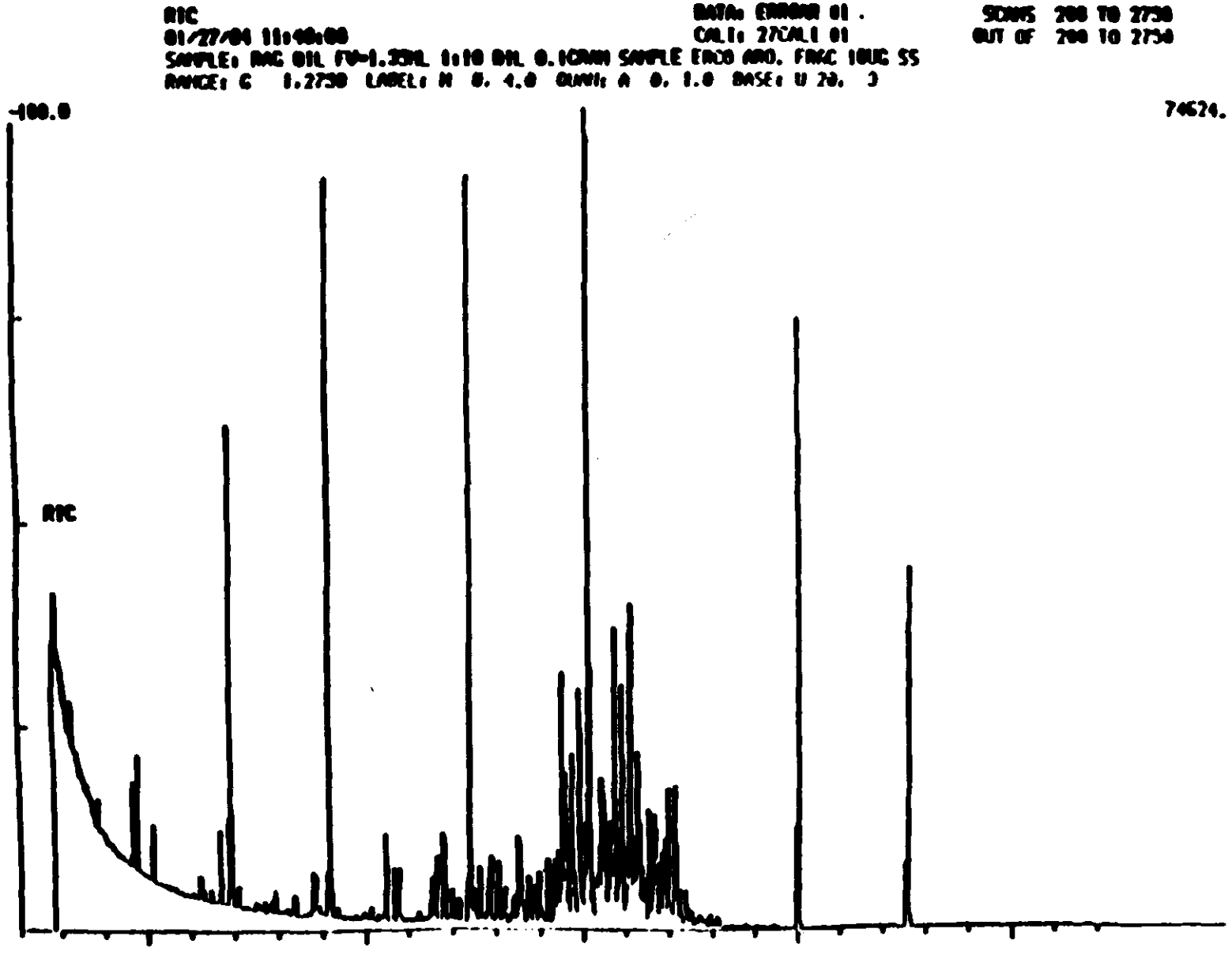


Figure 1. Reconstructed ion chromatogram from GC/MS analysis of the aromatic fraction from Rag Oil

Figure 1

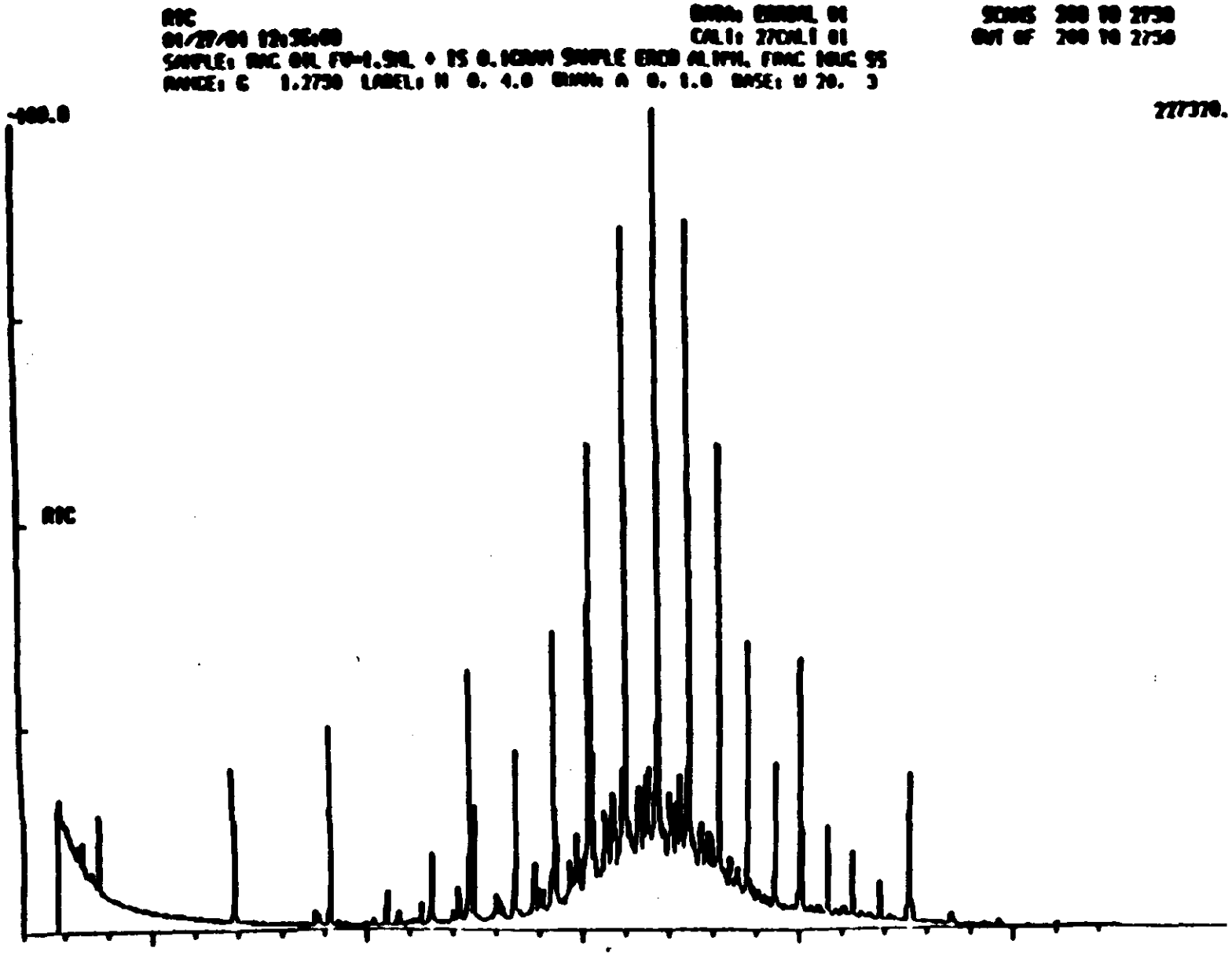
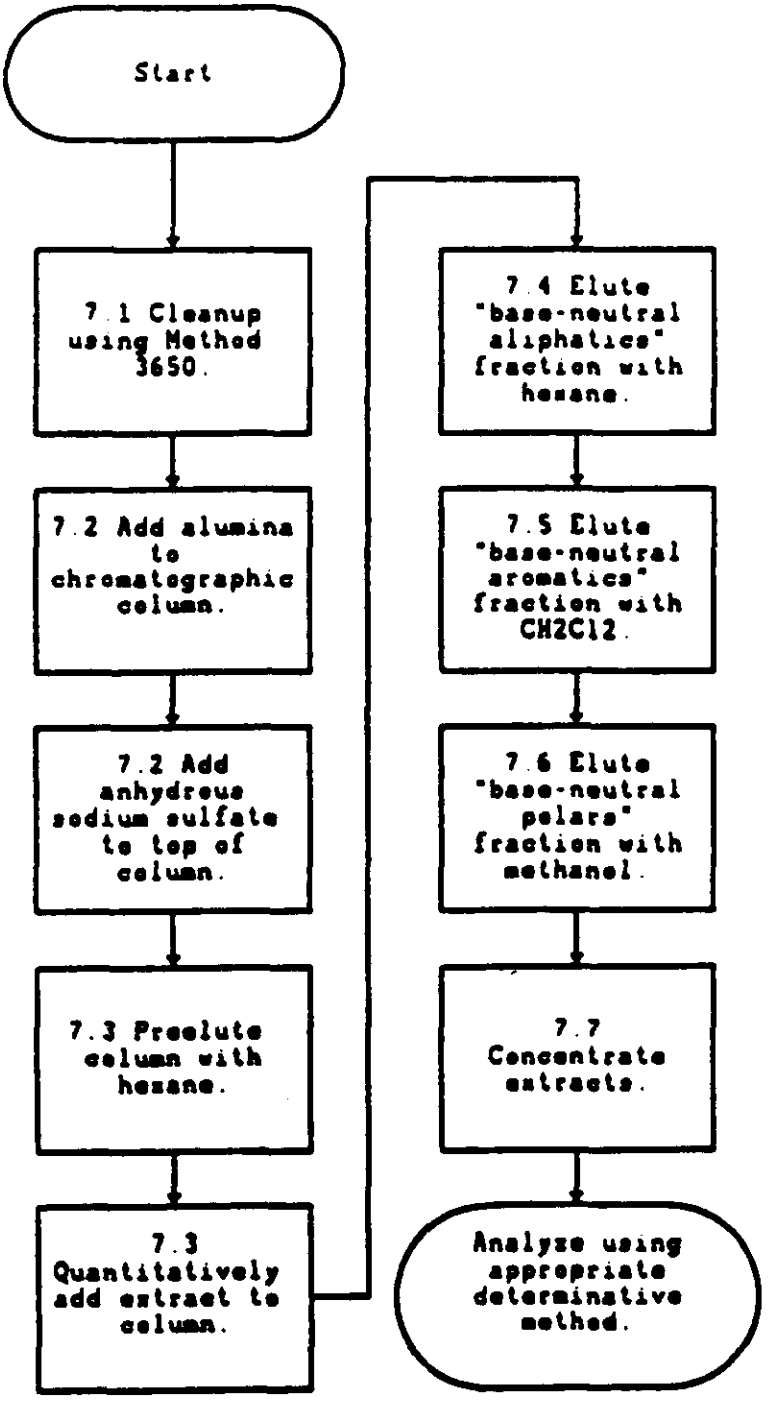


Figure 2. Reconstructed ion chromatogram from GC/MS analysis of the aliphatic fraction from Rag Oil


Start
7.1 Cleanup using Method 3650.
7.2 Add alumina to chromatographic column.
7.2 Add anhydrous sodium sulfate to top of column.
7.3 Preelute column with hexane.
7.3 Quantitatively add extract to column.
7.4 Elute "base-neutral aliphatics" fraction with hexane.
7.5 Elute "base-neutral aromatics" fraction with CH2Cl2.
7.6 Elute "base-neutral polars" fraction with methanol.
7.7 Concentrate extracts.
Analyze using appropriate determinative method.

METHOD 3620A

FLORISIL COLUMN CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Florisil, a registered tradename of the Floridin Co., is a magnesium silicate with acidic properties. It is used for general column chromatography as a cleanup procedure prior to sample analysis by gas chromatography.

1.2 General applications: Cleanup of pesticide residues and other chlorinated hydrocarbons; the separation of nitrogen compounds from hydrocarbons; the separation of aromatic compounds from aliphatic-aromatic mixtures; and similar applications for use with fats, oils, and waxes (Floridin). Additionally, Florisil is considered good for separations with steroids, esters, ketones, glycerides, alkaloids, and some carbohydrates (Gordon and Ford).

1.3 Specific applications: This method includes guidance for cleanup of sample extracts containing the following analyte groups: phthalate esters; nitrosamines; organochlorine pesticides; nitroaromatics; haloethers; chlorinated hydrocarbons; and organophosphorus pesticides.

2.0 SUMMARY OF METHOD

2.1 The column is packed with the required adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution is effected with a suitable solvent(s) leaving the interfering compounds on the column. The eluate is then concentrated.

3.0 INTERFERENCES

3.1 A reagent blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

4.0 APPARATUS AND MATERIALS

4.1 Beaker - 500 mL.

4.2 Chromatographic column - 300 mm long x 10 mm ID or 400 mm long x 20 mm ID, as specified in Section 7.0; with Pyrex glass wool at bottom and a Teflon stopcock.

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.

4.3 Kuderna-Danish (K-D) apparatus.

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

4.3.2 Evaporation flask - 500 mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

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

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

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

4.4 Muffle furnace.

4.5 Reagent bottle - 500 mL.

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

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

4.8 Erlenmeyer flasks - 50 and 250 mL.

4.9 Top-loading balance - 0.01 g.

5.0 REAGENTS

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

5.2 Florisil - Pesticide residue (PR) grade (60/100 mesh); purchase activated at 1250°F (677°C), stored in glass containers with ground-glass stoppers or foil-lined screw caps.

5.2.1 Deactivation of Florisil - for cleanup of phthalate esters. To prepare for use, place 100 g of Florisil into a 500 mL beaker and heat for approximately 16 hr at 40°C. After heating, transfer to a 500 mL reagent bottle. Tightly seal and cool to room temperature. When cool add 3 mL of organic-free reagent water. Mix thoroughly by shaking or rolling for 10 min and let stand for at least 2 hr. Keep the bottle sealed tightly.

5.2.2 Activation of Florisil - for cleanup of nitrosamines, organochlorine pesticides and PCBs, nitroaromatics, haloethers, chlorinated hydrocarbons, and organophosphorus pesticides. Just before use, activate each batch at least 16 hr at 130°C in a glass container loosely covered with aluminum foil. Alternatively, store the Florisil in an oven at 130°C. Cool the Florisil before use in a desiccator. (Florisil from different batches or sources may vary in adsorptive capacity. To standardize the amount of Florisil which is used, the use of lauric acid value is suggested. The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per g of Florisil. The amount of Florisil to be used for each column is calculated by dividing 110 by this ratio and multiplying by 20 g (Mills).

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. 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 Eluting solvents

5.4.1 Diethyl ether, $C_2H_5OC_2H_5$ - Pesticide quality or equivalent. Must be free of peroxides, as indicated by test strips (EM Quant or equivalent). Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 mL ethyl alcohol preservative must be added to each liter of ether.

5.4.2 Acetone, CH_3COCH_3 - Pesticide quality or equivalent.

5.4.3 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.4.4 Methylene chloride, CH_2Cl_2 - Pesticide quality or equivalent.

5.4.5 Pentane, $CH_3(CH_2)_3CH_3$ - Pesticide quality or equivalent.

5.4.6 Petroleum ether (boiling range 30-60°C) - Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Phthalate esters

7.1.1 Reduce the sample extract volume to 2 mL prior to cleanup. The extract solvent must be hexane.

7.1.2 Place approximately 10 g of deactivated Florisil (Section 5.1.1) into a 10 mm ID chromatographic column. Tap the column to settle

the Florisil and add approximately 1 cm of anhydrous sodium sulfate to the top.

7.1.3 Preelute the column with 40 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2 mL sample extract onto the column using an additional 2 mL of hexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 40 mL of hexane and continue the elution of the column. Discard this hexane eluate.

7.1.4 Next, elute the column with 100 mL of 20% ethyl ether in hexane (v/v) into a 500 mL K-D flask equipped with a 10 mL concentrator tube. Concentrate the collected fraction as needed. No solvent exchange is necessary. Adjust the volume of the cleaned-up extract to whatever volume is required (10 mL for Method 8060) and analyze by gas chromatography. Compounds that elute in this fraction are:

Bis(2-ethylhexyl) phthalate
Butyl benzyl phthalate
Di-n-butyl phthalate
Diethyl phthalate
Dimethyl phthalate
Di-n-octyl phthalate

7.2 Nitrosamines

7.2.1 Reduce the sample extract volume to 2 mL prior to cleanup.

7.2.2 Add a weight of activated Florisil (nominally 22 g) predetermined by calibration (Section 5.1.2) into a 20 mm ID chromatographic column. Tap the column to settle the Florisil and add about 5 mm of anhydrous sodium sulfate to the top.

7.2.3 Pre-elute the column with 40 mL of ethyl ether/pentane (15:85) (v/v). Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2 mL sample extract onto the column using an additional 2 mL of pentane to complete the transfer.

7.2.4 Elute the column with 90 mL of ethyl ether/pentane (15:85) (v/v) and discard the eluate. This fraction will contain the diphenylamine, if it is present in the extract.

7.2.5 Next, elute the column with 100 mL of acetone/ethyl ether (5:95) (v/v) into a 500 mL K-D flask equipped with a 10 mL concentrator tube. This fraction will contain all of the nitrosamines listed in the scope of the method.

7.2.6 Add 15 mL of methanol to the collected fraction, concentrate using pentane to prewet the K-D column and set the water bath at 70 to 75°C. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of pentane.

7.3 Organochlorine pesticides, haloethers, and organophosphorus pesticides (see Tables 1 and 2 for fractionation patterns of compounds tested)

7.3.1 Reduce the sample extract volume to 10 mL prior to cleanup. The extract solvent must be hexane.

7.3.2 Add a weight of activated Florisil (nominally 20 g), predetermined by calibration (Section 5.1.2), to a 20 mm ID chromatographic column. Settle the Florisil by tapping the column. Add anhydrous sodium sulfate to the top of the Florisil to form a layer 1 to 2 cm deep. Add 60 mL of hexane to wet and rinse the sodium sulfate and Florisil. Just prior to exposure of the sodium sulfate to air, stop the elution of the hexane by closing the stopcock on the chromatographic column. Discard the eluate.

7.3.3 Adjust the sample extract volume to 10 mL with hexane and transfer it from the K-D concentrator tube to the Florisil column. Rinse the tube twice with 1-2 mL hexane, adding each rinse to the column.

7.3.4 Place a 500 mL K-D flask and clean concentrator tube under the chromatographic column. Drain the column into the flask until the sodium sulfate layer is nearly exposed. Elute the column with 200 mL of 6% ethyl ether in hexane (v/v) (Fraction 1) using a drip rate of about 5 mL/min. All of the haloethers are in this fraction. Remove the K-D flask and set aside for later concentration. Elute the column again, using 200 mL of 15% ethyl ether in hexane (v/v) (Fraction 2), into a second K-D flask. Perform a third elution using 200 mL of 50% ethyl ether in hexane (v/v) (Fraction 3), and a final elution with 200 mL of 100% ethyl ether (Fraction 4), into separate K-D flasks.

7.3.5 Concentrate the eluates by standard K-D techniques using the water bath at about 85°C (75°C for Fraction 4). Adjust the final volume to whatever volume is required (1-10 mL).

7.4 Nitroaromatics and isophorone

7.4.1 Reduce the sample extract volume to 2 mL prior to cleanup.

7.4.2 Add a weight of activated Florisil (nominally 10 g) predetermined by calibration (Section 5.1.2) into a 10 mm ID chromatographic column. Tap the column to settle the Florisil and add about 1 cm of anhydrous sodium sulfate to the top.

7.4.3 Pre-elute the column with methylene chloride/hexane (1:9) (v/v) at about 2 mL/min. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the sample extract onto the column using an additional 2 mL of hexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 30 mL of methylene chloride/hexane (1:9) (v/v) and continue the elution of the column. Discard the eluate.

7.4.4 Elute the column with 90 mL of ethyl ether/pentane (15:85) (v/v) and discard the eluate. This fraction will contain the diphenylamine, if it is present in the extract.

7.4.5 Next, elute the column with 100 mL of acetone/ethyl ether (5:95) (v/v) into a 500 mL K-D flask equipped with a 10 mL concentrator tube. This fraction will contain all of the nitrosamines listed in the scope of the method.

7.4.6 Add 15 mL of methanol to the collected fraction, concentrate using pentane to prewet the K-D column, and set the water bath at 70 to 75°C. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of pentane.

7.4.7 Next, elute the column with 30 mL of acetone/methylene chloride (1:9) (v/v) into a 500 mL K-D flask equipped with a 10 mL concentrator tube. Concentrate the collected fraction, while exchanging the solvent to hexane. To exchange the solvent, reduce the elution solvent to about 10 mL. Add 50 mL of hexane, a fresh boiling chip, and return the reassembled K-D apparatus to the hot water bath. Adjust the final volume of the cleaned-up extract to whatever volume is required (1-10 mL). Compounds that elute in this fraction are:

2,4-Dinitrotoluene
2,6-Dinitrotoluene
Isophorone
Nitrobenzene.

7.5 Chlorinated hydrocarbons

7.5.1 Reduce the sample extract volume to 2 mL prior to cleanup. The extract solvent must be hexane.

7.5.2 Add a weight of activated Florisil (nominally 12 g) predetermined by calibration (Section 5.1.2) into a 10 mm ID chromatographic column. Tap the column to settle the Florisil and add about 1 to 2 cm of anhydrous sodium sulfate to the top.

7.5.3 Preelute the column with 100 mL of petroleum ether. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the sample extract to the column by decantation and subsequent petroleum ether washings. Discard the eluate. Just prior to exposure of the sodium sulfate layer to the air, begin eluting the column with 200 mL of petroleum ether and collect the eluate in a 500 mL K-D flask equipped with a 10 mL concentrator tube. This fraction should contain all of the chlorinated hydrocarbons:

2-Chloronaphthalene
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachloroethane
1,2,4-Trichlorobenzene.

7.5.4 Concentrate the fraction, using hexane to prewet the column. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with hexane. Adjust the final volume of the cleaned-up extract to whatever volume is required (1-10 mL).

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

8.3 For sample extracts that are cleaned up using this method, the associated quality control samples should also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 Table 1 indicates the distribution of chlorinated pesticides, PCB's, and haloethers in various Florisil column fractions.

9.2 Table 2 indicates the distribution of organophosphorus pesticides in various Florisil column fractions.

10.0 REFERENCES

1. Gordon, A.J. and R.A. Ford, The Chemist's Companion: A Handbook of Practical Data, Techniques, and References (New York: John Wiley & Sons, Inc.), pp. 372, 374, and 375, 1972.

2. Floridin of ITT System, Florisil: Properties, Application, Bibliography, Pittsburgh, Pennsylvania, 5M381DW.

3. Mills, P.A., "Variation of Florisil Activity; Simple Method for Measuring Absorbent Capacity and its use in Standardizing Florisil Columns," Journal of the Association of Official Analytical Chemists, 51, 29, 1968.

4. U.S. Food and Drug Association, Pesticides Analytical Manual (Volume 1), July 1985.

5. 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.

TABLE 1

DISTRIBUTION OF CHLORINATED PESTICIDES, PCBs, AND HALOETHERS INTO FLORISIL COLUMN FRACTIONS

Parameter	Percent Recovery by Fraction[a]		
	1	2	3
Aldrin	100		
α-BHC	100		
B-BHC	97		
γ-BHC	98		
δ-BHC	100		
Chlordane	100		
4,4'-DDD	99		
4,4'-DDE	98		
4,4'-DDT	100		
Dieldrin	0	100	
Endosulfan I	37	64	
Endosulfan II	0	7	91
Endosulfan sulfate	0	0	106
Endrin	4	96	
Endrin aldehyde	0	68	26
Haloethers	R		
Heptachlor	100		
Heptachlor epoxide	100		
Toxaphene	96		
PCB-1016	97		
PCB-1221	97		
PCB-1232	95	4	
PCB-1242	97		
PCB-1248	103		
PCB-1254	90		
PCB-1260	95		

[a] Eluant composition: Fraction 1 - 6% ethyl ether in hexane
Fraction 2 - 15% ethyl ether in hexane
Fraction 3 - 50% ethyl ether in hexane

R = Recovered (no percent recovery data presented).

SOURCE: U.S. EPA and FDA data.

TABLE 2

DISTRIBUTION OF ORGANOPHOSPHORUS PESTICIDES
INTO FLORISIL COLUMN FRACTIONS

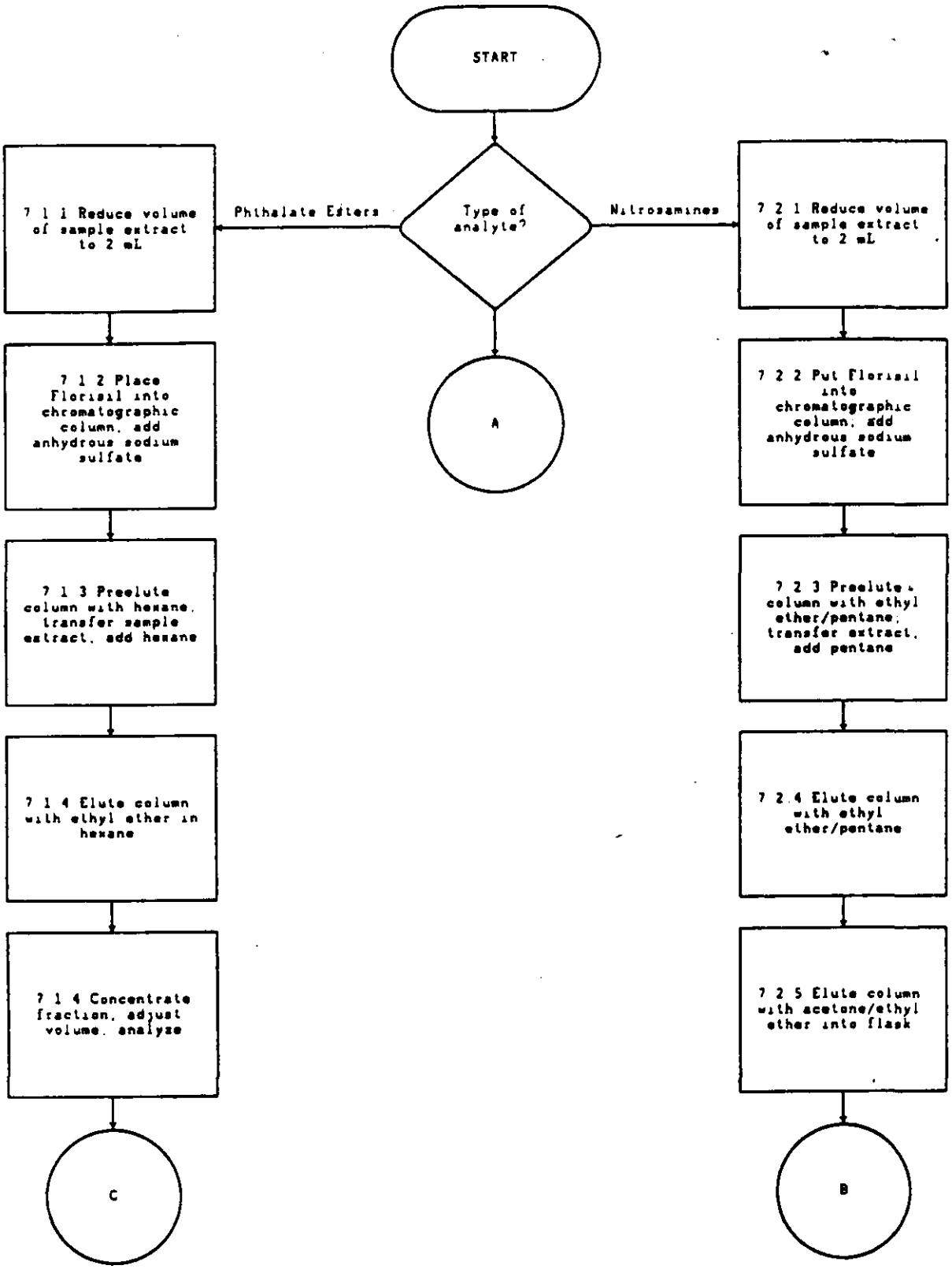
Parameter	Percent Recovery by Fraction[a]			
	1	2	3	4
Azinphos methyl			20	80
Bolstar (Sulprofos)	ND	ND	ND	ND
Chlorpyrifos	>80			
Coumaphos	NR	NR	NR	
Demeton	100			
Diazinon		100		
Dichlorvos	NR	NR	NR	
Dimethoate	ND	ND	ND	ND
Disulfoton	25-40			
EPN		>80		
Ethoprop	V	V	V	
Fensulfothion	ND	ND	ND	ND
Fenthion	R	R		
Malathion		5	95	
Merphos	V	V	V	
Mevinphos	ND	ND	ND	ND
Monochrotophos	ND	ND	ND	ND
Naled	NR	NR	NR	
Parathion		100		
Parathion methyl		100		
Phorate	0-62			
Ronnel	>80			
Stirophos (Tetrachlorvinphos)	ND	ND	ND	ND
Sulfotepp	V	V		
TEPP	ND	ND	ND	ND
Tokuthion (Prothiofos)	>80			
Trichloronate	>80			

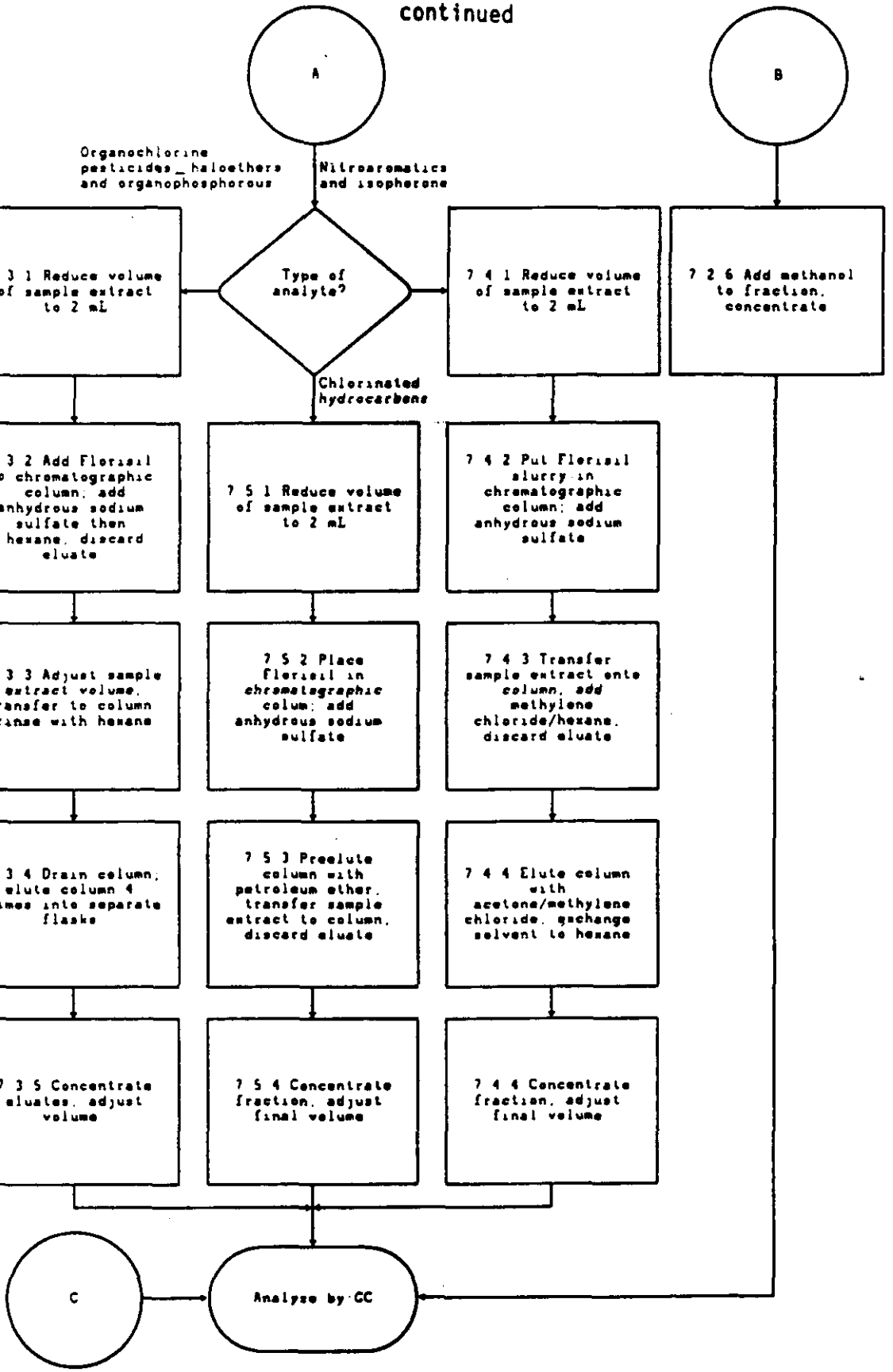
[a] Eluant composition: Fraction 1 - 200 mL of 6% ethyl ether in hexane
Fraction 2 - 200 mL of 15% ethyl ether in hexane
Fraction 3 - 200 mL of 50% ethyl ether in hexane
Fraction 4 - 200 mL of 100% ethyl ether

R = Recovered (no percent recovery information presented) (U.S. FDA).
NR = Not recovered (U.S. FDA).
V = Variable recovery (U.S. FDA).
ND = Not determined.

SOURCE: U.S. EPA and FDA data.

METHOD 3620A
FLORISIL COLUMN CLEANUP




A
B
Organochlorine pesticides, haloethers and organophosphorous
Nitroaromatics and isophorone
Type of analyte?
Chlorinated hydrocarbons
7 3 1 Reduce volume of sample extract to 2 mL
7 4 1 Reduce volume of sample extract to 2 mL
7 2 6 Add methanol to fraction, concentrate
7 3 2 Add Florisil to chromatographic column, add anhydrous sodium sulfate then hexane, discard eluate
7 5 1 Reduce volume of sample extract to 2 mL
7 4 2 Put Florisil slurry in chromatographic column; add anhydrous sodium sulfate
7 3 3 Adjust sample extract volume, transfer to column rinse with hexane
7 5 2 Place Florisil in chromatographic colum; add anhydrous sodium sulfate
7 4 3 Transfer sample extract onto column, add methylene chloride/hexane, discard eluate
7 3 4 Drain column, elute column 4 times into separate flasks
7 5 3 Preelute column with petroleum ether, transfer sample extract to column, discard eluate
7 4 4 Elute column with acetone/methylene chloride, exchange solvent to hexane
7 3 5 Concentrate eluates, adjust volume
7 5 4 Concentrate fraction, adjust final volume
7 4 4 Concentrate fraction, adjust final volume
C
Analyze by GC

METHOD 3630A

SILICA GEL CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Silica gel is a regenerative adsorbent of amorphous silica with weakly acidic properties. It is produced from sodium silicate and sulfuric acid. Silica gel can be used for column chromatography and is for separating the analytes from interfering compounds of a different chemical polarity.

1.2 General applications (Gordon and Ford):

1.2.1 Activated: Heated at 150-160°C for several hours. USES: Separation of hydrocarbons.

1.2.2 Deactivated: Containing 10-20% water. USES: An adsorbent for most functionalities with ionic or nonionic characteristics, including alkaloids, sugar esters, glycosides, dyes, alkali metal cations, lipids, glycerides, steroids, terpenoids and plasticizers. The disadvantages of deactivated silica gel are that the solvents methanol and ethanol decrease adsorbent activity.

1.3 Specific applications: This method includes guidance for cleanup of sample extracts containing polynuclear aromatic hydrocarbons, derivatized phenolic compounds.

2.0 SUMMARY OF METHOD

2.1 The column is packed with the required amount of adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution of the analytes is effected with a suitable solvent(s) leaving the interfering compounds on the column. The eluate is then concentrated.

3.0 INTERFERENCES

3.1 A reagent blank should be analyzed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

4.0 APPARATUS AND MATERIALS

4.1 Chromatographic column - 250 mm long x 10 mm ID; with Pyrex glass wool at bottom and a Teflon stopcock.

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.

4.2 Beakers - 500 mL.

4.3 Kuderna-Danish (K-D) apparatus

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

4.3.2 Evaporation flask - 500 mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

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

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

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

4.4 Vials - 10, 25 mL, glass with Teflon lined screw-caps or crimp tops.

4.5 Muffle furnace.

4.6 Reagent bottle - 500 mL.

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

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

4.9 Erlenmeyer flasks - 50 and 250 mL.

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 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 Silica gel. 100/200 mesh desiccant (Davison Chemical grade 923 or equivalent). Before use, activate for at least 16 hr. at 130°C in a shallow glass tray, loosely covered with foil.

5.4 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. 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.

5.5 Eluting solvents

5.5.1 Cyclohexane, C_6H_{12} - Pesticide quality or equivalent.

5.5.2 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.5.3 2-Propanol, $(CH_3)_2CHOH$ - Pesticide quality or equivalent.

5.5.4 Toluene, $C_6H_5CH_3$ - Pesticide quality or equivalent.

5.5.5 Methylene chloride, CH_2Cl_2 - Pesticide quality or equivalent.

5.5.6 Pentane, C_5H_{12} - Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Polynuclear aromatic hydrocarbons

7.1.1 Before the silica gel cleanup technique can be utilized, the extract solvent must be exchanged to cyclohexane. The exchange is performed as follows:

7.1.1.1 Following K-D concentration of the extract to 1-2 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 minutes. Add one or two clean boiling chips to the K-D flask. Add 4 mL of exchange solvent and attach a two ball micro-Snyder column. Prewet the Snyder column by adding about 0.5 mL of methylene chloride 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 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 apparent volume of liquid reaches 0.5-1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

Caution: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.1.1.2 Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a minimum amount of exchange solvent. Adjust the extract volume to about 2 mL.

7.1.2 Prepare a slurry of 10 g of activated silica gel in methylene chloride and place this into a 10 mm ID chromatographic column. Tap the column to settle the silica gel and elute the methylene chloride. Add 1 to 2 cm of anhydrous sodium sulfate to the top of the silica gel.

7.1.3 Preelute the column with 40 mL of pentane. The rate for all elutions should be about 2 mL/min. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, transfer the 2 mL cyclohexane sample extract onto the column using an additional 2 mL cyclohexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 25 mL of pentane and continue the elution of the column. Discard this pentane eluate.

7.1.4 Next, elute the column with 25 mL of methylene chloride/pentane (2:3)(v/v) into a 500 mL K-D flask equipped with a 10 mL concentrator tube. Concentrate the collected fraction to whatever volume is required (1-10 mL). Proceed with HPLC or GC analysis. Components that elute in this fraction are:

Acenaphthene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(g,h,i)perylene
Benzo(k)fluoranthene
Chrysene
Dibenzo(a,h)anthracene
Fluoranthene
Fluorene
Indeno(1,2,3-cd)pyrene
Naphthalene
Phenanthrene
Pyrene

7.2 Derivatized phenols

7.2.1 This silica gel cleanup procedure is performed on sample extracts that have undergone pentafluorobenzyl bromide derivatization as described in Method 8040.

7.2.2 Place 4.0 g of activated silica gel into a 10 mm ID chromatographic column. Tap the column to settle the silica gel and add about 2 g of anhydrous sodium sulfate to the top of the silica gel.

7.2.3 Preelute the column with 6 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, pipet onto the column 2 mL

of the hexane solution that contains the derivatized sample or standard. Elute the column with 10.0 mL of hexane and discard the eluate.

7.2.4 Elute the column, in order, with 10.0 mL of 15% toluene in hexane (Fraction 1); 10.0 mL of 40% toluene in hexane (Fraction 2); 10.0 mL of 75% toluene in hexane (Fraction 3); and 10.0 mL of 15% 2-propanol in toluene (Fraction 4). All elution mixtures are prepared on a volume:volume basis. Elution patterns for the phenolic derivatives are shown in Table 1. Fractions may be combined, as desired, depending upon the specific phenols of interest or level of interferences. Proceed with GC analysis (Method 8040).

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

8.3 For sample extracts that are cleaned up using this method, the associated quality control samples must also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 Table 1 provides performance information on the fractionation of phenolic derivatives using this method.

10.0 REFERENCES

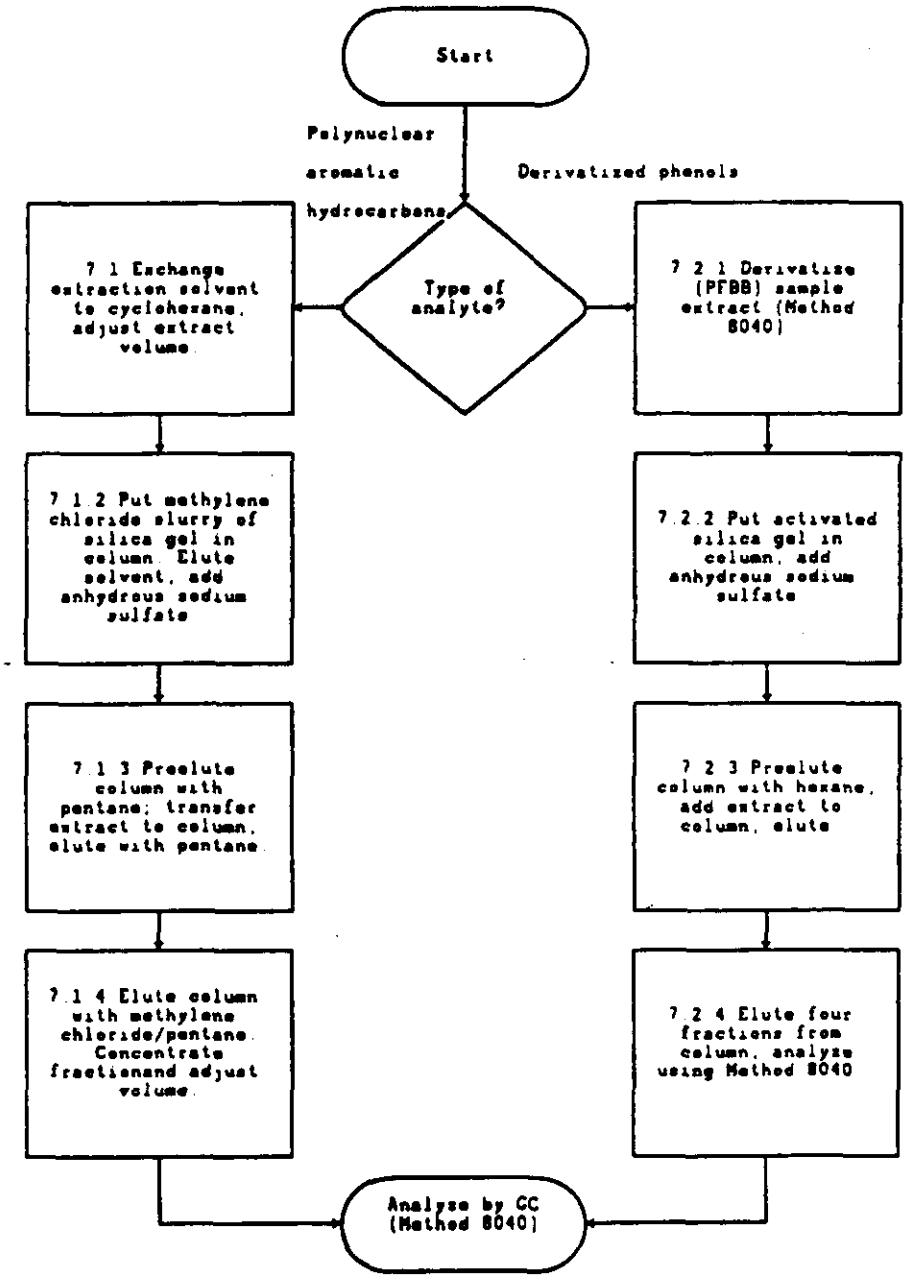
1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

TABLE 1
SILICA GEL FRACTIONATION OF PFBB DERIVATIVES

Parameter	Percent Recovery by Fraction*			
	1	2	3	4
2-Chlorophenol		90	1	
2-Nitrophenol			9	90
Phenol		90	10	
2,4-Dimethylphenol		95	7	
2,4-Dichlorophenol		95	1	
2,4,6-Trichlorophenol	50	50		
4-Chloro-3-methylphenol		84	14	
Pentachlorophenol	75	20		
4-Nitrophenol			1	90

* Eluant composition:

Fraction 1 - 15% toluene in hexane.
Fraction 2 - 40% toluene in hexane.
Fraction 3 - 75% toluene in hexane.
Fraction 4 - 15% 2-propanol in toluene.


Start
Polynuclear aromatic hydrocarbons
Derivatized phenols
Type of analyte?
7.1 Exchange extraction solvent to cyclohexane, adjust extract volume.
7.1.2 Put methylene chloride slurry of silica gel in column. Elute solvent, add anhydrous sodium sulfate
7.1.3 Preelute column with pentane; transfer extract to column, elute with pentane.
7.1.4 Elute column with methylene chloride/pentane. Concentrate fractionand adjust volume.
7.2.1 Derivatize (PFBB) sample extract (Method 8040)
7.2.2 Put activated silica gel in column, add anhydrous sodium sulfate
7.2.3 Preelute column with hexane, add extract to column, elute
7.2.4 Elute four fractions from column, analyze using Method 8040
Analyze by GC (Method 8040)

METHOD 3640

GEL-PERMEATION CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Gel-permeation chromatography (GPC) is a size exclusion procedure using organic solvents and hydrophobic gels in the separation of synthetic macromolecules (Gordon and Ford). The packing gel is porous and is characterized by the range or uniformity (exclusion range) of that pore size. In the choice of gels, the exclusion range must be greater than those of the molecules to be separated (Shugar, et al.).

1.2 General application: GPC is recommended for the elimination from the sample of lipids, polymers, copolymers, proteins, natural resins and polymers, cellular components, viruses, steroids, and dispersed high-molecular-weight compounds (Shugar, et al.).

1.3 Specific application: This method includes guidance for cleanup of sample extracts containing the compounds listed in Tables 2-1 through 2-9 of Chapter 2.

2.0 SUMMARY OF METHOD

2.1 The column is packed with the required amount of preswelled absorbent and is flushed with solvent for an extended period. The column is calibrated and then loaded with the sample to be analyzed. Elution is effected with a suitable solvent(s) and the product is then concentrated.

3.0 INTERFERENCES

3.1 A reagent blank should be analyzed for the compound of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

4.0 APPARATUS

4.1 Gel permeation chromatography system: (Analytical Biochemical Laboratories, Inc. GPC autoprep Model 1002A or equivalent). An automated system of this type is not required; however, if not used, equivalency of an alternative system must be shown.

4.1.1 Chromatographic column: 600- to 700-mm x 25-mm I.D. glass column fitted for upward flow operation.

4.1.2 Bio-beads S-X3: 70 g per column.

4.1.3 Pump: Capable of constant flow of 0.1 to 5 mL/min at up to 100 psi.

4.1.4 Injector: With 5-mL loop.

4.1.5 Ultraviolet detector: 254-nm (optional).

4.1.6 Strip-chart recorder: (optional).

4.1.7 Syringe: 10-mL with Luerlok fitting.

4.1.8 Syringe filter holder and filter: BioRad "Prep Disc" sample filter # 343-0005 and 5-um size filters or equivalent.

4.2 Beakers: 400-mL.

5.0 REAGENTS

5.1 Methylene chloride: Pesticide quality or equivalent.

5.2 GPC calibration solutions:

5.2.1 Corn oil: 200 mg/mL in methylene chloride.

5.2.2 Bis(2-ethylhexyl)phthalate and pentachlorophenol solution: 4.0 mg/mL in methylene chloride.

5.2.3 Mix the corn oil with the phthalate/phenol solution if a UV detector is used. The concentrations should remain the same.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Packing the column: Place approximately 70 g of Bio Beads SX-3 in a 400-mL beaker. Cover the beads with methylene chloride; allow the beads to swell overnight (before packing the columns). Transfer the swelled beads to the column and start pumping solvent through the column, from bottom to top, at 5.0 mL/min. After approximately 1 hr, adjust the pressure on the column to 7-10 psi and pump an additional 4 hr to remove air from the column. Adjust the column pressure periodically as required to maintain 7-10 psi. (See the instrument manual for more details on packing the column.) The pressure should not be permitted to exceed 25 psi.

7.2 Calibration of the column: The column can either be calibrated manually by gravimetric/GC/FID techniques or automatically if a recording UV detector with a flow through cell is available.

7.2.1 **Manual calibration:** Load 5 mL of the corn oil solution into sample loop No. 1 and 5 mL of the phthalate-phenol solution into loop No. 2. Inject the corn oil and collect 10-mL fractions (i.e., change fractions at 2-min intervals) for 36 min. Inject the phthalate-phenol solution and collect 15 mL fractions for 60 min. Determine the corn oil elution pattern by evaporation of each fraction to dryness followed by a gravimetric determination of the residue. Analyze the phthalate-phenol fractions by GC/FID using a DB-5 capillary column, a UV spectrophotometer, or a GC/MS system. Plot the concentration of each component in each fraction versus total eluant volume (or time) from the injection points. Choose a dump time which allows $\geq$ 85% removal of the corn oil and $\geq$ 85% recovery of the bis(2-ethylhexyl)phthalate. Choose the collect time to extend at least 10 min after the elution of pentachlorophenol. Wash the column with methylene chloride at least 15 min between samples. Typical parameters selected are: Dump time, 30 min (150 mL); collect time, 36 min (180 mL); and wash time, 15 min (75 mL).

7.2.2 **Automated calibration:** The column can also be calibrated by the use of a 254-nm detector in place of gravimetric and GC analyses of fractions. Use the corn oil/phthalate/phenol mixture when using a UV detector. Load 5 mL into sample loop No. 1. Use the same criteria for choosing dump time and collect time as in the manual calibration.

7.2.3 The SX-3 Bio Beads column may be reused for several months, even if discoloration occurs. Recalibrate the system once a week.

7.3 GPC Extract Cleanup: The extract must be in methylene chloride or, primarily methylene chloride. All other solvents must be concentrated to 1 mL and diluted to 10.0 mL with methylene chloride. Prefilter or load all extracts via the filter holder to avoid particulates that might cause flow stoppage or damage the valve. Load one 5.0 mL aliquot of the extract onto the GPC column. Do not apply excessive pressure when loading. Purge the sample loading tubing thoroughly with solvent between extracts. After especially dirty extracts, run a GPC blank (methylene chloride) to check for carry-over. Process the extracts using the dump, collect, and wash parameters determined from the calibration, and collect the cleaned extracts in 400-mL beakers tightly covered with aluminum foil.

NOTE: Half of the 10.0 mL extract is lost during the loading of the GPC. Therefore, divide the sample size by two when calculating analyte concentration.

7.4 Concentrate the extract by the standard K-D technique (see any of the extraction methods, Section 4.2 of this chapter). See the determinative methods (Chapter Four, Section 4.3) for the required final volume.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedure.

8.2 The analyst should demonstrate that the compound(s) of interest are being quantitatively recovered before applying this method to actual samples.

8.2 For sample extracts that are cleaned up using this method, the associated quality control samples must also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

1. Gordon, A.J., and R.A. Ford, The Chemist's Companion: A Handbook of Practical Data, Techniques, and References (New York: John Wiley & Sons, Inc.) pp. 372, 374, and 375, 1972.

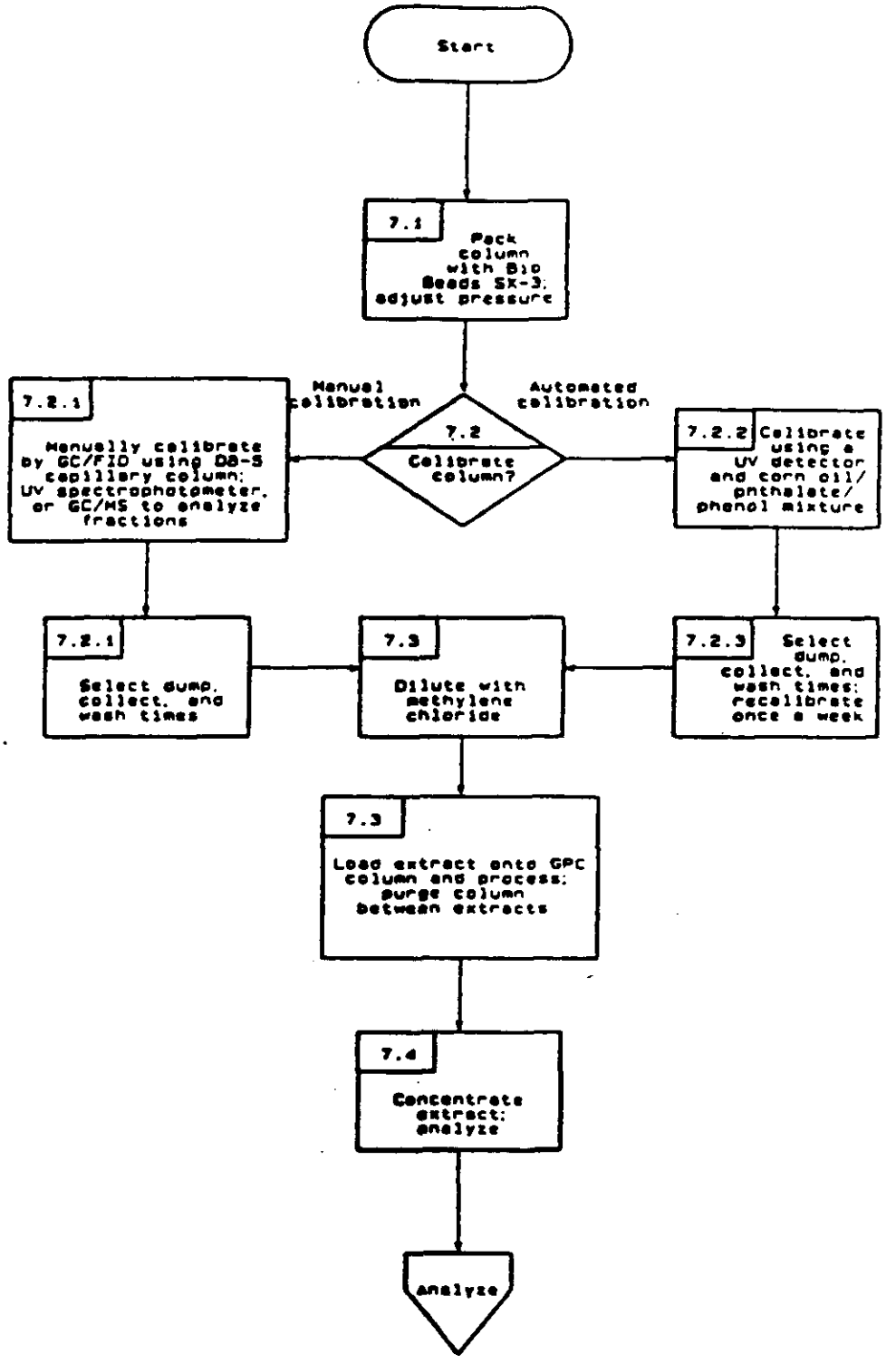
2. Shugar G.J., et al., Chemical Technician's Ready Reference Handbook, 2nd ed. (New York: McGraw-Hill Book Co.) pp. 764-766, 1981.

3. Wise, R.H., D.F. Bishop, R.T. Williams, and B.M. Austern, "Gel Permeation Chromatography in the GC/MS Analysis of Organics in Sludges," U.S. EPA, Municipal Environmental Research Laboratory, Cincinnati, Ohio 45268.

4. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, Revision, July 1985.

METHOD 3640

GEL-PERMEATION CLEANUP



METHOD 3650A

ACID-BASE PARTITION CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Method 3650 was formerly Method 3530 in the second edition of this manual.

1.2 Method 3650 is a liquid-liquid partitioning cleanup method to separate acid analytes, e.g. organic acids and phenols, from base/neutral analytes, e.g. amines, aromatic hydrocarbons, and halogenated organic compounds, using pH adjustment. It may be used for cleanup of petroleum waste prior to analysis or further cleanup (e.g., alumina cleanup). The following compounds can be separated by this method:

Compound Name	CAS No.[a]	Fraction
Benz(a)anthracene	56-55-3	Base-neutral
Benzo(a)pyrene	50-32-8	Base-neutral
Benzo(b)fluoranthene	205-99-2	Base-neutral
Chlordane	57-74-9	Base-neutral
Chlorinated dibenzodioxins		Base-neutral
2-Chlorophenol	95-57-8	Acid
Chrysene	218-01-9	Base-neutral
Creosote	8001-58-9	Base-neutral and Acid
Cresol(s)		Acid
Dichlorobenzene(s)		Base-neutral
Dichlorophenoxyacetic acid	94-75-7	Acid
2,4-Dimethylphenol	105-67-9	Acid
Dinitrobenzene	25154-54-5	Base-neutral
4,6-Dinitro-o-cresol	534-52-1	Acid
2,4-Dinitrotoluene	121-14-2	Base-neutral
Heptachlor	76-44-8	Base-neutral
Hexachlorobenzene	118-74-1	Base-neutral
Hexachlorobutadiene	87-68-3	Base-neutral
Hexachloroethane	67-72-1	Base-neutral
Hexachlorocyclopentadiene	77-47-4	Base-neutral
Naphthalene	91-20-3	Base-neutral
Nitrobenzene	98-95-3	Base-neutral
4-Nitrophenol	100-02-7	Acid
Pentachlorophenol	87-86-5	Acid
Phenol	108-95-2	Acid
Phorate	298-02-2	Base-neutral
2-Picoline	109-06-8	Base-neutral
Pyridine	110-86-1	Base-neutral
Tetrachlorobenzene(s)		Base-neutral
Tetrachlorophenol(s)		Acid
Toxaphene	8001-35-2	Base-neutral

Compound Name	CAS No.[a]	Fraction
Trichlorophenol(s)		Acid
2,4,5-TP (Silvex)	93-72-1	Acid

[a] Chemical Abstract Services Registry Number.

2.0 SUMMARY OF METHOD

2.1 The solvent extract from a prior solvent extraction method is shaken with water that is strongly basic. The acid analytes partition into the aqueous layer, whereas, the basic and neutral compounds stay in the organic solvent. The base/neutral fraction is concentrated and is then ready for further cleanup, if necessary, or analysis. The aqueous layer is acidified and extracted with an organic solvent. This extract is concentrated and is then ready for analysis of the acid analytes.

3.0 INTERFERENCES

3.1 More extensive procedures than those outlined in this method may be necessary for reagent purification.

3.2 A method blank must be run for the compounds of interest prior to use of the method. The interferences must be below the method detection limit before this method is applied to actual samples.

4.0 APPARATUS AND MATERIALS

4.1 Drying column - 20 mm ID Pyrex chromatographic column with Pyrex glass wool at bottom, or equivalent.

NOTE: Fritted glass discs are difficult to clean after highly contaminated extracts have been passed through them. Columns without frits are recommended. 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.

4.2 Kuderna-Danish (K-D) apparatus (Kontes K-570025-0500 or equivalent).

4.2.1 Concentrator tube - 10 mL graduated (Kontes K570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of the extracts.

4.2.2 Evaporation flask - 500 mL (K-570001-0500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

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

4.2.4 Snyder column - Two ball micro (Kontes K569001-0219 or equivalent).

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

4.3 Vials - Glass, 2 mL capacity with Teflon lined screw-caps or crimp tops.

4.4 Water bath - Heated, concentric ring cover, temperature control of ± 2°C. Use this bath in a hood.

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

4.6 pH indicator paper - pH range including the desired extraction pH.

4.7 Separatory funnel - 125 mL.

4.8 Erlenmeyer flask - 125 mL.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, 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 hydroxide, NaOH, (10N) - Dissolve 40 g of sodium hydroxide in 100 mL of organic-free reagent water.

5.4 Sulfuric acid, H_2SO_4, (1:1 v/v in water) - Slowly add 50 mL H_2SO_4 to 50 mL of organic-free reagent water.

5.5 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. 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.

5.6 Solvents:

5.6.1 Methylene chloride, CH_2Cl_2 - Pesticide quality or equivalent.

5.6.2 Acetone, CH_3COCH_3 - Pesticide quality or equivalent.

5.6.3 Methanol, CH_3OH - Pesticide quality or equivalent.

5.6.4 Diethyl Ether, $C_2H_5OC_2H_5$ - Pesticide quality or equivalent. Must be free of peroxides as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Place 10 mL of the solvent extract from a prior extraction procedure into a 125 mL separatory funnel.

7.2 Add 20 mL of methylene chloride to the separatory funnel.

7.3 Slowly add 20 mL of prechilled organic-free reagent water which has been previously adjusted to a pH of 12-13 with 10N sodium hydroxide.

7.4 Seal and shake the separatory funnel for at least 2 minutes with periodic venting to release excess pressure.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel should be vented into a hood to prevent unnecessary exposure of the analyst to the organic vapor.

7.5 Allow the organic layer to separate from the aqueous phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.

7.6 Separate the aqueous phase and transfer it to a 125 mL Erlenmeyer flask. Repeat the extraction two more times using 20 mL aliquots of dilute sodium hydroxide (pH 12-13). Combine the aqueous extracts.

7.7 Water soluble organic acids and phenols will be primarily in the aqueous phase. Base/neutral analytes will be in the methylene chloride. If the analytes of interest are only in the aqueous phase, discard the methylene chloride and proceed to Section 7.8. If the analytes of interest are only in the methylene chloride, discard the aqueous phase and proceed to Section 7.10.

7.8 Externally cool the 125 mL Erlenmeyer flask with ice while adjusting the aqueous phase to a pH of 1-2 with sulfuric acid (1:1). Quantitatively transfer the cool aqueous phase to a clean 125 mL separatory funnel. Add 20 mL of methylene chloride to the separatory funnel and shake for at least 2 minutes. Allow the methylene chloride to separate from the aqueous phase and collect the methylene chloride in an Erlenmeyer flask.

7.9 Add 20 mL of methylene chloride to the separatory funnel and extract at pH 1-2 a second time. Perform a third extraction in the same manner combining the extracts in the Erlenmeyer flask.

7.10 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporation flask.

7.11 Dry both acid and base/neutral fractions by passing them through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried fractions in K-D concentrators. Rinse the Erlenmeyer flasks which contained the solvents and the columns with 20 mL of methylene chloride to complete the quantitative transfer.

7.12 Concentrate both acid and base/neutral fractions as follows: Add one or two boiling chips to the flask and attach a three ball macro-Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the warm water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 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 cool. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride. Concentrate the extract to the final volume using either the micro-Snyder column technique (7.12.1) or nitrogen blowdown technique (7.12.2).

7.12.1 Micro-Snyder Column Technique

7.12.1.1 Add another one or two boiling chips to the concentrator tube and attach a two ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride to the top of the column. Place the K-D apparatus in a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus 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 apparent volume of the liquid reaches 0.5 mL, remove the K-D apparatus and allow it to cool. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 0.2 mL of methylene chloride. Adjust the final volume to 1 mL with methylene chloride.

7.12.2 Nitrogen Blowdown Technique

7.12.2.1 Place the concentrator tube in a warm water bath (35°C) and evaporate the solvent volume to 1.0-2.0 mL 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.

7.12.2.2 The internal wall of the concentrator tube must be rinsed down several times with the appropriate solvent during the operation. During evaporation, the tube solvent level must be positioned to avoid condensation water. Under normal procedures, the extract must not be allowed to become dry.

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

7.13 The acid fraction is now ready for analysis. If the base/neutral fraction requires further cleanup by the alumina column cleanup for petroleum waste (Method 3611), the solvent may have to be changed to hexane. If a solvent exchange is required, momentarily remove the Snyder column, add approximately 5 mL of the exchange solvent and a new boiling chip, and reattach the Snyder column. Concentrate the extract as described in Section 7.12.1.1, raising the temperature of the water bath, if necessary, to maintain proper distillation. When the apparent volume again reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Repeat the exchange 2 more times. If no further cleanup of the base/neutral extract is required, it is also ready for analysis.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for general quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst must demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

8.3 For samples that are cleaned using this method, the associated quality control samples must be processed through this cleanup method.

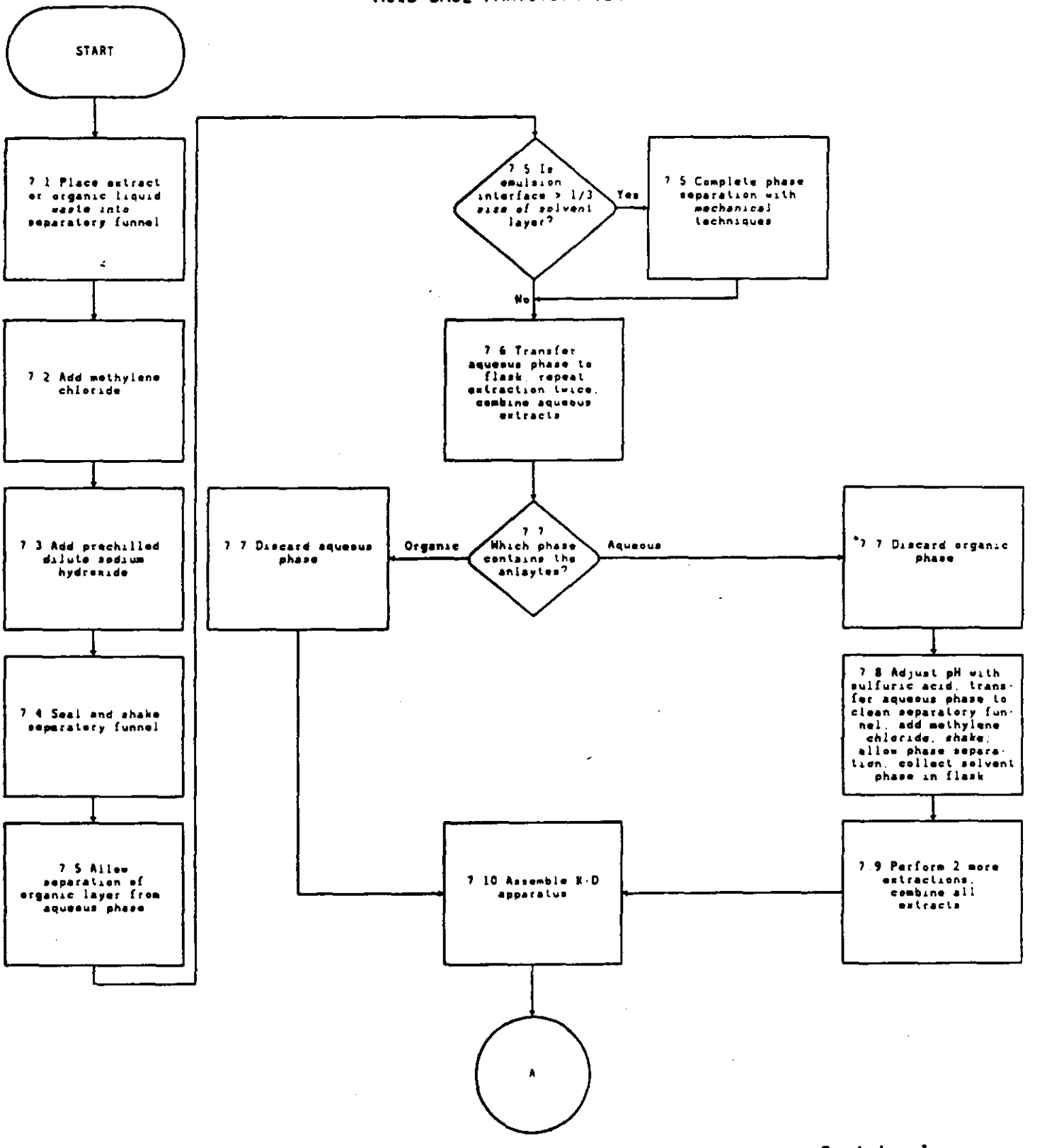
9.0 METHOD PERFORMANCE

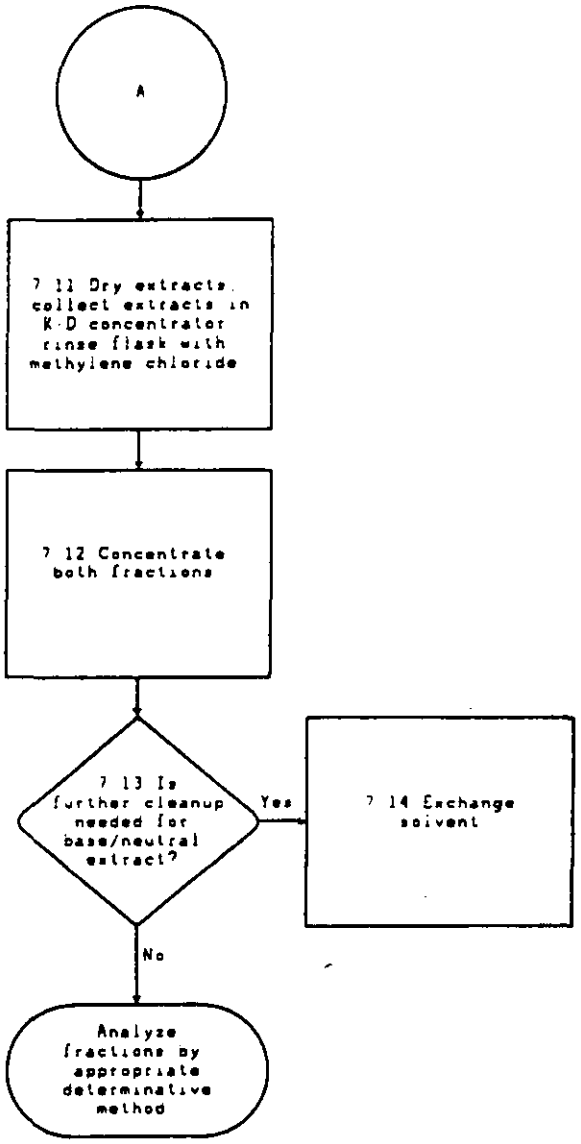
9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

1. Test Methods: Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1982; EPA-600/4-82-057.

METHOD 3650
ACID-BASE PARTITION CLEANUP




A
7.11 Dry extracts, collect extracts in K-D concentrator rinse flask with methylene chloride
7.12 Concentrate both fractions
7.13 Is further cleanup needed for base/neutral extract?
Yes
7.14 Exchange solvent
No
Analyze fractions by appropriate determinative method

SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS): CAPILLARY COLUMN TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 Method 8270 is used to determine the concentration of semivolatile organic compounds in extracts prepared from all types of solid waste matrices, soils, and ground water. Direct injection of a sample may be used in limited applications. *The following compounds can be determined by this method:*

		Appropriate Preparation Techniques				
Compounds	CAS No[a]	3510	3520	3540	3550	3580
Acenaphthene	83-32-9	X	X	X	X	X
Acenaphthene-d_{10} (I.S.)		X	X	X	X	X
Acenaphthylene	208-96-8	X	X	X	X	X
Acetophenone	98-86-2	X	ND	ND	ND	X
2-Acetylaminofluorene	53-96-3	X	ND	ND	ND	X
1-Acetyl-2-thiourea	591-08-2	LR	ND	ND	ND	LR
Aldrin	309-00-2	X	X	X	X	X
2-Aminoanthraquinone	117-79-3	X	ND	ND	ND	X
Aminoazobenzene	60-09-3	X	ND	ND	ND	X
4-Aminobiphenyl	92-67-1	X	ND	ND	ND	X
Anilazine	101-05-3	X	ND	ND	ND	X
Aniline	62-53-3	X	X	ND	X	X
o-Anisidine	90-04-0	X	ND	ND	ND	X
Anthracene	120-12-7	X	X	X	X	X
Aramite	140-57-8	HS(43)	ND	ND	ND	X
Aroclor - 1016	12674-11-2	X	X	X	X	X
Aroclor - 1221	11104-28-2	X	X	X	X	X
Aroclor - 1232	11141-16-5	X	X	X	X	X
Aroclor - 1242	53469-21-9	X	X	X	X	X
Aroclor - 1248	12672-29-6	X	X	X	X	X
Aroclor - 1254	11097-69-1	X	X	X	X	X
Aroclor - 1260	11096-82-5	X	X	X	X	X
Azinphos-methyl	86-50-0	HS(62)	ND	ND	ND	X
Barban	101-27-9	LR	ND	ND	ND	LR
Benzidine	92-87-5	CP	CP	CP	CP	CP
Benzoic acid	65-85-0	X	X	ND	X	X
Benz(a)anthracene	56-55-3	X	X	X	X	X
Benzo(b)fluoranthene	205-99-2	X	X	X	X	X
Benzo(k)fluoranthene	207-08-9	X	X	X	X	X
Benzo(g,h,i)perylene	191-24-2	X	X	X	X	X
Benzo(a)pyrene	50-32-8	X	X	X	X	X
p-Benzoquinone	106-51-4	OE	ND	ND	ND	X
Benzyl alcohol	100-51-6	X	X	ND	X	X

Compounds	CAS No[a]	Appropriate Preparation Techniques 3510	3520	3540	3550	3580
α-BHC	319-84-6	X	X	X	X	X
β-BHC	319-85-7	X	X	X	X	X
δ-BHC	319-86-8	X	X	X	X	X
γ-BHC (Lindane)	58-89-9	X	X	X	X	X
Bis(2-chloroethoxy)methane	111-91-1	X	X	X	X	X
Bis(2-chloroethyl) ether	111-44-4	X	X	X	X	X
Bis(2-chloroisopropyl) ether	108-60-1	X	X	X	X	X
Bis(2-ethylhexyl) phthalate	117-81-7	X	X	X	X	X
4-Bromophenyl phenyl ether	101-55-3	X	X	X	X	X
Bromoxynil	1689-84-5	X	ND	ND	ND	X
Butyl benzyl phthalate	85-68-7	X	X	X	X	X
Captafol	2425-06-1	HS(55)	ND	ND	ND	X
Captan	133-06-2	HS(40)	ND	ND	ND	X
Carbaryl	63-25-2	X	ND	ND	ND	X
Carbofuran	1563-66-2	X	ND	ND	ND	X
Carbophenothion	786-19-6	X	ND	ND	ND	X
Chlordane	57-74-9	X	X	X	X	X
Chlorfenvinphos	470-90-6	X	ND	ND	ND	X
4-Chloroaniline	106-47-8	X	ND	ND	ND	X
Chlorobenzilate	510-15-6	X	ND	ND	ND	X
5-Chloro-2-methylaniline	95-79-4	X	ND	ND	ND	X
4-Chloro-3-methylphenol	59-50-7	X	X	X	X	X
3-(Chloromethyl)pyridine hydrochloride	6959-48-4	X	ND	ND	ND	X
1-Chloronaphthalene	90-13-1	X	X	X	X	X
2-Chloronaphthalene	91-58-7	X	X	X	X	X
2-Chlorophenol	95-57-8	X	X	X	X	X
4-Chlorophenyl phenyl ether	7005-72-3	X	X	X	X	X
Chrysene	218-01-9	X	X	X	X	X
Chrysene-d_{12} (I.S.)		X	X	X	X	X
Coumaphos	56-72-4	X	ND	ND	ND	X
p-Cresidine	120-71-8	X	ND	ND	ND	X
Crotoxyphos	7700-17-6	X	ND	ND	ND	X
2-Cyclohexyl-4,6-dinitro-phenol	131-89-5	X	ND	ND	ND	LR
4,4'-DDD	72-54-8	X	X	X	X	X
4,4'-DDE	72-55-9	X	X	X	X	X
4,4'-DDT	50-29-3	X	X	X	X	X
Demeton-o	298-03-3	HS(68)	ND	ND	ND	X
Demeton-s	126-75-0	X	ND	ND	ND	X
Diallate (cis or trans)	2303-16-4	X	ND	ND	ND	X
2,4-Diaminotoluene	95-80-7	DC,OE(42)	ND	ND	ND	X
Dibenz(a,j)acridine	224-42-0	X	ND	ND	ND	X
Dibenz(a,h)anthracene	53-70-3	X	X	X	X	X
Dibenzofuran	132-64-9	X	X	ND	X	X
Dibenzo(a,e)pyrene	192-65-4	ND	ND	ND	ND	X
Di-n-butyl phthalate	84-74-2	X	X	X	X	X

Compounds	CAS No*	Appropriate Preparation Techniques 3510	3520	3540	3550	3580
Dichlone	117-80-6	OE	ND	ND	ND	X
1,2-Dichlorobenzene	95-50-1	X	X	X	X	X
1,3-Dichlorobenzene	541-73-1	X	X	X	X	X
1,4-Dichlorobenzene	106-46-7	X	X	X	X	X
1,4-Dichlorobenzene-d_4 (I.S)		X	X	X	X	X
3,3'-Dichlorobenzidine	91-94-1	X	X	X	X	X
2,4-Dichlorophenol	120-83-2	X	X	X	X	X
2,6-Dichlorophenol	87-65-0	X	ND	ND	ND	X
Dichlorovos	62-73-7	X	ND	ND	ND	X
Dicrotophos	141-66-2	X	ND	ND	ND	X
Dieldrin	60-57-1	X	X	X	X	X
Diethyl phthalate	84-66-2	X	X	X	X	X
Diethylstilbestrol	56-53-1	AW,OS(67)	ND	ND	ND	X
Diethyl sulfate	64-67-5	LR	ND	ND	ND	LR
Dimethoate	60-51-5	HE,HS(31)	ND	ND	ND	X
3,3'-Dimethoxybenzidine	119-90-4	X	ND	ND	ND	LR
Dimethylaminoazobenzene	60-11-7	X	ND	ND	ND	X
7,12-Dimethylbenz(a)-anthracene	57-97-6	CP(45)	ND	ND	ND	CP
3,3'-Dimethylbenzidine	119-93-7	X	ND	ND	ND	X
α,α-Dimethylphenethylamine	122-09-8	ND	ND	ND	ND	X
2,4-Dimethylphenol	105-67-9	X	X	X	X	X
Dimethyl phthalate	131-11-3	X	X	X	X	X
1,2-Dinitrobenzene	528-29-0	X	ND	ND	ND	X
1,3-Dinitrobenzene	99-65-0	X	ND	ND	ND	X
1,4-Dinitrobenzene	100-25-4	HE(14)	ND	ND	ND	X
4,6-Dinitro-2-methylphenol	534-52-1	X	X	X	X	X
2,4-Dinitrophenol	51-28-5	X	X	X	X	X
2,4-Dinitrotoluene	121-14-2	X	X	X	X	X
2,6-Dinitrotoluene	606-20-2	X	X	X	X	X
Dinocap	39300-45-3	CP,HS(28)	ND	ND	ND	CP
Dinoseb	88-85-7	X	ND	ND	ND	X
Diphenylamine	122-39-4	X	X	X	X	X
5,5-Diphenylhydantoin	57-41-0	X	ND	ND	ND	X
1,2-Diphenylhydrazine	122-66-7	X	X	X	X	X
Di-n-octyl phthalate	117-84-0	X	X	X	X	X
Disulfoton	298-04-4	X	ND	ND	ND	X
Endosulfan I	959-98-8	X	X	X	X	X
Endosulfan II	33213-65-9	X	X	X	X	X
Endosulfan sulfate	1031-07-8	X	X	X	X	X
Endrin	72-20-8	X	X	X	X	X
Endrin aldehyde	7421-93-4	X	X	X	X	X
Endrin ketone	53494-70-5	X	X	ND	X	X
EPN	2104-64-5	X	ND	ND	ND	X
Ethion	563-12-2	X	ND	ND	ND	X
Ethyl carbamate	51-79-6	DC(28)	ND	ND	ND	X

Compounds	CAS No[a]	Appropriate Preparation Techniques 3510	3520	3540	3550	3580
Ethyl methanesulfonate	62-50-0	X	ND	ND	ND	X
Famphur	52-85-7	X	ND	ND	ND	X
Fensulfothion	115-90-2	X	ND	ND	ND	X
Fenthion	55-38-9	X	ND	ND	ND	X
Fluchloralin	33245-39-5	X	ND	ND	ND	X
Fluoranthene	206-44-0	X	X	X	X	X
Fluorene	86-73-7	X	X	X	X	X
2-Fluorobiphenyl (surr.)	321-60-8	X	X	X	X	X
2-Fluorophenol (surr.)	367-12-4	X	X	X	X	X
Heptachlor	76-44-8	X	X	X	X	X
Heptachlor epoxide	1024-57-3	X	X	X	X	X
Hexachlorobenzene	118-74-1	X	X	X	X	X
Hexachlorobutadiene	87-68-3	X	X	X	X	X
Hexachlorocyclopentadiene	77-47-4	X	X	X	X	X
Hexachloroethane	67-72-1	X	X	X	X	X
Hexachlorophene	70-30-4	AW,CP(62)	ND	ND	ND	CP
Hexachloropropene	1888-71-7	X	ND	ND	ND	X
Hexamethyl phosphoramide	680-31-9	X	ND	ND	ND	X
Hydroquinone	123-31-9	ND	ND	ND	ND	X
Indeno(1,2,3-cd)pyrene	193-39-5	X	X	X	X	X
Isodrin	465-73-6	X	ND	ND	ND	X
Isophorone	78-59-1	X	X	X	X	X
Isosafrole	120-58-1	DC(46)	ND	ND	ND	X
Kepone	143-50-0	X	ND	ND	ND	X
Leptophos	21609-90-5	X	ND	ND	ND	X
Malathion	121-75-5	HS(5)	ND	ND	ND	X
Maleic anhydride	108-31-6	HE	ND	ND	ND	X
Mestranol	72-33-3	X	ND	ND	ND	X
Methapyrilene	91-80-5	X	ND	ND	ND	X
Methoxychlor	72-43-5	X	ND	ND	ND	X
3-Methylcholanthrene	56-49-5	X	ND	ND	ND	X
4,4'-Methylenebis(2-chloraniline)	101-14-4	OE,OS(0)	ND	ND	ND	LR
Methyl methanesulfonate	66-27-3	X	ND	ND	ND	X
2-Methylnaphthalene	91-57-6	X	X	ND	X	X
Methyl parathion	298-00-0	X	ND	ND	ND	X
2-Methylphenol	95-48-7	X	ND	ND	ND	X
3-Methylphenol	108-39-4	X	ND	ND	ND	X
4-Methylphenol	106-44-5	X	ND	ND	ND	X
Mevinphos	7786-34-7	X	ND	ND	ND	X
Mexacarbate	315-18-4	HE,HS(68)	ND	ND	ND	X
Mirex	2385-85-5	X	ND	ND	ND	X
Monocrotophos	6923-22-4	HE	ND	ND	ND	X
Naled	300-76-5	X	ND	ND	ND	X
Naphthalene	91-20-3	X	X	X	X	X
Naphthalene-d_8 (I.S.)		X	X	X	X	X
1,4-Naphthoquinone	130-15-4	X	ND	ND	ND	X
1-Naphthylamine	134-32-7	OS(44)	ND	ND	ND	X

Compounds	CAS No[a]	Appropriate Preparation Techniques				
		3510	3520	3540	3550	3580
2-Naphthylamine	91-59-8	X	ND	ND	ND	X
Nicotine	54-11-5	DE(67)	ND	ND	ND	X
5-Nitroacenaphthene	602-87-9	X	ND	ND	ND	X
2-Nitroaniline	88-74-4	X	X	ND	X	X
3-Nitroaniline	99-09-2	X	X	ND	X	X
4-Nitroaniline	100-01-6	X	X	ND	X	X
5-Nitro-o-anisidine	99-59-2	X	ND	ND	ND	X
Nitrobenzene	98-95-3	X	X	X	X	X
Nitrobenzene-d_5 (surr.)		X	X	X	X	X
4-Nitrobiphenyl	92-93-3	X	ND	ND	ND	X
Nitrofen	1836-75-5	X	ND	ND	ND	X
2-Nitrophenol	88-75-5	X	X	X	X	X
4-Nitrophenol	100-02-7	X	X	X	X	X
5-Nitro-o-toluidine	99-55-8	X	ND	ND	ND	X
Nitroquinoline-1-oxide	56-57-5	X	ND	ND	ND	X
N-Nitrosodibutylamine	924-16-3	X	ND	ND	ND	X
N-Nitrosodiethylamine	55-18-5	X	ND	ND	ND	X
N-Nitrosodimethylamine	62-75-9	X	X	X	X	X
N-Nitrosomethylethylamine	10595-95-6	X	ND	ND	ND	X
N-Nitrosodiphenylamine	86-30-6	X	X	X	X	X
N-Nitrosodi-n-propylamine	621-64-7	X	X	X	X	X
N-Nitrosomorpholine	59-89-2	ND	ND	ND	ND	X
N-Nitrosopiperidine	100-75-4	X	ND	ND	ND	X
N-Nitrosopyrrolidine	930-55-2	X	ND	ND	ND	X
Octamethyl pyrophosphoramide	152-16-9	LR	ND	ND	ND	LR
4,4'-Oxydianiline	101-80-4	X	ND	ND	ND	X
Parathion	56-38-2	X	ND	ND	ND	X
Pentachlorobenzene	608-93-5	X	ND	ND	ND	X
Pentachloronitrobenzene	82-68-8	X	ND	ND	ND	X
Pentachlorophenol	87-86-5	X	X	X	X	X
Perylene-d_{12} (I.S.)		X	X	X	X	X
Phenacetin	62-44-2	X	ND	ND	ND	X
Phenanthrene	85-01-8	X	X	X	X	X
Phenanthrene-d_{10} (I.S.)		X	X	X	X	X
Phenobarbital	50-06-6	X	ND	ND	ND	X
Phenol	108-95-2	DC(28)	X	X	X	X
Phenol-d_6 (surr.)		DC(28)	X	X	X	X
1,4-Phenylenediamine	106-50-3	X	ND	ND	ND	X
Phorate	298-02-2	X	ND	ND	ND	X
Phosalone	2310-17-0	HS(65)	ND	ND	ND	X
Phosmet	732-11-6	HS(15)	ND	ND	ND	X
Phosphamidon	13171-21-6	HE(63)	ND	ND	ND	X
Phthalic anhydride	85-44-9	CP,HE(1)	ND	ND	ND	CP
2-Picoline	109-06-8	ND	ND	ND	ND	ND
Piperonyl sulfoxide	120-62-7	X	ND	ND	ND	X
Pronamide	23950-58-5	X	ND	ND	ND	X
Propylthiouracil	51-52-5	LR	ND	ND	ND	LR

Compounds	CAS No[a]	Appropriate Preparation Techniques 3510	3520	3540	3550	3580
Pyrene	129-00-0	X	X	X	X	X
Pyridine	110-86-1	ND	ND	ND	ND	ND
Resorcinol	108-46-3	DC,OE(10)	ND	ND	ND	X
Safrole	94-59-7	X	ND	ND	ND	X
Strychnine	60-41-3	AW,OS(55)	ND	ND	ND	X
Sulfallate	95-06-7	X	ND	ND	ND	X
Terbufos	13071-79-9	X	ND	ND	ND	X
Terphenyl-d_{14}(surr.)		X	X	ND	X	X
1,2,4,5-Tetrachlorobenzene	95-94-3	X	ND	ND	ND	X
2,3,4,6-Tetrachlorophenol	58-90-2	X	ND	ND	ND	X
Tetrachlorvinphos	961-11-5	X	ND	ND	ND	X
Tetraethyl pyrophosphate	107-49-3	X	ND	ND	ND	X
Thionazine	297-97-2	X	ND	ND	ND	X
Thiophenol (Benzenethiol)	108-98-5	X	ND	ND	ND	X
Toluene diisocyanate	584-84-9	HE(6)	ND	ND	ND	X
o-Toluidine	95-53-4	X	ND	ND	ND	X
Toxaphene	8001-35-2	X	X	X	X	X
2,4,6-Tribromophenol (surr.)		X	X	X	X	X
1,2,4-Trichlorobenzene	120-82-1	X	X	X	X	X
2,4,5-Trichlorophenol	95-95-4	X	X	ND	X	X
2,4,6-Trichlorophenol	88-06-2	X	X	X	X	X
Trifluralin	1582-09-8	X	ND	ND	ND	X
2,4,5-Trimethylaniline	137-17-7	X	ND	ND	ND	X
Trimethyl phosphate	512-56-1	HE(60)	ND	ND	ND	X
1,3,5-Trinitrobenzene	99-35-4	X	ND	ND	ND	X
Tris(2,3-dibromopropyl) phosphate	126-72-7	X	ND	ND	ND	LR
Tri-p-tolyl phosphate	78-32-0	X	ND	ND	ND	X
0,0,0-Triethyl phosphorothioate	126-68-1	X	ND	ND	ND	X

a Chemical Abstract Service Registry Number.

AW = Adsorption to walls of glassware during extraction and storage.
CP = Nonreproducible chromatographic performance.
DC = Unfavorable distribution coefficient (number in parenthesis is percent recovery).
HE = Hydrolysis during extraction accelerated by acidic or basic conditions (number in parenthesis is percent recovery).
HS = Hydrolysis during storage (number in parenthesis is percent stability).
LR = Low response.
ND = Not determined.
OE = Oxidation during extraction accelerated by basic conditions (number in parenthesis is percent recovery).
OS = Oxidation during storage (number in parenthesis is percent stability).
X = Greater than 70 percent recovery by this technique.

Percent Stability = Average Recovery (Day 7) x 100/Average Recovery (Day 0).

1.2 Method 8270 can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. See Table 1 for a list of compounds and their characteristic ions that have been evaluated on the specified GC/MS system.

1.3 The following compounds may require special treatment when being determined by this method. Benzidine can be subject to oxidative losses during solvent concentration. Also, chromatography is poor. Under the alkaline conditions of the extraction step, α-BHC, γ-BHC, endosulfan I and II, and endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

1.4 The estimated quantitation limit (EQL) of Method 8270 for determining an individual compound is approximately 1 mg/Kg (wet weight) for soil/sediment samples, 1-200 mg/Kg for wastes (dependent on matrix and method of preparation), and 10 μg/L for ground water samples (see Table 2). EQLs will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Prior to using this method, the samples should be prepared for chromatography using the appropriate sample preparation and cleanup methods. This method describes chromatographic conditions that will allow for the separation of the compounds in the extract.

3.0 INTERFERENCES

3.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation

and/or cleanup of the samples and take corrective action to eliminate the problem.

3.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph/mass spectrometer system

4.1.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

4.1.2 Column - 30 m x 0.25 mm ID (or 0.32 mm ID) 1 μm film thickness silicone-coated fused-silica capillary column (J&W Scientific DB-5 or equivalent).

4.1.3 Mass spectrometer - Capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 3 when 1 μL of the GC/MS tuning standard is injected through the GC (50 ng of DFTPP).

4.1.4 GC/MS interface - Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria may be used.

4.1.5 Data system - A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

4.2 Syringe - 10 μL.

4.3 Volumetric flasks, Class A - 10 mL to 1000 mL.

4.4 Balance - Analytical, 0.0001 g.

4.5 Bottles - glass with Teflon-lined screw caps or crimp tops.

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 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 Stock standard solutions (1000 mg/L) - Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.3.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 10 mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.2 Transfer the stock standard solutions into bottles with Teflon lined screw-caps. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.3.3 Stock standard solutions must be replaced after 1 year or sooner if comparison with quality control check samples indicates a problem.

5.4 Internal standard solutions - The internal standards recommended are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}. Other compounds may be used as internal standards as long as the requirements given in Section 7.3.2 are met. Dissolve 0.200 g of each compound with a small volume of carbon disulfide. Transfer to a 50 mL volumetric flask and dilute to volume with methylene chloride so that the final solvent is approximately 20% carbon disulfide. Most of the compounds are also soluble in small volumes of methanol, acetone, or toluene, except for perylene-d_{12}. The resulting solution will contain each standard at a concentration of 4,000 ng/μL. Each 1 mL sample extract undergoing analysis should be spiked with 10 μL of the internal standard solution, resulting in a concentration of 40 ng/μL of each internal standard. Store at 4°C or less when not being used.

5.5 GC/MS tuning standard - A methylene chloride solution containing 50 ng/μL of decafluorotriphenylphosphine (DFTPP) should be prepared. The standard should also contain 50 ng/μL each of 4,4'-DDT, pentachlorophenol, and

benzidine to verify injection port inertness and GC column performance. Store at 4°C or less when not being used.

5.6 Calibration standards - A minimum of five calibration standards should be prepared. One of the calibration standards should be at a concentration near, but above, the method detection limit; the others should correspond to the range of concentrations found in real samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method (e.g. some or all of the compounds listed in Table 1 may be included). Each 1 mL aliquot of calibration standard should be spiked with 10 µL of the internal standard solution prior to analysis. All standards should be stored at -10°C to -20°C and should be freshly prepared once a year, or sooner if check standards indicate a problem. The daily calibration standard should be prepared weekly and stored at 4°C.

5.7 Surrogate standards - The recommended surrogate standards are phenol-d_6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d_5, 2-fluorobiphenyl, and p-terphenyl-d_{14}. See Method 3500 for the instructions on preparing the surrogate standards. Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards in all blanks, spikes, and sample extracts. Take into account all dilutions of sample extracts.

5.8 Matrix spike standards - See Method 3500 for instructions on preparing the matrix spike standard. Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards in all matrix spikes. Take into account all dilutions of sample extracts.

5.9 Acetone, hexane, methylene chloride, isooctane, carbon disulfide, toluene, and other appropriate solvents - Pesticide quality or equivalent

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Sample preparation - Samples must be prepared by one of the following methods prior to GC/MS analysis.

Matrix	Methods
Water	3510, 3520
Soil/sediment	3540, 3550
Waste	3540, 3550, 3580

7.1.1 Direct injection - In very limited applications direct injection of the sample into the GC/MS system with a 10 µL syringe may be appropriate. The detection limit is very high (approximately

10,000 µg/L); therefore, it is only permitted where concentrations in excess of 10,000 µg/L are expected. The system must be calibrated by direct injection.

7.2 Extract cleanup - Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

Compounds	Methods
Phenols	3630, 3640, 8040*
Phthalate esters	3610, 3620, 3640
Nitrosamines	3610, 3620, 3640
Organochlorine pesticides & PCBs	3620, 3660
Nitroaromatics and cyclic ketones	3620, 3640
Polynuclear aromatic hydrocarbons	3611, 3630, 3640
Haloethers	3620, 3640
Chlorinated hydrocarbons	3620, 3640
Organophosphorus pesticides	3620
Petroleum waste	3611, 3650
All priority pollutant base, neutral, and acids	3640

*Method 8040 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered on GC/FID.

7.3 Initial calibration - The recommended GC/MS operating conditions:

Mass range:	35-500 amu
Scan time:	1 sec/scan
Initial temperature:	40°C, hold for 4 minutes
Temperature program:	40-270°C at 10°C/min
Final temperature:	270°C, hold until benzo[g,h,i]perylene has eluted
Injector temperature:	250-300°C
Transfer line temperature:	250-300°C
Source temperature:	According to manufacturer's specifications
Injector:	Grob-type, splitless
Sample volume:	1-2 µL
Carrier gas:	Hydrogen at 50 cm/sec or helium at 30 cm/sec

7.3.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 3 for a 50 ng injection of DFTPP. Analyses should not begin until all these criteria are met. Background subtraction should be straightforward and designed only to eliminate column bleed or instrument background ions. The GC/MS tuning standard should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD should not exceed 20%. Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible. If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning. It may also be necessary to break off the first 6-12 in. of the capillary column.

7.3.2 The internal standards selected in Section 5.1 should permit most of the components of interest in a chromatogram to have retention

times of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 1). If interferences are noted, use the next most intense ion as the quantitation ion (i.e. for 1,4-dichlorobenzene-d_4 use m/z 152 for quantitation).

7.3.3 Analyze 1 μL of each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each compound (as indicated in Table 1). Figure 1 shows a chromatogram of a calibration standard containing base/neutral and acid analytes. Calculate response factors (RFs) for each compound as follows:

$$RF = (A_x C_{is})/(A_{is} C_x)$$

where:

A_x = Area of the characteristic ion for the compound being measured.

A_{is} = Area of the characteristic ion for the specific internal standard.

C_{is} = Concentration of the specific internal standard (ng/μL).

C_x = Concentration of the compound being measured (ng/μL).

7.3.4 The average RF should be calculated for each compound. The percent relative standard deviation (%RSD = 100[SD/RF]) should also be calculated for each compound. The %RSD should be less than 30% for each compound. However, the %RSD for each individual Calibration Check Compound (CCC) (see Table 4) must be less than 30%. The relative retention times of each compound in each calibration run should agree within 0.06 relative retention time units. Late-eluting compounds usually have much better agreement.

7.3.5 A system performance check must be performed to ensure that minimum average RFs are met before the calibration curve is used. For semivolatiles, the System Performance Check Compounds (SPCCs) are: N-nitroso-di-n-propylamine; hexachlorocyclopentadiene; 2,4-dinitro-phenol; and 4-nitrophenol. The minimum acceptable average RF for these compounds SPCCs is 0.050. These SPCCs typically have very low RFs (0.1-0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

7.4 Daily GC/MS calibration

7.4.1 Prior to analysis of samples, the GC/MS tuning standard must be analyzed. A 50 ng injection of DFTPP must result in a mass spectrum for DFTPP which meets the criteria given in Table 3. These criteria must be demonstrated during each 12 hour shift.

7.4.2 A calibration standard(s) at mid-concentration, containing each compound of interest, including all required surrogates, must be performed every 12 hours during analysis. Compare the response factor data from the standards every 12 hours with the average response factor from the initial calibration for a specific instrument as per the SPCC (Section 7.4.3) and CCC (Section 7.4.4) criteria.

7.4.3 System Performance Check Compounds (SPCCs): A system performance check must be made during every 12 hour shift. If the SPCC criteria are met, a comparison of response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. The minimum RF for semivolatile SPCCs is 0.050. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before analysis begins.

7.4.4 Calibration Check Compounds (CCCs): After the system performance check is met, CCCs listed in Table 4 are used to check the validity of the initial calibration. Calculate the percent difference using:

$$\% \text{ Difference} = \frac{\overline{RF_i} - RF_c}{\overline{RF_i}} \times 100$$

where:

$\overline{RF_i}$ = Average response factor from initial calibration.
RF_c = Response factor from current verification check standard.

If the percent difference for any compound is greater than 20, the laboratory should consider this a warning limit. If the percent difference for each CCC is less than 30%, the initial calibration is assumed to be valid. If the criterion is not met (> 30% difference) for any one CCC, corrective action must be taken. Problems similar to those listed under SPCCs could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration must be generated. This criterion must be met before sample analysis begins.

7.4.5 The internal standard responses and retention times in the calibration check standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the last check calibration (12 hours), the chromatographic system must be inspected for malfunctions and corrections must be made, as required. If the EICP area for any of the internal standards changes by a factor of two (-50% to +100%) from the last daily calibration standard check, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate.

7.5 GC/MS analysis

7.5.1 It is highly recommended that the extract be screened on a GC/FID or GC/PID using the same type of capillary column. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

7.5.2 Spike the 1 mL extract obtained from sample preparation with 10 µL of the internal standard solution just prior to analysis.

7.5.3 Analyze the 1 mL extract by GC/MS using a 30 m x 0.25 mm (or 0.32 mm) silicone-coated fused-silica capillary column. The volume to be injected should ideally contain 100 ng of base/neutral and 200 ng of acid surrogates (for a 1 µL injection). The recommended GC/MS operating conditions to be used are specified in Section 7.3.

7.5.4 If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution must take place. Additional internal standard must be added to the diluted extract to maintain the required 40 ng/µL of each internal standard in the extracted volume. The diluted extract must be reanalyzed.

7.5.5 Perform all qualitative and quantitative measurements as described in Section 7.6. Store the extracts at 4°C, protected from light in screw-cap vials equipped with unpierced Teflon lined septa.

7.6 Data interpretation

7.6.1 Qualitative analysis

7.6.1.1 An analyte (e.g. those listed in Table 1) is identified by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference should be obtained on the user's GC/MS within the same 12 hours as the sample analysis. These standard reference spectra may be obtained through analysis of the calibration standards. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC relative retention time (RRT) as the standard component; and (2) correspondence of the sample component and the standard component mass spectrum.

7.6.1.1.1 The sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run within the same 12 hours as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

7.6.1.1.2 All ions present in the standard mass spectrum at a relative intensity greater than 10% (most abundant ion

in the spectrum equals 100% must be present in the sample spectrum.

7.6.1.1.3 The relative intensities of ions specified in Section 7.6.1.1.2 must agree within plus or minus 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample abundance must be between 30 and 70 percent.)

7.6.1.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. For example, the RCRA permit or waste delisting requirements may require the reporting of nontarget analytes. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%.)

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

7.6.2 Quantitative analysis

7.6.2.1 When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte (e.g. see Table 5).

7.6.2.2 Calculate the concentration of each identified analyte in the sample as follows:

Water

$$\text{concentration } (\mu g/L) = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_o)(V_i)}$$

where:

A_x = Area of characteristic ion for compound being measured.
I_s = Amount of internal standard injected (ng).
V_t = Volume of total extract, taking into account dilutions (i.e. a 1-to-10 dilution of a 1 mL extract will mean V_t = 10,000 μL. If half the base/neutral extract and half the acid extract are combined, V_t = 2,000).
A_{is} = Area of characteristic ion for the internal standard.
RF = Response factor for compound being measured (Section 7.3.3).
V_o = Volume of water extracted (mL).
V_i = Volume of extract injected (μL).

Sediment/Soil Sludge (on a dry-weight basis) and Waste (normally on a wet-weight basis

$$\text{concentration } (\mu g/Kg) = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_i)(W_s)(D)}$$

where:

A_x, I_s, V_t, A_{is}, RF, V_i = Same as for water.
W_s = Weight of sample extracted or diluted in grams.
D = % dry weight of sample/100, or 1 for a wet-weight basis.

7.6.2.3 Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formulas given above should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.6.2.5 Quantitation of multicomponent compounds (e.g. Aroclors) is beyond the scope of Method 8270. Normally, quantitation is performed using a GC/ECD by Method 8080.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures.

8.2 Required instrument QC is found in the following sections:

8.2.1 The GC/MS system must be tuned to meet the DFTPP specifications in Sections 7.3.1 and 7.4.1.

8.2.2 There must be an initial calibration of the GC/MS system as specified in Section 7.3.

8.2.3 The GC/MS system must meet the SPCC criteria specified in Section 7.4.3 and the CCC criteria in Section 7.4.4, each 12 hours.

8.3 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.3.1 A quality control (QC) reference sample concentrate is required containing each analyte at a concentration of 100 mg/L in methanol. The QC reference sample concentrate may be prepared from pure standard materials or purchased as certified solutions. If prepared by the laboratory, the QC reference sample concentrate must be made using stock standards prepared independently from those used for calibration.

8.3.2 Using a pipet, prepare QC reference samples at a concentration of 100 µg/L by adding 1.00 mL of QC reference sample concentrate to each of four 1 L aliquots of organic-free reagent water.

8.3.3 Analyze the well-mixed QC reference samples according to the method beginning in Section 7.1 with extraction of the samples.

8.3.4 Calculate the average recovery ($\bar{x}$) in µg/L, and the standard deviation of the recovery (s) in µg/L, for each analyte of interest using the four results.

8.3.5 For each analyte, compare s and $\bar{x}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 6. If s and $\bar{x}$ for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{x}$ falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

NOTE: The large number of analytes in Table 6 present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes of a given method are determined.

8.3.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.3.6.1 or 8.3.6.2.

8.3.6.1 Locate and correct the source of the problem and repeat the test for all analytes beginning with Section 8.3.2.

8.3.6.2 Beginning with Section 8.3.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.3.2.

8.4 For aqueous and soil matrices, laboratory established surrogate control limits should be compared with the control limits listed in Table 8. The limits given in Table 8 are multilaboratory performance based limits for soil and aqueous samples, and therefore, the single laboratory limits must fall within those given in Table 8 for these matrices.

8.4.1 If recovery is not within limits, the following procedures are required.

8.4.1.1 Check to be sure that there are no errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly.

8.4.1.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the extract.

8.4.1.3 If no problem is found, re-extract and re-analyze the sample.

8.4.1.4 If, upon re-analysis, the recovery is again not within limits, flag the data as "estimated concentration".

8.4.2 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

9.0 METHOD PERFORMANCE

9.1 Method 8250 (the packed column version of Method 8270) was tested by 15 laboratories using Organic-free reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5-1,300 µg/L. Single operator accuracy and precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 7. Method performance data for Method 8270 is being developed.

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, Method 625," October 26, 1984.

2. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, July 1985, Revision.

3. Eichelberger, J.W., L.E. Harris, and W.L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems," Analytical Chemistry, 47, 995-1000, 1975.

4. "Method Detection Limit for Methods 624 and 625," Olynyk, P., W.L. Budde, and J.W. Eichelberger, Unpublished report, October 1980.

5. "Interlaboratory Method Study for EPA Method 625-Base/Neutrals, Acids, and Pesticides," Final Report for EPA Contract 68-03-3102 (in preparation).

6. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

7. Lucas, S.V.; Kornfeld, R.A. "GC-MS Suitability Testing of RCRA Appendix VIII and Michigan List Analytes "; U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, February 20, 1987, Contract No. 68-03-3224.

8. Engel, T.M.; Kornfeld, R.A.; Warner, J.S.; Andrews, K.D. "Screening of Semivolatile Organic Compounds for Extractability and Aqueous Stability by SW-846, Method 3510"; U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, June 5, 1987, Contract 68-03-3224.

TABLE 1.
CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS

Compound	Retention Time (min.)	Primary Ion	Secondary Ion(s)
2-Picoline	3.75[a]	93	66,92
Aniline	5.68	93	66,65
Phenol	5.77	94	65,66
Bis(2-chloroethyl) ether	5.82	93	63,95
2-Chlorophenol	5.97	128	64,130
1,3-Dichlorobenzene	6.27	146	148,111
1,4-Dichlorobenzene-d_4 (I.S.)	6.35	152	150,115
1,4-Dichlorobenzene	6.40	146	148,111
Benzyl alcohol	6.78	108	79,77
1,2-Dichlorobenzene	6.85	146	148,111
N-Nitrosomethylethylamine	6.97	88	42,88,43,56
Bis(2-chloroisopropyl) ether	7.22	45	77,121
Ethyl carbamate	7.27	62	62,44,45,74
Thiophenol (Benzenethiol)	7.42	110	110,66,109,84
Methyl methanesulfonate	7.48	80	80,79,65,95
N-Nitrosodi-n-propylamine	7.55	70	42,101,130
Hexachloroethane	7.65	117	201,199
Maleic anhydride	7.65	54	54,98,53,44
Nitrobenzene	7.87	77	123,65
Isophorone	8.53	82	95,138
N-Nitrosodiethylamine	8.70	102	102,42,57,44,56
2-Nitrophenol	8.75	139	109,65
2,4-Dimethylphenol	9.03	122	107,121
p-Benzoquinone	9.13	108	54,108,82,80
Bis(2-chloroethoxy)methane	9.23	93	95,123
Benzoic acid	9.38	122	105,77
2,4-Dichlorophenol	9.48	162	164,98
Trimethyl phosphate	9.53	110	110,79,95,109,140
Ethyl methanesulfonate	9.62	79	79,109,97,45,65
1,2,4-Trichlorobenzene	9.67	180	182,145
Naphthalene-d_8 (I.S.)	9.75	136	68
Naphthalene	9.82	128	129,127
Hexachlorobutadiene	10.43	225	223,227
Tetraethyl pyrophosphate	11.07	99	99,155,127,81,109
Diethyl sulfate	11.37	139	139,45,59,99,111,125
4-Chloro-3-methylphenol	11.68	107	144,142
2-Methylnaphthalene	11.87	142	141
2-Methylphenol	12.40	107	107,108,77,79,90
Hexachloropropene	12.45	213	213,211,215,117,106,141
Hexachlorocyclopentadiene	12.60	237	235,272
N-Nitrosopyrrolidine	12.65	100	100,41,42,68,69
Acetophenone	12.67	105	71,105,51,120
4-Methylphenol	12.82	107	107,108,77,79,90
2,4,6-Trichlorophenol	12.85	196	198,200
o-Toluidine	12.87	106	106,107,77,51,79
3-Methylphenol	12.93	107	107,108,77,79,90
2-Chloronaphthalene	13.30	162	127,164

TABLE 1.
(Continued)

Compound	Retention Time (min.)	Primary Ion	Secondary Ion(s)
N-Nitrosopiperidine	13.55	114	42,114,55,56,41
1,4-Phenylenediamine	13.62	108	108,80,53,54,52
1-Chloronaphthalene	13.65[a]	162	127,164
2-Nitroaniline	13.75	65	92,138
5-Chloro-2-methylaniline	14.28	106	106,141,140,77,89
Dimethyl phthalate	14.48	163	194,164
Acenaphthylene	14.57	152	151,153
2,6-Dinitrotoluene	14.62	165	63,89
Phthalic anhydride	14.62	104	104,76,50,148
o-Anisidine	15.00	108	80,108,123,52
3-Nitroaniline	15.02	138	108,92
Acenaphthene-d_{10} (I.S.)	15.05	164	162,160
Acenaphthene	15.13	154	153,152
2,4-Dinitrophenol	15.35	184	63,154
2,6-Dinitrophenol	15.47	162	162,164,126,98,63
4-Chloroaniline	15.50	127	127,129,65,92
Isosafrole	15.60	162	162,131,104,77,51
Dibenzofuran	15.63	168	139
2,4-Diaminotoluene	15.78	121	121,122,94,77,104
2,4-Dinitrotoluene	15.80	165	63,89
4-Nitrophenol	15.80	139	109,65
2-Naphthylamine	16.00[a]	143	115,116
1,4-Naphthoquinone	16.23	158	158,104,102,76,50,130
p-Cresidine	16.45	122	122,94,137,77,93
Dichlorovos	16.48	109	109,185,79,145
Diethyl phthalate	16.70	149	177,150
Fluorene	16.70	166	165,167
2,4,5-Trimethylaniline	16.70	120	120,135,134,91,77
N-Nitrosodibutylamine	16.73	84	84,57,41,116,158
4-Chlorophenyl phenyl ether	16.78	204	206,141
Hydroquinone	16.93	110	110,81,53,55
4,6-Dinitro-2-methylphenol	17.05	198	51,105
Resorcinol	17.13	110	110,81,82,53,69
N-Nitrosodiphenylamine	17.17	169	168,167
Safrole	17.23	162	162,162,104,77,103,135
Hexamethyl phosphoramide	17.33	135	135,44,179,92,42
3-(Chloromethyl)pyridine hydrochloride	17.50	92	92,127,129,65,39
Diphenylamine	17.54[a]	169	168,167
1,2,4,5-Tetrachlorobenzene	17.97	216	216,214,179,108,143,218
1-Naphthylamine	18.20	143	143,115,89,63
1-Acetyl-2-thiourea	18.22	118	43,118,42,76
4-Bromophenyl phenyl ether	18.27	248	250,141
Toluene diisocyanate	18.42	174	174,145,173,146,132,91
2,4,5-Trichlorophenol	18.47	196	196,198,97,132,99
Hexachlorobenzene	18.65	284	142,249
Nicotine	18.70	84	84,133,161,162
Pentachlorophenol	19.25	266	264,268

TABLE 1.
(Continued)

Compound	Retention Time (min.)	Primary Ion	Secondary Ion(s)
5-Nitro-o-toluidine	19.27	152	77,152,79,106,94
Thionazine	19.35	107	96,107,97,143,79,68
4-Nitroaniline	19.37	138	138,65,108,92,80,39
Phenanthrene-d_{10}(i.s.)	19.55	188	94,80
Phenanthrene	19.62	178	179,176
Anthracene	19.77	178	176,179
1,4-Dinitrobenzene	19.83	168	168,75,50,76,92,122
Mevinphos	19.90	127	127,192,109,67,164
Naled	20.03	109	109,145,147,301,79,189
1,3-Dinitrobenzene	20.18	168	168,76,50,75,92,122
Diallate (cis or trans)	20.57	86	86,234,43,70
1,2-Dinitrobenzene	20.58	168	168,50,63,74
Diallate (trans or cis)	20.78	86	86,234,43,70
Pentachlorobenzene	21.35	250	250,252,108,248,215,254
5-Nitro-o-anisidine	21.50	168	168,79,52,138,153,77
Pentachloronitrobenzene	21.72	237	237,142,214,249,295,265
4-Nitroquinoline-1-oxide	21.73	174	174,101,128,75,116
Di-n-butyl phthalate	21.78	149	150,104
2,3,4,6-Tetrachlorophenol	21.88	232	232,131,230,166,234,168
Demeton-o	22.72	88	88,89,60,61,115,171
Fluoranthene	23.33	202	101,203
1,3,5-Trinitrobenzene	23.68	75	75,74,213,120,91,63
Dicrotophos	23.82	127	127,67,72,109,193,237
Benzidine	23.87	184	92,185
Trifluralin	23.88	306	306,43,264,41,290
Bromoxynil	23.90	277	277,279,88,275,168
Pyrene	24.02	202	200,203
Monocrotophos	24.08	127	127,192,67,97,109
Phorate	24.10	75	75,121,97,93,260
Sulfallate	24.23	188	188,88,72,60,44
Demeton-s	24.30	88	88,60,81,89,114,115
Phenacetin	24.33	108	180,179,109,137,80
Dimethoate	24.70	87	87,93,125,143,229
Phenobarbital	24.70	204	204,117,232,146,161
Carbofuran	24.90	164	164,149,131,122
Octamethyl pyrophosphoramide	24.95	135	135,44,199,286,153,243
4-Aminobiphenyl	25.08	169	169,168,170,115
Terbufos	25.35	231	231,57,97,153,103
a,a-Dimethylphenylamine	25.43	58	58,91,65,134,42
Pronamide	25.48	173	173,175,145,109,147
Aminoazobenzene	25.72	197	92,197,120,65,77
Dichlone	25.77	191	191,163,226,228,135,193
Dinoseb	25.83	211	211,163,147,117,240
Disulfoton	25.83	88	88,97,89,142,186
Fluchloralin	25.88	306	306,63,326,328,264,65
Mexacarbate	26.02	165	165,150,134,164,222
4,4'-Oxydianiline	26.08	200	200,108,171,80,65

TABLE 1.
(Continued)

Compound	Retention Time (min.)	Primary Ion	Secondary Ion(s)
Butyl benzyl phthalate	26.43	149	91,206
4-Nitrobiphenyl	26.55	199	199,152,141,169,151
Phosphamidon	26.85	127	127,264,72,109,138
2-Cyclohexyl-4,6-Dinitrophenol	26.87	231	231,185,41,193,266
Methyl parathion	27.03	109	109,125,263,79,93
Carbaryl	27.17	144	144,115,116,201
Dimethylaminoazobenzene	27.50	225	225,120,77,105,148,42
Propylthiouracil	27.68	170	170,142,114,83
Benz(a)anthracene	27.83	228	229,226
Chrysene-d_{12} (I.S.)	27.88	240	120,236
3,3'-Dichlorobenzidine	27.88	252	254,126
Chrysene	27.97	228	226,229
Malathion	28.08	173	173,125,127,93,158
Kepone	28.18	272	272,274,237,178,143,270
Fenthion	28.37	278	278,125,109,169,153
Parathion	28.40	109	109,97,291,139,155
Anilazine	28.47	239	239,241,143,178,89
Bis(2-ethylhexyl) phthalate	28.47	149	167,279
3,3'-Dimethylbenzidine	28.55	212	212,106,196,180
Carbophenothion	28.58	157	157,97,121,342,159,199
5-Nitroacenaphthene	28.73	199	199,152,169,141,115
Methapyrilene	28.77	97	97,50,191,71
Isodrin	28.95	193	193,66,195,263,265,147
Captan	29.47	79	79,149,77,119,117
Chlorfenvinphos	29.53	267	267,269,323,325,295
Crotoxyphos	29.73	127	127,105,193,166
Phosmet	30.03	160	160,77,93,317,76
EPN	30.11	157	157,169,185,141,323
Tetrachlorvinphos	30.27	329	109,329,331,79,333
Di-n-octyl phthalate	30.48	149	167,43
2-Aminoanthraquinone	30.63	223	223,167,195
Barban	30.83	222	222,51,87,224,257,153
Aramite	30.92	185	185,191,319,334,197,321
Benzo(b)fluoranthene	31.45	252	253,125
Nitrofen	31.48	283	283,285,202,139,253
Benzo(k)fluoranthene	31.55	252	253,125
Chlorobenzilate	31.77	251	251,139,253,111,141
Fensulfothion	31.87	293	293,97,308,125,292
Ethion	32.08	231	231,97,153,125,121
Diethylstilbestrol	32.15	268	268,145,107,239,121,159
Famphur	32.67	218	218,125,93,109,217
Tri-p-tolyl phosphate[b]	32.75	368	368,367,107,165,198
Benzo(a)pyrene	32.80	252	253,125
Perylene-d_{12} (I.S.)	33.05	264	260,265
7,12-Dimethylbenz(a)anthracene	33.25	256	256,241,239,120
5,5-Diphenylhydantoin	33.40	180	180,104,252,223,209
Captafol	33.47	79	79,77,80,107

TABLE 1.
(Continued)

Compound	Retention Time (min.)	Primary Ion	Secondary Ion(s)
Dinocap	33.47	69	69,41,39
Methoxychlor	33.55	227	227,228,152,114,274,212
2-Acetylaminofluorene	33.58	181	181,180,223,152
4,4'-Methylenebis(2-chloroaniline)	34.38	231	231,266,268,140,195
3,3'-Dimethoxybenzidine	34.47	244	244,201,229
3-Methylcholanthrene	35.07	268	268,252,253,126,134,113
Phosalone	35.23	182	182,184,367,121,379
Azinphos-methyl	35.25	160	160,132,93,104,105
Leptophos	35.28	171	171,377,375,77,155,379
Mirex	35.43	272	272,237,274,270,239,235
Tris(2,3-dibromopropyl) phosphate	35.68	201	137,201,119,217,219,199
Dibenz(a,j)acridine	36.40	279	279,280,277,250
Mestranol	36.48	277	277,310,174,147,242
Coumaphos	37.08	362	362,226,210,364,97,109
Indeno(1,2,3-cd)pyrene	39.52	276	138,227
Dibenz(a,h)anthracene	39.82	278	139,279
Benzo(g,h,i)perylene	41.43	276	138,277
1,2:4,5-Dibenzopyrene	41.60	302	302,151,150,300
Strychnine	45.15	334	334,335,333
Piperonyl sulfoxide	46.43	162	162,135,105,77
Hexachlorophene	47.98	196	196,198,209,211,406,408
Aldrin	--	66	263,220
Aroclor-1016	--	222	260,292
Aroclor-1221	--	190	224,260
Aroclor-1232	--	190	224,260
Aroclor-1242	--	222	256,292
Aroclor-1248	--	292	362,326
Aroclor-1254	--	292	362,326
Aroclor-1260	--	360	362,394
α-BHC	--	183	181,109
β-BHC	--	181	183,109
δ-BHC	--	183	181,109
γ-BHC (Lindane)	--	183	181,109
4,4'-DDD	--	235	237,165
4,4'-DDE	--	246	248,176
4,4'-DDT	--	235	237,165
Dieldrin	--	79	263,279
1,2-Diphenylhydrazine	--	77	105,182
Endosulfan I	--	195	339,341
Endosulfan II	--	337	339,341
Endosulfan sulfate	--	272	387,422
Endrin	--	263	82,81
Endrin aldehyde	--	67	345,250
Endrin ketone	--	317	67,319
2-Fluorobiphenyl (surr.)	--	172	171
2-Fluorophenol (surr.)	--	112	64

TABLE 1.
(Continued)

Compound	Retention Time (min.)	Primary Ion	Secondary Ion(s)
Heptachlor	--	100	272,274
Heptachlor epoxide	--	353	355,351
Nitrobenzene-d_5 (surr.)	--	82	128,54
N-Nitrosodimethylamine	--	42	74,44
Phenol-d_6 (surr.)	--	99	42,71
Terphenyl-d_{14} (surr.)	--	244	122,212
2,4,6-Tribromophenol (surr.)	--	330	332,141
Toxaphene	--	159	231,233

I.S. = internal standard.
surr. = surrogate.
[a]Estimated retention times.
[b]Substitute for the non-specific mixture, tricresyl phosphate.

TABLE 2.
ESTIMATED QUANTITATION LIMITS (EQLs) FOR SEMIVOLATILE ORGANICS[a]

Semivolatiles	Estimated Quantitation Limits[b] Ground water µg/L	Low Soil/Sediment[c] µg/Kg
Acenaphthene	10	660
Acenaphthylene	10	660
Acetophenone	10	ND
2-Acetylaminofluorene	20	ND
1-Acetyl-2-thiourea	1000	ND
2-Aminoanthraquinone	20	ND
Aminoazobenzene	10	ND
4-Aminobiphenyl	20	ND
Anilazine	100	ND
o-Anisidine	10	ND
Anthracene	10	660
Aramite	20	ND
Azinphos-methyl	100	ND
Barban	200	ND
Benz(a)anthracene	10	660
Benzo(b)fluoranthene	10	660
Benzo(k)fluoranthene	10	660
Benzoic acid	50	3300
Benzo(g,h,i)perylene	10	660
Benzo(a)pyrene	10	660
p-Benzoquinone	10	ND
Benzyl alcohol	20	1300
Bis(2-chloroethoxy)methane	10	660
Bis(2-chloroethyl) ether	10	660
Bis(2-chloroisopropyl) ether	10	660
4-bromophenyl phenyl ether	10	660
Bromoxynil	10	ND
Butyl benzyl phthalate	10	660
Captafol	20	ND
Captan	50	ND
Carbaryl	10	ND
Carbofuran	10	ND
Carbophenothion	10	ND
Chlorfenvinphos	20	ND
4-Chloroaniline	20	1300
Chlorobenzilate	10	ND
5-Chloro-2-methylaniline	10	ND
4-Chloro-3-methylphenol	20	1300
3-(Chloromethyl)pyridine hydrochloride	100	ND
2-Chloronaphthalene	10	660
2-Chlorophenol	10	660
4-Chlorophenyl phenyl ether	10	660
Chrysene	10	660
Coumaphos	40	ND

TABLE 2.
(Continued)

Semivolatiles	Estimated Quantitation Limits[b] Ground water µg/L	Low Soil/Sediment[1] µg/Kg
p-Cresidine	10	ND
Crotoxyphos	20	ND
2-Cyclohexyl-4,6-dinitrophenol	100	ND
Demeton-o	10	ND
Demeton-s	10	ND
Diallate (cis or trans)	10	ND
Diallate (trans or cis)	10	ND
2,4-Diaminotoluene	20	ND
Dibenz(a,j)acridine	10	ND
Dibenz(a,h)anthracene	10	660
Dibenzofuran	10	660
Dibenzo(a,e)pyrene	10	ND
Di-n-butyl phthalate	10	ND
Dichlone	NA	ND
1,2-Dichlorobenzene	10	660
1,3-Dichlorobenzene	10	660
1,4-Dichlorobenzene	10	660
3,3'-Dichlorobenzidine	20	1300
2,4-Dichlorophenol	10	660
2,6-Dichlorophenol	10	ND
Dichlorovos	10	ND
Dicrotophos	10	ND
Diethyl phthalate	10	660
Diethylstilbestrol	20	ND
Diethyl sulfate	100	ND
Dimethoate	20	ND
3,3'-Dimethoxybenzidine	100	ND
Dimethylaminoazobenzene	10	ND
7,12-Dimethylbenz(a)anthracene	10	ND
3,3'-Dimethylbenzidine	10	ND
a,a-Dimethylphenethylamine	ND	ND
2,4-Dimethylphenol	10	660
Dimethyl phthalate	10	660
1,2-Dinitrobenzene	40	ND
1,3-Dinitrobenzene	20	ND
1,4-Dinitrobenzene	40	ND
4,6-Dinitro-2-methylphenol	50	3300
2,4-Dinitrophenol	50	3300
2,4-Dinitrotoluene	10	660
2,6-Dinitrotoluene	10	660
Dinocap	100	ND
Dinoseb	20	ND
5,5-Diphenylhydantoin	20	ND
Di-n-octyl phthalate	10	660

TABLE 2.
(Continued)

Semivolatiles	Estimated Quantitation Limits[b] Ground water µg/L	Low Soil/Sediment[c] µg/Kg
Disulfoton	10	ND
EPN	10	ND
Ethion	10	ND
Ethyl carbamate	50	ND
Bis(2-ethylhexyl) phthalate	10	660
Ethyl methanesulfonate	20	ND
Famphur	20	ND
Fensulfothion	40	ND
Fenthion	10	ND
Fluchloralin	20	ND
Fluoranthene	10	660
Fluorene	10	660
Hexachlorobenzene	10	660
Hexachlorobutadiene	10	660
Hexachlorocyclopentadiene	10	660
Hexachloroethane	10	660
Hexachlorophene	50	ND
Hexachloropropene	10	ND
Hexamethyl phosphoramide	20	ND
Hydroquinone	ND	ND
Indeno(1,2,3-cd)pyrene	10	660
Isodrin	20	ND
Isophorone	10	660
Isosafrole	10	ND
Kepone	20	ND
Leptophos	10	ND
Malathion	50	ND
Maleic anhydride	NA	ND
Mestranol	20	ND
Methapyrilene	100	ND
Methoxychlor	10	ND
3-Methylcholanthrene	10	ND
4,4'-Methylenebis(2-chloroaniline)	NA	ND
Methyl methanesulfonate	10	ND
2-Methylnaphthalene	10	660
Methyl parathion	10	ND
2-Methylphenol	10	660
3-Methylphenol	10	ND
4-Methylphenol	10	660
Mevinphos	10	ND
Mexacarbate	20	ND
Mirex	10	ND
Monocrotophos	40	ND
Naled	20	ND

TABLE 2.
(Continued)

Semivolatiles	Estimated Quantitation Limits[b]	
	Ground water µg/L	Low Soil/Sediment[c] µg/Kg
Naphthalene	10	660
1,4-Naphthoquinone	10	ND
1-Naphthylamine	10	ND
2-Naphthylamine	10	ND
Nicotine	20	ND
5-Nitroacenaphthene	10	ND
2-Nitroaniline	50	3300
3-Nitroaniline	50	3300
4-Nitroaniline	20	ND
5-Nitro-o-anisidine	10	ND
Nitrobenzene	10	660
4-Nitrobiphenyl	10	ND
Nitrofen	20	ND
2-Nitrophenol	10	660
4-Nitrophenol	50	3300
5-Nitro-o-toluidine	10	ND
4-Nitroquinoline-1-oxide	40	ND
N-Nitrosodibutylamine	10	ND
N-Nitrosodiethylamine	20	ND
N-Nitrosodiphenylamine	10	660
N-Nitroso-di-n-propylamine	10	660
N-Nitrosopiperidine	20	ND
N-Nitrosopyrrolidine	40	ND
Octamethyl pyrophosphoramide	200	ND
4,4'-Oxydianiline	20	ND
Parathion	10	ND
Pentachlorobenzene	10	ND
Pentachloronitrobenzene	20	ND
Pentachlorophenol	50	3300
Phenacetin	20	ND
Phenanthrene	10	660
Phenobarbital	10	ND
Phenol	10	660
1,4-Phenylenediamine	10	ND
Phorate	10	ND
Phosalone	100	ND
Phosmet	40	ND
Phosphamidon	100	ND
Phthalic anhydride	100	ND
2-Picoline	ND	ND
Piperonyl sulfoxide	100	ND
Pronamide	10	ND
Propylthiouracil	100	ND
Pyrene	10	660

TABLE 2.
(Continued)

Semivolatiles	Estimated Quantitation Limits[b] Ground water µg/L	Low Soil/Sediment[a] µg/Kg
Pyridine	ND	ND
Resorcinol	100	ND
Safrole	10	ND
Strychnine	40	ND
Sulfallate	10	ND
Terbufos	20	ND
1,2,4,5-Tetrachlorobenzene	10	ND
2,3,4,6-Tetrachlorophenol	10	ND
Tetrachlorvinphos	20	ND
Tetraethyl pyrophosphate	40	ND
Thionazine	20	ND
Thiophenol (Benzenethiol)	20	ND
Toluene diisocyanate	100	ND
o-Toluidine	10	ND
1,2,4-Trichlorobenzene	10	660
2,4,5-Trichlorophenol	10	660
2,4,6-Trichlorophenol	10	660
Trifluralin	10	ND
2,4,5-Trimethylaniline	10	ND
Trimethyl phosphate	10	ND
1,3,5-Trinitrobenzene	10	ND
Tris(2,3-dibromopropyl) phosphate	200	ND
Tri-p-tolyl phosphate(h)	10	ND
0,0,0-Triethylphosphorothioate	NT	ND

a EQLs listed for soil/sediment are based on wet weight. Normally data is reported on a dry weight basis, therefore, EQLs will be higher based on the % dry weight of each sample. This is based on a 30 g sample and gel permeation chromatography cleanup.
b Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable.
ND = Not determined.
NA = Not applicable.
NT = Not tested.

Other Matrices	Factor[1]
High-concentration soil and sludges by sonicator	7.5
Non-water miscible waste	75

[1]EQL = [EQL for Low Soil/Sediment (Table 2)] X [Factor].

TABLE 3.
DFTPP KEY IONS AND ION ABUNDANCE CRITERIA[a]

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	40-60% of mass 198
197	< 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	> 40% of mass 198
443	17-23% of mass 442

[a]See Reference 4.

TABLE 4.
CALIBRATION CHECK COMPOUNDS

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitrosodiphenylamine	Phenol
Di-n-octyl phthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

TABLE 5.
SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}
Aniline	Acetophenone	Acenaphthene
Benzyl alcohol	Benzoic acid	Acenaphthylene
Bis(2-chloroethyl) ether	Bis(2-chloroethoxy)methane	1-Chloronaphthalene
Bis(2-chloroisopropyl) ether	4-Chloroaniline	2-Chloronaphthalene
2-Chlorophenol	4-Chloro-3-methylphenol	4-Chlorophenyl phenyl ether
1,3-Dichlorobenzene	2,4-Dichlorophenol	Dibenzofuran
1,4-Dichlorobenzene	2,6-Dichlorophenol	Diethyl phthalate
1,2-Dichlorobenzene	α,α-Dimethyl-phenethylamine	Dimethyl phthalate
Ethyl methanesulfonate	2,4-Dimethylphenol	2,4-Dinitrophenol
2-Fluorophenol (surr.)	Hexachlorobutadiene	2,4-Dinitrotoluene
Hexachloroethane	Isophorone	2,6-Dinitrotoluene
Methyl methanesulfonate	2-Methylnaphthalene	Fluorene
2-Methylphenol	Naphthalene	2-Fluorobiphenyl (surr.)
4-Methylphenol	Nitrobenzene	Hexachlorocyclo-pentadiene
N-Nitrosodimethylamine	Nitrobenzene-d_5 (surr.)	1-Naphthylamine.
N-Nitroso-di-n-propylamine	2-Nitrophenol	2-Naphthylamine
Phenol	N-Nitrosodibutylamine	2-Nitroaniline
Phenol-d_6 (surr.)	N-Nitrosopiperidine	3-Nitroaniline
2-Picoline	1,2,4-Trichlorobenzene	4-Nitroaniline
		4-Nitrophenol
		Pentachlorobenzene
		1,2,4,5-Tetra-chlorobenzene
		2,3,4,6-Tetra-chlorophenol
		2,4,6-Tribromo-phenol (surr.)
		2,4,6-Trichloro-phenol
		2,4,5-Trichloro-phenol

(surr.) = surrogate

TABLE 5.
(Continued)

Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
4-Aminobiphenyl	Benzidine	Benzo(b)fluoranthene
Anthracene	Benzo(a)anthracene	Benzo(k)fluoranthene
4-Bromophenyl phenyl ether	Bis(2-ethylhexyl) phthalate	Benzo(g,h,i)perylene
Di-n-butyl phthalate	Butyl benzyl phthalate	Benzo(a)pyrene
4,6-Dinitro-2-methylphenol	Chrysene	Dibenz(a,j)acridine
Diphenylamine	3,3'-Dichlorobenzidine	Dibenz(a,h)anthracene
1,2-Diphenylhydrazine	p-Dimethylaminoazobenzene	7,12-Dimethylbenz(a)anthracene
Fluoranthene	Pyrene	Di-n-octyl phthalate
Hexachlorobenzene	Terphenyl-d_{14} (surr.)	Indeno(1,2,3-cd)pyrene
N-Nitrosodiphenylamine		3-Methylcholanthrene
Pentachlorophenol		
Pentachloronitrobenzene		
Phenacetin		
Phenanthrene		
Pronamide		

(surr.) = surrogate

TABLE 6.
QC ACCEPTANCE CRITERIA[a]

Compound	Test conc. (µg/L)	Limit for s (µg/L)	Range for x (µg/L)(%)	Range p, p_s
Acenaphthene	100	27.6	60.1-132.3	47-145
Acenaphthylene	100	40.2	53.5-126.0	33-145
Aldrin	100	39.0	7.2-152.2	D-166
Anthracene	100	32.0	43.4-118.0	27.133
Benz(a)anthracene	100	27.6	41.8-133.0	33-143
Benzo(b)fluoranthene	100	38.8	42.0-140.4	24-159
Benzo(k)fluoranthene	100	32.3	25.2-145.7	11-162
Benzo(a)pyrene	100	39.0	31.7-148.0	17-163
Benzo(ghi)perylene	100	58.9	D-195.0	D-219
Benzyl butyl phthalate	100	23.4	D-139.9	D-152
β-BHC	100	31.5	41.5-130.6	24-149
δ-BHC	100	21.6	D-100.0	D-110
Bis(2-chloroethyl) ether	100	55.0	42.9-126.0	12-158
Bis(2-chloroethoxy)methane	100	34.5	49.2-164.7	33-184
Bis(2-chloroisopropyl) ether	100	46.3	62.8-138.6	36-166
Bis(2-ethylhexyl) phthalate	100	41.1	28.9-136.8	8-158
4-Bromophenyl phenyl ether	100	23.0	64.9-114.4	53-127
2-Chloronaphthalene	100	13.0	64.5-113.5	60-118
4-Chlorophenyl phenyl ether	100	33.4	38.4-144.7	25-158
Chrysene	100	48.3	44.1-139.9	17-168
4,4'-DDD	100	31.0	D-134.5	D-145
4,4'-DDE	100	32.0	19.2-119.7	4-136
4,4'-DDT	100	61.6	D-170.6	D-203
Dibenzo(a,h)anthracene	100	70.0	D-199.7	D-227
Di-n-butyl phthalate	100	16.7	8.4-111.0	1-118
1,2-Dichlorobenzene	100	30.9	48.6-112.0	32-129
1,3-Dichlorobenzene	100	41.7	16.7-153.9	D-172
1,4-Dichlorobenzene	100	32.1	37.3-105.7	20-124
3,3'-Dichlorobenzidine	100	71.4	8.2-212.5	D-262
Dieldrin	100	30.7	44.3-119.3	29-136
Diethyl phthalate	100	26.5	D-100.0	D-114
Dimethyl phthalate	100	23.2	D-100.0	D-112
2,4-Dinitrotoluene	100	21.8	47.5-126.9	39-139
2,6-Dinitrotoluene	100	29.6	68.1-136.7	50-158
Di-n-octylphthalate	100	31.4	18.6-131.8	4-146
Endosulfan sulfate	100	16.7	D-103.5	D-107
Endrin aldehyde	100	32.5	D-188.8	D-209
Fluoranthene	100	32.8	42.9-121.3	26-137
Fluorene	100	20.7	71.6-108.4	59-121
Heptachlor	100	37.2	D-172.2	D-192
Heptachlor epoxide	100	54.7	70.9-109.4	26.155
Hexachlorobenzene	100	24.9	7.8-141.5	D-152
Hexachlorobutadiene	100	26.3	37.8-102.2	24-116

TABLE 6.
(Continued)

Compound	Test conc. (µg/L)	Limit for s (µg/L)	Range for x (µg/L)(%)	Range p, p_s
Hexachloroethane	100	24.5	55.2-100.0	40-113
Indeno(1,2,3-cd)pyrene	100	44.6	D-150.9	D-171
Isophorone	100	63.3	46.6-180.2	21-196
Naphthalene	100	30.1	35.6-119.6	21-133
Nitrobenzene	100	39.3	54.3-157.6	35-180
N-Nitrosodi-n-propylamine	100	55.4	13.6-197.9	D-230
PCB-1260	100	54.2	19.3-121.0	D-164
Phenanthrene	100	20.6	65.2-108.7	54-120
Pyrene	100	25.2	69.6-100.0	52-115
1,2,4-Trichlorobenzene	100	28.1	57.3-129.2	44-142
4-Chloro-3-methylphenol	100	37.2	40.8-127.9	22-147
2-Chlorophenol	100	28.7	36.2-120.4	23-134
2,4-Chlorophenol	100	26.4	52.5-121.7	39-135
2,4-Dimethylphenol	100	26.1	41.8-109.0	32-119
2,4-Dinitrophenol	100	49.8	D-172.9	D-191
2-Methyl-4,6-dinitrophenol	100	93.2	53.0-100.0	D-181
2-Nitrophenol	100	35.2	45.0-166.7	29-182
4-Nitrophenol	100	47.2	13.0-106.5	D-132
Pentachlorophenol	100	48.9	38.1-151.8	14-176
Phenol	100	22.6	16.6-100.0	5-112
2,4,6-Trichlorophenol	100	31.7	52.4-129.2	37-144

s = Standard deviation of four recovery measurements, in µg/L.

$\bar{x}$ = Average recovery for four recovery measurements, in µg/L.

p, p_s = Percent recovery measured.

D = Detected; result must be greater than zero.

a Criteria from 40 CFR Part 136 for Method 625. These criteria are based directly on the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7.

TABLE 7.
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Compound	Accuracy, as recovery, x' (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S' (µg/L)
Acenaphthene	0.96C+0.19	0.15$\bar{x}$-0.12	0.21$\bar{x}$-0.67
Acenaphthylene	0.89C+0.74	0.24$\bar{x}$-1.06	0.26$\bar{x}$-0.54
Aldrin	0.78C+1.66	0.27$\bar{x}$-1.28	0.43$\bar{x}$+1.13
Anthracene	0.80C+0.68	0.21$\bar{x}$-0.32	0.27$\bar{x}$-0.64
Benz(a)anthracene	0.88C-0.60	0.15$\bar{x}$+0.93	0.26$\bar{x}$-0.21
Chloroethane	0.99C-1.53	0.14$\bar{x}$-0.13	0.17$\bar{x}$-0.28
Benzo(b)fluoranthene	0.93C-1.80	0.22$\bar{x}$+0.43	0.29$\bar{x}$+0.96
Benzo(k)fluoranthene	0.87C-1.56	0.19$\bar{x}$+1.03	0.35$\bar{x}$+0.40
Benzo(a)pyrene	0.90C-0.13	0.22$\bar{x}$+0.48	0.32$\bar{x}$+1.35
Benzo(ghi)perylene	0.98C-0.86	0.29$\bar{x}$+2.40	0.51$\bar{x}$-0.44
Benzyl butyl phthalate	0.66C-1.68	0.18$\bar{x}$+0.94	0.53$\bar{x}$+0.92
β-BHC	0.87C-0.94	0.20$\bar{x}$-0.58	0.30$\bar{x}$+1.94
δ-BHC	0.29C-1.09	0.34$\bar{x}$+0.86	0.93$\bar{x}$-0.17
Bis(2-chloroethyl) ether	0.86C-1.54	0.35$\bar{x}$-0.99	0.35$\bar{x}$+0.10
Bis(2-chloroethoxy)methane	1.12C-5.04	0.16$\bar{x}$+1.34	0.26$\bar{x}$+2.01
Bis(2-chloroisopropyl) ether	1.03C-2.31	0.24$\bar{x}$+0.28	0.25$\bar{x}$+1.04
Bis(2-ethylhexyl) phthalate	0.84C-1.18	0.26$\bar{x}$+0.73	0.36$\bar{x}$+0.67
4-Bromophenyl phenyl ether	0.91C-1.34	0.13$\bar{x}$+0.66	0.16$\bar{x}$+0.66
2-Chloronaphthalene	0.89C+0.01	0.07$\bar{x}$+0.52	0.13$\bar{x}$+0.34
4-Chlorophenyl phenyl ether	0.91C+0.53	0.20$\bar{x}$-0.94	0.30$\bar{x}$-0.46
Chrysene	0.93C-1.00	0.28$\bar{x}$+0.13	0.33$\bar{x}$-0.09
4,4'-DDD	0.56C-0.40	0.29$\bar{x}$-0.32	0.66$\bar{x}$-0.96
4,4'-DDE	0.70C-0.54	0.26$\bar{x}$-1.17	0.39$\bar{x}$-1.04
4,4'-DDT	0.79C-3.28	0.42$\bar{x}$+0.19	0.65$\bar{x}$-0.58
Dibenzo(a,h)anthracene	0.88C+4.72	0.30$\bar{x}$+8.51	0.59$\bar{x}$+0.25
Di-n-butyl phthalate	0.59C+0.71	0.13$\bar{x}$+1.16	0.39$\bar{x}$+0.60
1,2-Dichlorobenzene	0.80C+0.28	0.20$\bar{x}$+0.47	0.24$\bar{x}$+0.39
1,3-Dichlorobenzene	0.86C-0.70	0.25$\bar{x}$+0.68	0.41$\bar{x}$+0.11
1,4-Dichlorobenzene	0.73C-1.47	0.24$\bar{x}$+0.23	0.29$\bar{x}$+0.36
3,3'-Dichlorobenzidine	1.23C-12.65	0.28$\bar{x}$+7.33	0.47$\bar{x}$+3.45
Dieldrin	0.82C-0.16	0.20$\bar{x}$-0.16	0.26$\bar{x}$-0.07
Diethyl phthalate	0.43C+1.00	0.28$\bar{x}$+1.44	0.52$\bar{x}$+0.22
Dimethyl phthalate	0.20C+1.03	0.54$\bar{x}$+0.19	1.05$\bar{x}$-0.92
2,4-Dinitrotoluene	0.92C-4.81	0.12$\bar{x}$+1.06	0.21$\bar{x}$+1.50
2,6-Dinitrotoluene	1.06C-3.60	0.14$\bar{x}$+1.26	0.19$\bar{x}$+0.35
Di-n-octyl phthalate	0.76C-0.79	0.21$\bar{x}$+1.19	0.37$\bar{x}$+1.19
Endosulfan sulfate	0.39C+0.41	0.12$\bar{x}$+2.47	0.63$\bar{x}$-1.03
Endrin aldehyde	0.76C-3.86	0.18$\bar{x}$+3.91	0.73$\bar{x}$-0.62
Fluoranthene	0.81C+1.10	0.22$\bar{x}$-0.73	0.28$\bar{x}$-0.60
Fluorene	0.90C-0.00	0.12$\bar{x}$+0.26	0.13$\bar{x}$+0.61
Heptachlor	0.87C-2.97	0.24$\bar{x}$-0.56	0.50$\bar{x}$-0.23
Heptachlor epoxide	0.92C-1.87	0.33$\bar{x}$-0.46	0.28$\bar{x}$+0.64

TABLE 7.
(Continued)

Compound	Accuracy, as recovery, x' (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S' (µg/L)
Hexachlorobenzene	0.74C+0.66	0.18$\bar{x}$-0.10	0.43$\bar{x}$-0.52
Hexachlorobutadiene	0.71C-1.01	0.19$\bar{x}$+0.92	0.26$\bar{x}$+0.49
Hexachloroethane	0.73C-0.83	0.17$\bar{x}$+0.67	0.17$\bar{x}$+0.80
Indeno(1,2,3-cd)pyrene	0.78C-3.10	0.29$\bar{x}$+1.46	0.50$\bar{x}$-0.44
Isophorone	1.12C+1.41	0.27$\bar{x}$+0.77	0.33$\bar{x}$+0.26
Naphthalene	0.76C+1.58	0.21$\bar{x}$-0.41	0.30$\bar{x}$-0.68
Nitrobenzene	1.09C-3.05	0.19$\bar{x}$+0.92	0.27$\bar{x}$+0.21
N-Nitrosodi-n-propylamine	1.12C-6.22	0.27$\bar{x}$+0.68	0.44$\bar{x}$+0.47
PCB-1260	0.81C-10.86	0.35$\bar{x}$+3.61	0.43$\bar{x}$+1.82
Phenanthrene	0.87C+0.06	0.12$\bar{x}$+0.57	0.15$\bar{x}$+0.25
Pyrene	0.84C-0.16	0.16$\bar{x}$+0.06	0.15$\bar{x}$+0.31
1,2,4-Trichlorobenzene	0.94C-0.79	0.15$\bar{x}$+0.85	0.21$\bar{x}$+0.39
4-Chloro-3-methylphenol	0.84C+0.35	0.23$\bar{x}$+0.75	0.29$\bar{x}$+1.31
2-Chlorophenol	0.78C+0.29	0.18$\bar{x}$+1.46	0.28$\bar{x}$+0.97
2,4-Dichlorophenol	0.87C-0.13	0.15$\bar{x}$+1.25	0.21$\bar{x}$+1.28
2,4-Dimethylphenol	0.71C+4.41	0.16$\bar{x}$+1.21	0.22$\bar{x}$+1.31
2,4-Dinitrophenol	0.81C-18.04	0.38$\bar{x}$+2.36	0.42$\bar{x}$+26.29
2-Methyl-4,6-dinitrophenol	1.04C-28.04	0.10$\bar{x}$+42.29	0.26$\bar{x}$+23.10
2-Nitrophenol	0.07C-1.15	0.16$\bar{x}$+1.94	0.27$\bar{x}$+2.60
4-Nitrophenol	0.61C-1.22	0.38$\bar{x}$+2.57	0.44$\bar{x}$+3.24
Pentachlorophenol	0.93C+1.99	0.24$\bar{x}$+3.03	0.30$\bar{x}$+4.33
Phenol	0.43C+1.26	0.26$\bar{x}$+0.73	0.35$\bar{x}$+0.58
2,4,6-Trichlorophenol	0.91C-0.18	0.16$\bar{x}$+2.22	0.22$\bar{x}$+1.81

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in µg/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{x}$, in µg/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{x}$, in µg/L.

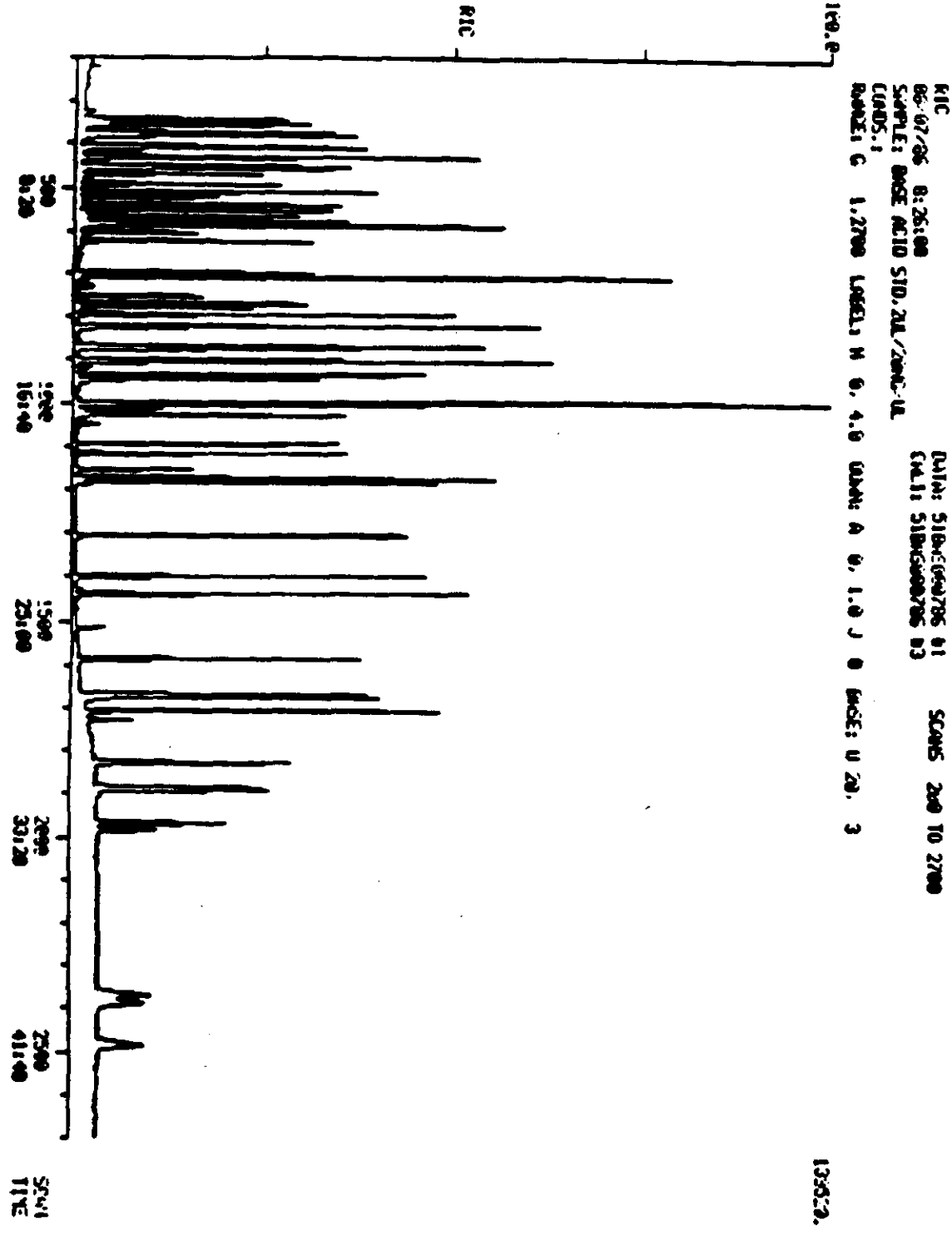
C = True value for the concentration, in µg/L.

$\bar{x}$ = Average recovery found for measurements of samples containing a concentration of C, in µg/L.

TABLE 8.
SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Low/High Water	Low/High Soil/Sediment
Nitrobenzene-d_5	35-114	23-120
2-Fluorobiphenyl	43-116	30-115
p-Terphenyl-d_{14}	33-141	18-137
Phenol-d_6	10-94	24-113
2-Fluorophenol	21-100	25-121
2,4,6-Tribromophenol	10-123	19-122

FIGURE 1.
GAS CHROMATOGRAM OF BASE/NEUTRAL AND ACID CALIBRATION STANDARD



METHOD 8270
GAS CHROMATOGRAPHY/MASS SPECTROMETRY FOR SEMIVOLATILE ORGANICS: CAPILLARY COLUMN TECHNIQUE