SW8463A

TEST METHODS FOR EVALUATING SOLID WASTE, PHYSICAL/CHEMICAL METHODS, SW-846, 3RD EDITION,

PROPOSED UPDATE II

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Revision 2 methods (methods which have been revised in the proposed Update II package) are designated by the letter "B" in the method number. Likewise, Revision 1 methods (methods which were previously revised in the promulgated Update I package or are being revised for the first time in the proposed Update II package) are designated by the letter "A" in the method number. In order to properly document the method revision used, the entire method number, including the letter designation, must be identified by the method user. A method reference found within the text of SW-846 methods and chapters refers to the latest promulgated revision of the method, even though the referenced method number is without an appropriate letter designation.

ORGANOCHLORINE PESTICIDES, HALOWAXES AND PCBs AS AROCLORS BY GAS CHROMATOGRAPHY: CAPILLARY COLUMN TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 Method 8081 is used to determine the concentrations of various organochlorine pesticides, Halowaxes and polychlorinated biphenyls (PCBs) as Aroclors, in extracts from solid and liquid matrices. Open-tubular, capillary columns were employed with electron capture detectors (ECD) or electrolytic conductivity detectors (ELCD). When compared to the packed columns, these fused-silica, open-tubular columns offer improved resolution, better selectivity, increased sensitivity, and faster analysis. The list below is annotated to show whether a single- or dual-column analysis system was used to identify each target analyte.

Compound Name	CAS Registry No.
Alachlor[a,b]	15972-60-8
Aldrin[a,b]	309-00-2
Aroclor-1016[a,b]	12674-11-2
Aroclor-1221[a,b]	1104-28-2
Aroclor-1232[a,b]	11141-16-5
Aroclor-1242[a,b]	53469-21-9
Aroclor-1248[a,b]	12672-29-6
Aroclor-1254[a,b]	11097-69-1
Aroclor-1260[a,b]	11096-82-5
α-BHC[a,b]	319-84-6
β-BHC[a,b]	319-85-7
γ-BHC (Lindane)[a,b]	58-89-9
δ-BHC[a,b]	319-86-8
Captafol[b]	2425-06-1
Captan[b]	133-06-2
Chlorobenzilate[b]	510-15-6
α-Chlordane[b]	5103-71-9
γ-Chlordane[a,b]	5103-74-2
Chloroneb[b]	2675-77-6
Chloropropylate[b]	99516-95-7
Chlorothalonil[b]	1897-45-6
DBCP[b]	96-12-8
DCPA[b]	1861-32-1
4,4'-DDD[a,b]	72-54-8

Compound Name	CAS Registry No.
4,4′-DDE[a,b]	72-55-9
4,4′-DDT[a,b]	50-29-3
Diallate[b]	2303-16-4
Dichlone[b]	117-80-6
Dicofol[b]	115-32-2
Dieldrin[a,b]	60-57-1
Endosulfan I[a,b]	959-98-8
Endosulfan II[a,b]	33213-65-9
Endosulfan sulfate[a,b]	1031-07-8
Endrin[a,b]	72-20-8
Endrin aldehyde[a,b]	7421-93-4
Endrin ketone[b]	53494-70-5
Etridiazole[b]	2593-15-9
Halowax-1000[b]	58718-66-4
Halowax-1001[b]	58718-67-5
Halowax-1013[b]	12616-35-2
Halowax-1014[b]	12616-36-3
Halowax-1051[b]	2234-13-1
Halowax-1099[b]	39450-05-0
Heptachlor[a,b]	76-44-8
Heptachlor epoxide[a,b]	1024-57-3
Hexachlorobenzene[b]	118-74-1
Hexachlorocyclopentadiene[b]	77-47-4
Isodrin[b]	465-73-6
Kepone[b]	143-50-0
Methoxychlor[a,b]	72-43-5
Mirex[b]	2385-85-5
Nitrofen[b]	1836-75-5
PCNB[b]	82-68-8
Perthane[b]	72-56-0
Propachlor[b]	1918-16-17
Strobane[b]	8001-50-1
Toxaphene[a,b]	8001-35-2
trans-Nonachlor[b]	39765-80-5
trans-Permethrin[b]	51877-74-8
Trifluralin[b]	1582-09-8

[a] Single-column analysis
[b] Dual-column analysis

1.2 The analyst must select columns, detectors and calibration procedures most appropriate for the specific analytes of interest in a study. Matrix-specific performance data must be established and the stability of the analytical system and instrument calibration must be established for each new matrix.

1.3 Although performance data are presented for many of the listed chemicals, it is unlikely that all of them could be determined in a single analysis. This limitation results because the chemical and chromatographic behavior of many of these chemicals can result in co-elution. Several cleanup/fractionation schemes are provided in this method and in Method 3600. Any listed chemical is a potential method interference when it is not a target analyte.

1.4 Several multi-component mixtures (i.e., Aroclors, Halowaxes, Toxaphene and Strobane) are listed as target compounds. When samples contain more than one multi-component analyte, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. The same is true of multi-component analytes that have been subjected to environmental degradation or degradation by treatment technologies. These result in "weathered" Aroclors (or any other multi-component mixtures) that may have significant differences in peak patterns than those of standards. In these cases, individual congener analyses may be preferred over total mixture analyses.

1.5 Compound identification based on single column analysis should be confirmed on a second column, or should be supported by at least one other qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm the measurements made with the primary column. GC/MS Method 8270 is also recommended as a confirmation technique if sensitivity permits (Section 8).

1.6 This method describes a dual column option. The option allows a hardware configuration of two analytical columns joined to a single injection port. The option allows one injection to be used for dual column analysis. Analysts are cautioned that the dual column option may not be appropriate when the instrument is subject to mechanical stress, many samples are to be run in a short period, or when contaminated samples are analyzed.

1.7 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph (GC) and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.8 Extracts suitable for analysis by this method may also be analyzed for organophosphorus pesticides (Method 8141). Some extracts may also be suitable for triazine herbicide analysis, if low recoveries (normally samples taken for triazine analysis must be preserved) are not a problem.

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample (approximately 1 L for liquids, 2 g to 30 g for solids) is extracted using the appropriate sample extraction technique. Liquid samples are extracted at neutral pH with methylene chloride using either a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Solid samples are extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using either Soxhlet extraction (Method 3540), Automated Soxhlet (Method 3541), or Ultrasonic Extraction (Method 3550). A variety of cleanup steps may be applied to the extract, depending on (1) the nature of the coextracted matrix interferences and (2) the target analytes.

After cleanup, the extract is analyzed by injecting a 1-μL sample into a gas chromatograph with a narrow- or wide-bore fused silica capillary column and electron capture detector (GC/ECD) or an electrolytic conductivity detector (GC/ELCD).

3.0 INTERFERENCES

3.1 Refer to Methods 3500 (Section 3, in particular), 3600, and 8000.

3.2 Sources of interference in this method can be grouped into three broad categories: contaminated solvents, reagents or sample processing hardware; contaminated GC carrier gas, parts, column surfaces or detector surfaces; and the presence of coeluting compounds in the sample matrix to which the ECD will respond. Interferences coextracted from the samples will vary considerably from waste to waste. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation.

3.3 Interferences by phthalate esters introduced during sample preparation can pose a major problem in pesticide determinations. These materials may be removed prior to analysis using Gel Permeation Cleanup - pesticide option (Method 3640) or as Fraction III of the silica gel cleanup procedure (Method 3630). Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations. Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalate esters can best be minimized by avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination. Exhaustive cleanup of solvents, reagents and glassware may be required to eliminate background phthalate ester contamination.

3.4 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water, and rinses with tap water and organic-free reagent water. Drain the glassware and dry in an oven at 130°C for several hours or rinse with methanol and drain. Store dry glassware in a clean environment.

3.5 The presence of elemental sulfur will result in broad peaks that interfere with the detection of early-eluting organochlorine pesticides. Sulfur contamination should be expected with sediment samples. Method 3660 is suggested for removal of sulfur. Since the recovery of Endrin aldehyde (using the TBA procedure) is drastically reduced, this compound must be determined prior to sulfur cleanup.

3.6 Waxes, lipids, and other high molecular weight co-extractables can be removed by Gel-Permeation Cleanup (Method 3640).

3.7 It may be difficult to quantitate Aroclor patterns and single component pesticides together. Some pesticides can be removed by sulfuric acid/permanganate cleanup (Method 3665) and silica fractionation (Method 3630). Guidance on the identification of PCBs is given in Section 7.

3.8 The following target analytes coelute using single column analysis:

DB 608	*Trifluralin/Diallate isomers*
	PCNP/Dichlone/Isodrin
	DDD/Endosulfan II
DB 1701	Captan/Chlorobenzilate
	Captafol/Mirex
	DDD/Endosulfan II
	Methoxychlor/Endosulfan sulfate

3.8.1 Other halogenated pesticides or industrial chemicals may interfere with the analysis of pesticides. Certain co-eluting organophosphorus pesticides are eliminated by the Gel Permeation Chromatography cleanup - pesticide option (Method 3640). Co-eluting chlorophenols are eliminated by Silica gel (Method 3630), Florisil (Method 3620), or Alumina (Method 3610) cleanup.

3.9 The following compounds coelute using the dual column analysis. Two temperature programs are provided for the same pair of columns as option 1 and option 2 for dual column analysis. In general, the DB-5 column resolves fewer compounds that the DB-1701:

3.9.1 DB-5/DB-1701, thin film, slow ramp: See Section 7 and Table 6.

DB-5	*trans*-Permethrin/Heptachlor epoxide
	Endosulfan I/α-Chlordane
	Perthane/Endrin
	Endosulfan II/Chloropropylate/Chlorobenzilate
	4,4'-DDT/Endosulfan sulfate
	Methoxychlor/Dicofol

Perthane/Endrin and Chlorobenzilate/Endosulfan II/Chloropropylate will also co-elute on DB-5 after moderate deterioration in column performance.

DB-1701	Chlorothalonil/ß-BHC
	δ-BHC/DCPA/*trans*-Permethrin
	α-Chlordane/*trans*-Nonachlor
	Captan/Dieldrin
	Chlorobenzilate/Chloropropylate

Chlorothalonil/ß-BHC and α-Chlordane/*trans*-Nonachlor will co-elute on the DB-1701 column after moderate deterioration in column performance.

Nitrofen, Dichlone, Carbophenothion, Dichloran and Kepone were removed from the composite mixture because of extensive peak tailing on both columns. Simazine and Atrazine give poor responses on the ECD detector. Triazine compounds should be analyzed using Method 8141 (NPD option).

3.9.2 DB-5/DB-1701, thick film, fast ramp: See Section 7 and Table 7.

DB-5	Diallate/α-BHC Perthane/Endosulfan II Chlorobenzilate/Chloropropylate Endrin/Nitrofen 4,4′-DDT/Endosulfan sulfate Methoxychlor/Dicolfol
DB-1701	α-Chlordane/*trans*-Nonachlor (partially resolved) 4,4′-DDD/Endosulfan II (partially resolved)

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph: an analytical system complete with gas chromatograph suitable for on-column and split-splitless injection and all required accessories including syringes, analytical columns, gases, electron capture detectors (ECD), and recorder/integrator or data system.

The columns listed in this section were used to develop the method performance data. Their specification is not intended to prevent laboratories from using columns that are developed after promulgation of the method. Laboratories may use other capillary columns if they document method performance data (e.g. chromatographic resolution, analyte breakdown, and MDLs) equal to or better than those provided with the method.

4.1.1 Single-column Analysis:

4.1.1.1 Narrow-bore columns:

4.1.1.1.1 Column 1 - 30 m x 0.25 or 0.32 mm internal diameter (ID) fused silica capillary column chemically bonded with SE-54 (DB 5 or equivalent), 1 μm film thickness.

4.1.1.1.2 Column 2 - 30 m x 0.25 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB 608, SPB 608, or equivalent), 25 μm coating thickness, 1 μm film thickness.

4.1.1.1.3 Narrow bore columns should be installed in split/splitless (Grob-type) injectors.

4.1.1.2 Wide-bore columns

4.1.1.2.1 Column 1 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB 608, SPB 608, RTx-35, or equivalent), 0.5 μm or 0.83 μm film thickness.

4.1.1.2.2 Column 2 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 50 percent phenyl

methylpolysiloxane (DB 1701, or equivalent), 1.0 μm film thickness.

4.1.1.2.3 Column 3 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with SE-54 (DB 5, SPB 5, RTx5, or equivalent), 1.5 μm film thickness.

4.1.1.2.4 Wide-bore columns should be installed in 1/4 inch injectors, with deactivated liners designed specifically for use with these columns.

4.1.2 Dual Column Analysis:

4.1.2.1 Column pair 1:

4.1.2.1.1 J&W Scientific press-fit Y-shaped glass 3-way union splitter (J&W Scientific, Catalog no. 705-0733) or Restek Y-shaped fused-silica connector (Restek, Catalog no. 20405), or equivalent.

4.1.2.1.2 30 m x 0.53 m ID DB-5 (J&W Scientific), 1.5 μm film thickness, or equivalent.

4.1.2.1.3 30 m x 0.53 mm ID DB-1701 (J&W Scientific), 1.0 μm film thickness, or equivalent.

4.1.2.2 Column pair 2:

4.1.2.2.1 Splitter 2 - Supelco 8 in. glass injection tee, deactivated (Supelco, Catalog no. 2-3665M), or equivalent.

4.1.2.2.2 30 m x 0.53 m ID DB-5 (J&W Scientific), 0.83 μm film thickness, or equivalent.

4.1.2.2.3 30 m x 0.53 mm ID DB-1701 (J&W Scientific), 1.0 μm film thickness, or equivalent.

4.1.3 Column rinsing kit: Bonded-phase column rinse kit (J&W Scientific, Catalog no. 430-3000 or equivalent).

4.2 Glassware (see Methods 3510, 3520, 3540, 3541, 3550, 3630, 3640, 3660, and 3665 for specifications).

4.3 Kuderna-Danish (K-D) apparatus. See extraction methods for specifics.

5.0 REAGENTS

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

NOTE: Store the standard solutions (stock, composite, calibration, internal, and surrogate) at 4°C in Teflon-sealed containers in the dark. When a lot of standards is prepared, it is recommended that aliquots of that lot be stored in individual small vials. All standard solutions must be replaced after six months or sooner if routine QC (Section 8) indicates a problem.

5.2 Solvents and reagents: As appropriate for Method 3510, 3520, 3540, 3541, 3550, 3630, 3640, 3660, or 3665: n-hexane, diethyl ether, methylene chloride, acetone, ethyl acetate, and isooctane (2,2,4-trimethylpentane). All solvents should be pesticide quality or equivalent, and each lot of solvent should be determined to be phthalate free. Solvents must be exchanged to hexane or isooctane prior to analysis.

5.2.1 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): Can be prepared from pure standard materials or can be purchased as certified solutions.

5.3.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure compound. Dissolve the compound in isooctane or hexane and dilute to volume in a 10-mL volumetric flask. If compound purity is 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard solution. Commercially prepared stock standard solutions can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.2 ß-BHC, Dieldrin and some other standards may not be adequately soluble in isooctane. A small amount of acetone or toluene should be used to dissolve these compounds during the preparation of the stock standard solutions.

5.4 Composite stock standard: Can be prepared from individual stock solutions. For composite stock standards containing less than 25 components, take exactly 1 mL of each individual stock solution at 1000 mg/L, add solvent, and mix the solutions in a 25-mL volumetric flask. For example, for a composite containing 20 individual standards, the resulting concentration of each component in the mixture, after the volume is adjusted to 25 mL, will be 1 mg/25 mL. This composite solution can be further diluted to obtain the desired concentrations. For composite stock standards containing more than 25 components, use volumetric flasks of the appropriate volume (e.g., 50 mL, 100 mL).

5.5 Calibration standards should be prepared at a minimum of five concentrations by dilution of the composite stock standard with isooctane or hexane. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector.

5.5.1 Although all single component analytes can be resolved on a new 35 percent phenyl methyl silicone (e.g., DB-608), two calibration

mixtures should be prepared for the single component analytes of this method.

5.5.2 This requirement is established to (1) minimize potential resolution and quantitation problems on confirmation columns or on older 35 percent phenyl methyl silicone (e.g. DB-608) columns and (2) allow determination of Endrin and DDT breakdown for method QC (Section 8).

5.5.3 Separate calibration standards are required for each multi-component target analyte with the exception of Aroclors 1016 and 1260, which can be run as a mixture.

5.6 Internal standard (optional):

5.6.1 Pentachloronitrobenzene is suggested as an internal standard for the single column analysis. Prepare the standard to complement the concentrations found in Section 5.5.

5.6.2 Make a solution of 1 mg/mL of 1-bromo-2-nitrobenzene for dual-column analysis. Dilute it to 5000 ng/µL for spiking, then use a spiking volume of 10 µL/mL of extract.

5.7 Surrogate standards: The performance of the method should be monitored using surrogate compounds. Surrogate standards are added to all samples, method blanks, matrix spikes, and calibration standards.

5.7.1 For the single column analysis, use decachlorobiphenyl as the primary surrogate. However, if recovery is low, or late-eluting compounds interfere with decachlorobiphenyl, then tetrachloro-m-xylene should be evaluated as a surrogate. Proceed with corrective action when both surrogates are out of limits for a sample (Section 8.2). Method 3500, Section 5, indicates the proper procedure for preparing these surrogates.

5.7.2 For the dual column analysis make a solution of 1 mg/mL of 4-chloro-3-nitrobenzotrifluoride and dilute to 500 ng/µL. Use a spiking volume of 100 µL for a 1 L aqueous sample. Store the spiking solutions at 4°C in Teflon-sealed containers in the dark.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 See Chapter 4, Organic Analytes, Section 4.

6.2 Extracts must be stored under refrigeration in the dark and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction:

7.1.1 Refer to Chapter Two and Method 3500 for guidance in choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral pH with methylene chloride as a solvent using a

separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Extract solid samples with hexane-acetone (1:1) using one of the Soxhlet extraction (Method 3540 or 3541) or ultrasonic extraction (Method 3550) procedures.

NOTE: Hexane/acetone (1:1) may be more effective as an extraction solvent for organochlorine pesticides and PCBs in some environmental and waste matrices than is methylene chloride/acetone (1:1). Use of hexane/acetone generally reduces the amount of co-extracted interferences and improves signal/noise.

7.1.2 Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. Each sample must be spiked with the compounds of interest to determine the percent recovery and the limit of detection for that sample (Section 5). See Method 8000 for guidance on demonstration of initial method proficiency as well as guidance on matrix spikes for routine sample analysis.

7.2 Cleanup/Fractionation:

7.2.1 Cleanup procedures may not be necessary for a relatively clean sample matrix, but most extracts from environmental and waste samples will require additional preparation before analysis. The specific cleanup procedure used will depend on the nature of the sample to be analyzed and the data quality objectives for the measurements. General guidance for sample extract cleanup is provided in this section and in Method 3600.

7.2.1.1 If a sample is of biological origin, or contains high molecular weight materials, the use of GPC cleanup/pesticide option (Method 3640) is recommended. Frequently, one of the adsorption chromatographic cleanups may also be required following the GPC cleanup.

7.2.1.2 If only PCBs are to be measured in a sample, the sulfuric acid/permanganate cleanup (Method 3665) is recommended. Additional cleanup/fractionation by Alumina Cleanup (Method 3610), Silica-Gel Cleanup (Method 3630), or Florisil Cleanup (Method 3620), may be necessary.

7.2.1.3 If both PCBs and pesticides are to be measured in the sample, isolation of the PCB fraction by Silica Cleanup (Method 3630) is recommended.

7.2.1.4 If only pesticides are to be measured, cleanup by Method 3620 or Method 3630 is recommended.

7.2.1.5 Elemental sulfur, which may appear in certain sediments and industrial wastes, interferes with the electron capture gas chromatography of certain pesticides. Sulfur should be removed by the technique described in Method 3660, Sulfur Cleanup.

7.3 GC Conditions: This method allows the analyst to choose between a single column or a dual column configuration in the injector port. Either

wide- or narrow-bore columns may be used. Identifications based on retention times from a single column must be confirmed on a second column or with an alternative qualitative technique.

7.3.1 Single Column Analysis:

7.3.1.1 This capillary GC/ECD method allows the analyst the option of using 0.25-0.32 mm ID capillary columns (narrow-bore) or 0.53 mm ID capillary columns (wide-bore). Performance data are provided for both options. Figures 1-6 provide example chromatograms.

7.3.1.2 The use of narrow-bore columns is recommended when the analyst requires greater chromatographic resolution. Use of narrow-bore columns is suitable for relatively clean samples or for extracts that have been prepared with one or more of the clean-up options referenced in the method. Wide-bore columns (0.53 mm) are suitable for more complex environmental and waste matrices.

7.3.1.3 For the single column method of analysis, using wide-bore capillary columns, Table 1 lists average retention times and method detection limits (MDLs) for the target analytes in water and soil matrices. For the single column method of analysis, using narrow-bore capillary columns, Table 2 lists average retention times and method detection limits (MDLs) for the target analytes in water and soil matrices. The MDLs for the components of a specific sample may differ from those listed in Tables 1 and 2 because they are dependent upon the nature of interferences in the sample matrix. Table 3 lists the Estimated Quantitation Limits (EQLs) for other matrices. Table 4 lists the GC operating conditions for the single column method of analysis.

7.3.2 Dual Column Analysis:

7.3.2.1 The dual-column/dual-detector approach involves the use of two 30 m x 0.53 mm ID fused-silica open-tubular columns of different polarities, thus different selectivities towards the target compounds. The columns are connected to an injection tee and ECD detectors. Retention times for the organochlorine analytes on dual columns are in Table 5. The GC operating conditions for the compounds in Table 5 are in Table 6. Multicomponent mixtures of Toxaphene and Strobane were analyzed separately (Figures 7 and 8) using the GC operating conditions found in Table 7. Seven Aroclor mixtures and six Halowax mixtures were analyzed under the conditions outlined in Table 7 (Figures 9 through 21). Figure 22 is a sample chromatogram for a mixture of organochlorine pesticides. The retention times of the individual components detected in these mixtures are given in Tables 8 and 9.

7.3.2.1.1 Operating conditions for a more heavily loaded DB-5/DB-1701 pair are given in Table 7. This column pair was used for the detection of multicomponent organochlorine compounds.

7.3.2.1.2 Operating conditions for a DB-5/DB-1701 column pair with thinner films, a different type of splitter, and a slower temperature programming rate are provided in Table 6. These conditions gave better peak shapes for compounds such as Nitrofen and Dicofol. Table 5 lists the retention times for the compounds detected on this column pair.

7.4 Calibration:

7.4.1 Prepare calibration standards using the procedures in Section 5. Refer to Method 8000 (Section 7) for proper calibration techniques for both initial calibration and calibration verification. The procedure for either internal or external calibration may be used, however, in most cases external standard calibration is used with Method 8081. This is because of the sensitivity of the electron capture detector and the probability of the internal standard being affected by interferences. Because several of the pesticides may co-elute on any single column, analysts should use two calibration mixtures (Section 7.3.3). The specific mixture should be selected to minimize the problem of peak overlap.

NOTE: Because of the sensitivity of the electron capture detector, the injection port and column should always be cleaned prior to performing the initial calibration.

7.4.1.1 Method 8081 has many multi-component target analytes. For this reason, the choice of target analytes chosen for calibration should be limited to those specified in the project plan. Sites may require analysis for the organochlorine pesticides only or the PCBs only. Toxaphene and/or technical Chlordane may also not be specified at certain sites. In addition, where PCBs are specified in the project plan, a mixture of Aroclors 1016 and 1260 will suffice for the initial calibration of all Aroclors since they include all congeners present in the different regulated Aroclors. A mid-point calibration standard of all Aroclors must be included with the initial calibration so that the analyst is familiar with each Aroclor pattern and retention times on each column.

7.4.1.2 For calibration verification (each 12 hr shift) all target analytes required in the project plan must be injected with the following exception for the Aroclors. For sites that require PCB analysis, include only the Aroclors that are expected to be found at the site. If PCBs are required but it is unknown which Aroclors may be present, the mid-concentration Aroclors 1016/1260 mixture only, may be injected. However, if specific Aroclors are found at the site during the initial screening, it is required that the samples containing Aroclors be reinjected with the proper mid-concentration Aroclor standards.

7.4.2 Because of the low concentration of pesticide standards injected on a GC/ECD, column adsorption may be a problem when the GC has not been used for a day or more. Therefore, the GC column should be primed or deactivated by injecting a PCB or pesticide standard mixture

approximately 20 times more concentrated than the mid-concentration standard. Inject this standard mixture prior to beginning the initial calibration or calibration verification.

CAUTION: Several analytes, including Aldrin, may be observed in the injection just following this system priming. Always run an acceptable blank prior to running any standards or samples.

7.4.3 Retention time windows:

7.4.3.1 Before establishing the retention time windows, make sure the gas chromatographic system is within optimum operating conditions. The width of the retention time window should be based upon actual retention times of standards measured over the course of 72 hours. See Method 8000 for details.

7.4.3.2 Retention time windows shall be defined as plus or minus three times the standard deviation of the absolute retention times for each standard. However, the experience of the analyst should weigh heavily in the interpretation of the chromatograms. For multicomponent standards (i.e., PCBs), the analyst should use the retention time window but should primarily rely on pattern recognition. Section 7.5.4 provides guidance on the establishment of absolute retention time windows.

7.4.3.3 Certain analytes, particularly Kepone, are subject to changes in retention times. Dry Kepone standards prepared in hexane or isooctane can produce gaussian peaks. However, Kepone extracted from samples or standards exposed to water or methanol may produce peaks with broad tails that elute later than the standard (0-1 minute). This shift is presumably the result of the formation of a hemi-acetal from the ketone functionality. Method 8270 is recommended for Kepone.

7.5 Gas chromatographic analysis:

7.5.1 Set up the GC system using the conditions described in Tables 4, 6, or 7. An initial oven temperature at or below 140-150°C is required to resolve the four BHC isomers. A final temperature of 240-270°C is required to elute decachlorobiphenyl. Use of injector pressure programming will improve the chromatography of late eluting peaks.

7.5.2 Verify calibration each 12 hour shift by injecting calibration verification standards prior to conducting any analyses. See Section 7.4.1.2 for special guidance on calibration verification of PCBs. A calibration standard must also be injected at intervals of not less than once every twenty samples (after every 10 samples is recommended to minimize the number of samples requiring re-injection when QC is exceeded) and at the end of the analysis sequence. The calibration factor for each analyte to be quantitated must not exceed a ±15 percent difference when compared to the initial calibration curve. When this criterion is exceeded, inspect the gas chromatographic system to determine the cause and perform whatever maintenance is necessary before verifying calibration

and proceeding with sample analysis. If routine maintenance does not return the instrument performance to meet the QC requirements (Section 8.2) based on the last initial calibration, then a new initial calibration must be performed.

7.5.2.1 Analysts should use high and low concentrations of mixtures of single-component analytes and multi-component analytes for calibration verification.

7.5.3 Continuation of sample injection may continue for as long as the calibration verification standards and standards interspersed with the samples meet instrument QC requirements. It is recommended that standards be analyzed after every 10 (required after every 20 samples), and at the end of a set. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

7.5.3.1 Each sample analysis must be bracketed with an acceptable initial calibration, calibration verification standard(s) (each 12 hr shift), or calibration standards interspersed within the samples. All samples that were injected after the standard that last met the QC criteria must be reinjected.

7.5.3.2 Although analysis of a single mid-concentration standard (standard mixture or multi-component analyte) will satisfy the minimum requirements, analysts are urged to use different calibration verification standards during organochlorine pesticide/PCB analyses. Also, multi-level standards (mixtures or multi-component analytes) are highly recommended to ensure that detector response remains stable for all analytes over the calibration range.

7.5.4 Establish absolute retention time windows for each analyte. Use the absolute retention time for each analyte from standards analyzed during that 12 hour shift as the midpoint of the window. The daily retention time window equals the midpoint $\pm$ three times the standard deviations.

7.5.4.1 Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window.

7.5.4.2 Validation of gas chromatographic system qualitative performance: Use the calibration standards analyzed during the sequence to evaluate retention time stability. If any of the standards fall outside their daily retention time windows, the system is out of control. Determine the cause of the problem and correct it.

7.5.5 Record the volume injected to the nearest 0.05 μL and the resulting peak size in area units. Using either the internal or the external calibration procedure (Method 8000), determine the identity and the quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes.

7.5.5.1 If the responses exceed the calibration range of the system, dilute the extract and reanalyze. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

7.5.5.2 If partially overlapping or coeluting peaks are found, change columns or try GC/MS quantitation, see Section 8 and Method 8270.

7.5.5.3 If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The analyst should consult with the source of the sample to determine whether further concentration of the sample is warranted.

7.5.6 Identification of mixtures (i.e. PCBs and Toxaphene) is based on the characteristic "fingerprint" retention time and shape of the indicator peak(s); and quantitation is based on the area under the characteristic peaks as compared to the area under the corresponding calibration peak(s) of the same retention time and shape generated using either internal or external calibration procedures.

7.5.7 Quantitation of the target compounds is based on: 1) a reproducible response of the ECD or ELCD within the calibration range; and 2) a direct proportionality between the magnitude of response of the detector to peaks in the sample extract and the calibration standards. Proper quantitation requires the appropriate selection of a baseline from which the area or height of the characteristic peak(s) can be determined.

7.5.8 If compound identification or quantitation are precluded due to interference (e.g., broad, rounded peaks or ill-defined baselines are present) cleanup of the extract or replacement of the capillary column or detector is warranted. Rerun sample on another instrument to determine if the problem results from analytical hardware or the sample matrix. Refer to Method 3600 for the procedures to be followed in sample cleanup.

7.6 Quantitation of Multiple Component Analytes:

7.6.1 Multi-component analytes present problems in measurement. Suggestions are offered in the following sections for handing Toxaphene, Chlordane, PCB, DDT, and BHC.

7.6.2 Toxaphene: Toxaphene is manufactured by the chlorination of camphenes, whereas Strobane results from the chlorination of a mixture of camphenes and pinenes. Quantitative calculation of Toxaphene or Strobane is difficult, but reasonable accuracy can be obtained. To calculate toxaphene on GC/ECD: (a) adjust the sample size so that the major Toxaphene peaks are 10-70% of full-scale deflection (FSD); (b) inject a Toxaphene standard that is estimated to be within $\pm$10 ng of the sample; (c) quantitate using the five major peaks or the total area of the Toxaphene pattern.

7.6.2.1 To measure total area, construct the baseline of standard Toxaphene between its extremities; and construct the

baseline under the sample, using the distances of the peak troughs to baseline on the standard as a guide. This procedure is made difficult by the fact that the relative heights and widths of the peaks in the sample will probably not be identical to the standard.

7.6.2.2 A series of Toxaphene residues have been calculated using the total peak area for comparison to the standard and also using the area of the last four peaks only, in both sample and standard. The agreement between the results obtained by the two methods justifies the use of the latter method for calculating Toxaphene in a sample where the early eluting portion of the Toxaphene chromatogram shows interferences from other substances such as DDT.

7.6.3 Chlordane is a technical mixture of at least 11 major components and 30 or more minor components. *Trans*- and *cis*-Chlordane (α and γ), respectively, are the two major components of technical Chlordane. However, the exact percentage of each in the technical material is not completely defined, and is not consistent from batch to batch.

7.6.3.1 The GC pattern of a chlordane residue may differ considerably from that of the technical standard. Depending on the sample substrate and its history, residues of Chlordane can consist of almost any combination of: constituents from the technical Chlordane, plant and/or animal metabolites, and products of degradation caused by exposure to environmental factors such as water and sunlight.

7.6.3.2 Whenever possible, when Chlordane residue does not resemble technical Chlordane, the analyst should quantitate the peaks of α-Chlordane,γ-Chlordane, and heptachlor separately against the appropriate reference materials, and report the individual residues.

7.6.3.3 When the GC pattern of the residue resembles that of technical Chlordane, the analyst may quantitate Chlordane residues by comparing the total area of the Chlordane chromatogram using the five major peaks or the total area. If the heptachlor epoxide peak is relatively small, include it as part of the total Chlordane area for calculation of the residue. If heptachlor and/or heptachlor epoxide are much out of proportion, calculate these separately and subtract their areas from the total area to give a corrected chlordane area. (Note that octachloro epoxide, a metabolite of Chlordane, can easily be mistaken for heptachlor epoxide on a nonpolar GC column.)

7.6.3.4 To measure the total area of the Chlordane chromatogram, inject an amount of technical chlordane standard which will produce a chromatogram in which the major peaks are approximately the same size as those in the sample chromatograms.

7.6.4 Polychlorinated biphenyls (PCBs): Quantitation of residues of PCB involves problems similar to those encountered in the quantitation of Toxaphene, Strobane, and Chlordane. In each case, the chemical is made up

of numerous compounds which generate multi-peak chromatograms. Also, in each case, the chromatogram of the residue may not match that of the standard.

7.6.4.1 Mixtures of PCBs of various chlorine contents were sold for many years in the U.S. by the Monsanto Co. under the trade name Aroclor (1200 series and 1016). Although these Aroclors are no longer marketed, the PCBs remain in the environment and are sometimes found as residues in foods, especially fish. The Aroclors most commonly found in the environment are 1242, 1254, and 1260.

7.6.4.2 PCB residues are generally quantitated by comparison to the most similar Aroclor standard. A choice must be made as to which Aroclor is most similar to that of the residue and whether that standard is truly representative of the PCBs in the sample.

7.6.4.3 PCB Quantitation option #1- Quantitate the PCB residues by comparing the total area of the chlorinated biphenyl peaks to the total area of peaks from the appropriate Aroclor reference material. Measure the total area or height response from the common baseline under all the peaks. Use only those peaks from the sample that can be attributed to chlorobiphenyls. These peaks must also be present in the chromatogram of the reference materials. Option #1 should not be used if there are interference peaks within the Aroclor pattern, especially if they overlap PCB congeners.

7.6.4.4 PCB Quantitation option #2- Quantitate the PCB residues by comparing the responses of 3 to 5 major peaks in each appropriate Aroclor standard with the peaks obtained from the chlorinated biphenyls in the sample extract. The amount of Aroclor is calculated using an individual response factor for each of the major peaks. The results of the 3 to 5 determinations are averaged. Major peaks are defined as those peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. Late-eluting Aroclor peaks are generally the most stable in the environment.

7.6.4.5 When samples appear to contain weathered PCBs, treated PCBs or mixtures of Aroclors, use of Aroclor standards is not appropriate. Several diagnostic peaks useful for identifying non-Aroclor PCBs are identified in Table 10. Analysts should examine chromatographs containing these peaks carefully, as these samples may contain PCBs. PCB concentrations may be estimated from specific congeners by adding the concentration of the congener peaks listed in Table 11. The congeners are analyzed as single components. This approach will provide reasonable accuracy for Aroclors 1016, 1232, 1242 and 1248 but will underestimate the concentrations of Aroclors 1254, 1260 and 1221. It is highly recommended that heavily weathered, treated or mixed Aroclors be analyzed using GC/MS if concentration permits.

7.6.5 Hexachlorocyclohexane (BHC, from the former name, benzene hexachloride): Technical grade BHC is a cream-colored amorphous solid

with a very characteristic musty odor; it consists of a mixture of six chemically distinct isomers and one or more heptachlorocyclohexanes and octachlorocyclohexanes. Commercial BHC preparations may show a wide variance in the percentage of individual isomers present. Quantitate each isomer (α, β, γ, and δ) separately against a standard of the respective pure isomer.

7.6.6 DDT: Technical DDT consists primarily of a mixture of 4,4'-DDT (approximately 75%) and 2,4'-DDT (approximately 25%). As DDT weathers, 4,4'-DDE, 2,4'-DDE, 4,4'-DDD, and 2,4'-DDD are formed. Since the 4,4'-isomers of DDT, DDE, and DDD predominate in the environment, these are the isomers normally regulated by US EPA and should be quantitated against standards of the respective pure isomer.

7.7 Suggested chromatography maintenance: Corrective measures may require any one or more of the following remedial actions.

7.7.1 Splitter connections: For dual columns which are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector (J&W Scientific or Restek), clean and deactivate the splitter port insert or replace with a cleaned and deactivated splitter. Break off the first few inches (up to one foot) of the injection port side of the column. Remove the columns and solvent backflush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the columns.

7.7.1.1 GC injector ports can be of critical concern, especially in the analysis of DDT and Endrin. Injectors that are contaminated, chemically active, or too hot can cause the degradation ("breakdown") of the analytes. Endrin and DDT breakdown to endrin aldehyde, endrin ketone, DDD, or DDE. When such breakdown is observed, clean and deactivate the injector port, break off at least 0.5 M of the column and remount it. Check the injector temperature and lower it to 205°C, if required. Endrin and DDT breakdown is less of a problem when ambient on-column injectors are used.

7.7.2 Metal injector body: Turn off the oven and remove the analytical columns when the oven has cooled. Remove the glass injection port insert (instruments with on-column injection). Lower the injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

7.7.2.1 Place a beaker beneath the injector port inside the oven. Using a wash bottle, serially rinse the entire inside of the injector port with acetone and then toluene; catch the rinsate in the beaker.

7.7.2.2 Prepare a solution of a deactivating agent (Sylon-CT or equivalent) following manufacturer's directions. After all metal surfaces inside the injector body have been thoroughly coated

with the deactivation solution, rinse the injector body with toluene, methanol, acetone, then hexane. Reassemble the injector and replace the columns.

7.7.3 Column rinsing: The column should be rinsed with several column volumes of an appropriate solvent. Both polar and nonpolar solvents are recommended. Depending on the nature of the sample residues expected, the first rinse might be water, followed by methanol and acetone; methylene chloride is a good final rinse and in some cases may be the only solvent required. The column should then be filled with methylene chloride and allowed to stand flooded overnight to allow materials within the stationary phase to migrate into the solvent. The column is then flushed with fresh methylene chloride, drained, and dried at room temperature with a stream of ultrapure nitrogen.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control (QC) procedures including matrix spikes, duplicates and blanks. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If an extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Quality control requirements for the GC system, including calibration and corrective actions, are found in Method 8000. The following steps are recommended as additional method QC.

8.2.1 The laboratory control sample (LCS) concentrate (Method 8000) should contain the organochlorine pesticides at 10 mg/L for water samples. If this method is to be used for analysis of Aroclors, Chlordane or Toxaphene only, the LCS should contain the most representative multi-component mixture at a concentration of 50 mg/L in acetone. The frequency of analysis of the QC reference sample analysis is equivalent to a minimum of 1 per 20 samples or 1 per batch if less than 20 samples. If the recovery of any compound found in the QC reference sample is less than 80 percent or greater than 120 percent of the certified value, the laboratory performance is judged to be out of control, and the problem must be corrected. A new set of calibration standards should be prepared and analyzed.

8.2.2 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000).

If recovery is not within limits, the following are required:

8.2.2.1 Confirm that there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.

8.2.2.2 Examine chromatograms for interfering peaks and for integrated areas.

8.2.2.3 Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

8.2.2.4 Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.2.3 Include a calibration standard after each group of 20 samples (it is recommended that a calibration standard be included after every 10 samples to minimize the number of repeat injections) in the analysis sequence as a calibration check. The response factors for the calibration should be within 15 percent of the initial calibration. When this continuing calibration is out of this acceptance window, the laboratory should stop analyses and take corrective action.

8.2.4 Whenever quantitation is accomplished using an internal standard, internal standards must be evaluated for acceptance. The measured area of the internal standard must be no more than 50 percent different from the average area calculated during calibration. When the internal standard peak area is outside the limit, all samples that fall outside the QC criteria must be reanalyzed.

8.3 DDT and Endrin are easily degraded in the injection port. Breakdown occurs when the injection port liner is contaminated high boiling residue from sample injection or when the injector contains metal fittings. Check for degradation problems by injecting a standard containing only 4,4'-DDT and Endrin. Presence of 4,4'-DDE, 4,4'-DDD, Endrin ketone or Endrin indicates breakdown. If degradation of either DDT or Endrin exceeds 15%, take corrective action before proceeding with calibration.

8.3.1 Calculate percent breakdown as follows:

$$\%\ \text{breakdown for 4,4'-DDT} = \frac{\text{Total DDT degradation peak area (DDE + DDD)}}{\text{peak areas (DDT + DDE + DDD)}} \times 100$$

$$\%\ \text{breakdown for Endrin} = \frac{\text{Total endrin degradation peak area (endrin aldehyde + endrin ketone)}}{\text{peak areas (endrin + aldehyde + ketone)}} \times 100$$

8.3.2 The breakdown of DDT and endrin should be measured before samples are analyzed and at the beginning of each 12 hour shift. Injector maintenance and recalibration should be completed if the breakdown is greater than 15% for either compound (Section 8.2.3).

8.4 GC/MS confirmation may be used for single column analysis. In addition, any compounds confirmed by two columns should also be confirmed by GC/MS if the concentration is sufficient for detection by GC/MS.

8.4.1 Full-scan GC/MS will normally require a minimum concentration near 10 ng/μL in the final extract for each single-component compound. Ion trap or selected ion monitoring will normally require a minimum concentration near 1 ng/ L.

8.4.2 The GC/MS must be calibrated for the specific target pesticides when it is used for quantitative analysis.

8.4.3 GC/MS may not be used for single column confirmation when concentrations are below 1 ng/ L.

8.4.4 GC/MS confirmation should be accomplished by analyzing the same extract used for GC/ECD analysis and the associated blank.

8.4.5 Use of the base/neutral-acid extract and associated blank may be used if the surrogates and internal standards do not interfere and it is demonstrated that the analyte is stable during acid/base partitioning. However, if the compounds are not detected in the base/neutral-acid extract even though the concentrations are high enough, a GC/MS analysis of the pesticide extract should be performed.

8.4.6 A QC reference sample of the compound must also be analyzed by GC/MS. The concentration of the QC reference standard must demonstrate the ability to confirm the pesticides/Aroclors identified by GC/ECD.

8.5 Whenever silica gel (Method 3630) or Florisil (Method 3620) cleanup is used, demonstrate that the fractionation scheme is reproducible. Batch to batch variation in the composition of the silica gel material or overloading the column may cause a change in the distribution patterns of the organochlorine pesticides and PCBs. When compounds are found in two fractions, add the concentrations in the fractions, and corrections for any additional dilution.

9.0 METHOD PERFORMANCE

9.1 The MDL is defined in Chapter One. The MDL concentrations listed in Tables 1 and 2 were obtained using organic-free reagent water and sandy loam soil.

9.2 The chromatographic separations in method has been tested in a single laboratory by using clean hexane and liquid and solid waste extracts that were spiked with the test compounds at three concentrations. Single-operator precision, overall precision, and method accuracy were found to be related to the concentration of the compound and the type of matrix.

9.3 This method has been applied in a variety of commercial laboratories for environmental and waste matrices. Performance data for a limited number of target analytes spiked into sewage sludge and dichloroethene still bottoms at high concentration levels. These data are provided in Tables 12 and 13.

9.4 The accuracy and precision obtainable following this method depends on the sample matrix, sample preparation technique, optional cleanup techniques, and calibration procedures used.

9.5 Single laboratory accuracy data were obtained for organochlorine pesticides in a clay soil. The spiking concentration was 500 µg/kg. The spiking solution was mixed into the soil during addition and then immediately transferred to the extraction device and immersed in the extraction solvent. The spiked sample was then extracted by Method 3541 (Automated Soxhlet). The data

represents a single determination. Analysis was by capillary column gas chromatography/electron capture detector following Method 8081 for the organochlorine pesticides. These data are listed in Table 14 and were taken from Reference 14.

9.6 Single laboratory recovery data were obtained for PCBs in clay and soil. Oak Ridge National Laboratory spiked Aroclors 1254 and 1260 at concentrations of 5 and 50 ppm into portions of clay and soil samples and extracted using the procedure outlined in Method 3541. Multiple extractions using two different extractors were performed. The extracts were analyzed by Method 8080. The data are listed in Table 15 and were taken from Reference 15.

9.7 Multi-laboratory accuracy and precision data were obtained for PCBs in soil. Eight laboratories spiked Aroclors 1254 and 1260 into three portions of 10 g of Fuller's Earth on three non-consecutive days followed by immediate extraction using Method 3541. Six of the laboratories spiked each Aroclor at 5 and 50 mg/kg and two laboratories spiked each Aroclor at 50 and 500 mg/kg. All extracts were analyzed by Oak Ridge National Laboratory, Oak Ridge, TN using Method 8080. These data are listed in Table 16 and were taken from Reference 13.

10.0 REFERENCES

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TABLE 1

GAS CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS FOR THE ORGANOCHLORINE PESTICIDES AND PCBs AS AROCLORS[a] USING WIDE-BORE CAPILLARY COLUMNS SINGLE COLUMN METHOD OF ANALYSIS

Compound	Retention Time (min) DB 608[c]	DB 1701[c]	MDL[b] Water (µg/L)	MDL[b] Soil (µg/kg)
Aldrin	11.84	12.50	0.034	2.2
α-BHC	8.14	9.46	0.035	1.9
ß-BHC	9.86	13.58	0.023	3.3
δ-BHC	11.20	14.39	0.024	1.1
γ-BHC (Lindane)	9.52	10.84	0.025	2.0
α-Chlordane	15.24	16.48	0.008	
γ-Chlordane	14.63	16.20	0.037	1.5
4,4'-DDD	18.43	19.56	0.050	4.2
4,4'-DDE	16.34	16.76	0.058	2.5
4,4'-DDT	19.48	20.10	0.081	3.6
Dieldrin	16.41	17.32	0.044	NA
Endosulfan I	15.25	15.96	0.030	2.1
Endosulfan II	18.45	19.72	0.040	2.4
Endosulfan Sulfate	20.21	22.36	0.035	3.6
Endrin	17.80	18.06	0.039	3.6
Endrin aldehyde	19.72	21.18	0.050	1.6
Heptachlor	10.66	11.56	0.040	2.0
Heptachlor epoxide	13.97	15.03	0.032	2.1
Methoxychlor	22.80	22.34	0.086	5.7
Toxaphene	MR	MR	NA	NA
Aroclor-1016	MR	MR	0.054	57.0
Aroclor-1221	MR	MR	NA	NA
Aroclor-1232	MR	MR	NA	NA
Aroclor-1242	MR	MR	NA	NA
Aroclor-1248	MR	MR	NA	NA
Aroclor-1254	MR	MR	NA	NA
Aroclor-1260	MR	MR	0.90	70.0

Water = Organic-free reagent water.
Soil = Sandy loam soil.
MR = Multiple peak responses.
NA = Data not available.

[a] Aqueous MDLs from U.S. EPA Method 8081. Organochlorine Pesticides and PCBs as Aroclors. Environmental Protection Agency. Office of Research and Development, Washington, DC 20460.

TABLE 1
(Continued)

[b] MDL is the method detection limit. MDL was determined from the analysis of seven replicate aliquots of each matrix processed through the entire analytical method (extraction, silica gel cleanup, and GC/ECD analysis). MDL = t(n-1, 0.99) x SD, where t(n-1, 0.99) is the student's t value appropriate for a 99% confidence interval and a standard deviation with n-1 degrees of freedom, and SD is the standard deviation of the seven replicate measurements.

[c] See Table 4 for GC operating conditions.

TABLE 2

GAS CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS FOR THE ORGANOCHLORINE PESTICIDES AND PCBs AS AROCLORS[a] USING NARROW-BORE CAPILLARY COLUMNS SINGLE COLUMN METHOD OF ANALYSIS

Compound	Retention Time (min) DB 608[c]	DB 5[d]	MDL[b] Water (µg/L)	MDL[b] Soil (µg/kg)
Aldrin	14.51	14.70	0.034	2.2
α-BHC	11.43	10.94	0.035	1.9
ß-BHC	12.59	11.51	0.023	3.3
δ-BHC	13.69	12.20	0.024	1.1
γ-BHC (Lindane)	12.46	11.71	0.025	2.0
α-Chlordane				
γ-Chlordane	17.34	17.02	0.037	1.5
4,4′-DDD	21.67	20.11	0.050	4.2
4,4′-DDE	19.09	18.30	0.058	2.5
4,4′-DDT	23.13	21.84	0.081	3.6
Dieldrin	19.67	18.74	0.044	NA
Endosulfan I	18.27	17.62	0.030	2.1
Endosulfan II	22.17	20.11	0.040	2.4
Endosulfan sulfate	24.45	21.84	0.035	3.6
Endrin	21.37	19.73	0.039	3.6
Endrin aldehyde	23.78	20.85	0.050	1.6
Heptachlor	13.41	13.59	0.040	2.0
Heptachlor epoxide	16.62	16.05	0.032	2.1
Methoxychlor	28.65	24.43	NA	NA
Toxaphene	MR	MR	0.086	5.7
Aroclor-1016	MR	MR	NA	NA
Aroclor-1221	MR	MR	0.054	57.0
Aroclor-1232	MR	MR	NA	NA
Aroclor-1242	MR	MR	NA	NA
Aroclor-1248	MR	MR	NA	NA
Aroclor-1254	MR	MR	NA	NA
Aroclor-1260	MR	MR	0.90	70.0

Liquid = Organic-free reagent water.
Solid = Sandy loam soil.
MR = Multiple peak responses.
NA = Data not available.

TABLE 2
(Continued)

[a] Aqueous MDLs from U.S. EPA Method 8081. Organochlorine Pesticides and PCBs as Aroclors. Environmental Protection Agency. Office of Research and Development, Washington, DC 20460.

[b] MDL is the method detection limit. MDL was determined from the analysis of seven replicate aliquots of each matrix processed through the entire analytical method (extraction, cleanup, and GC/ECD analysis). MDL = t(n-1, 0.99) x SD, where t(n-1, 0.99) is the student's t value appropriate for a 99% confidence interval and a standard deviation with n-1 degrees of freedom, and SD is the standard deviation of the seven replicate measurements.

[c] 30 m x 0.25 mm ID DB 608 1 µm film thickness, see Table 4 for GC operating conditions.

[d] 30 m x 0.25 mm ID DB 5 1 µm film thickness, see Table 4 for GC operating conditions.

TABLE 3

ESTIMATED QUANTITATION LIMITS (EQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-concentration soil by sonication with GPC cleanup	670
High-concentration soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a] Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

[b] EQL = [Method detection limit for water (Table 1) or (Table 2) wide bore or narrow bore options] x [Factor (Table 3)]. For nonaqueous samples, the factor is on a wet-weight basis.

TABLE 4
GC OPERATING CONDITIONS FOR ORGANOCHLORINE COMPOUNDS
SINGLE COLUMN ANALYSIS

Narrow-bore columns:

Narrow-bore Column 1 - 30 m x 0.25 or 0.32 mm internal diameter (ID) fused silica capillary column chemically bonded with SE-54 (DB 5 or equivalent), 1 μm film thickness.

Carrier gas (He)	16 psi
Injector temperature	225°C
Detector temperature	300°C
Initial temperature	100°C, hold 2 minutes
Temperature program	100°C to 160°C at 15°C/min, followed by 160°C to 270°C at 5°C/min
Final temperature	270°C

Narrow-bore Column 2 - 30 m x 0.25 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB 608, SPB 608, or equivalent), 25 μm coating thickness, 1 μm film thickness

Carrier gas (N_2)	20 psi
Injector temperature	225°C
Detector temperature	300°C
Initial temperature	160°C, hold 2 minutes
Temperature program	160°C to 290°C at 5°C/min
Final temperature	290°C, hold 1 min

Wide-bore columns:

Wide-bore Column 1 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB 608, SPB 608, RTx-35, or equivalent), 0.5 μm or 0.83 μm film thickness.

Wide-bore Column 2 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 50 percent phenyl methylpolysiloxane (DB 1701, or equivalent), 1.0 μm film thickness.

Carrier gas (He)	5-7 mL/minute
Makeup gas	
argon/methane (P-5 or P-10) or N_2	30 mL/min
Injector temperature	250°C
Detector temperature	290°C
Initial temperature	150°C, hold 0.5 minute
Temperature program	150°C to 270°C at 5°C/min
Final temperature	270°C, hold 10 min

TABLE 4 (Continued)
GC OPERATING CONDITIONS FOR ORGANOCHLORINE COMPOUNDS
SINGLE COLUMN ANALYSIS

Wide-bore Column 3 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with SE-54 (DB 5, SPB 5, RTx, or equivalent), 1.5 μm film thickness.

Carrier gas (He)	6 mL/minute
Makeup gas argon/methane (P-5 or P-10) or N_2	30 mL/min
Injector temperature	205°C
Detector temperature	290°C
Initial temperature	140°C, hold 2 min
Temperature program	140°C to 240°C at 10°C/min, hold 5 minutes at 240°C, 240°C to 265°C at 5°C/min
Final temperature	265°C, hold 18 min

TABLE 5
RETENTION TIMES OF THE ORGANOCHLORINE PESTICIDES[a]
DUAL COLUMN METHOD OF ANALYSIS

Compound No.	Compound	CAS No.	DB-5 RT(min)	DB-1701 RT(min)
1	DBCP	96-12-8	2.14	2.84
2	Hexachlorocyclopentadiene	77-47-4	4.49	4.88
3	Etridiazole	2593-15-9	6.38	8.42
4	Chloroneb	2675-77-6	7.46	10.60
5	Hexachlorobenzene	118-74-1	12.79	14.58
6	Diallate	2303-16-4	12.35	15.07
7	Propachlor	1918-16-17	9.96	15.43
8	Trifluralin	1582-09-8	11.87	16.26
9	α-BHC	319-84-6	12.35	17.42
10	PCNB	82-68-8	14.47	18.20
11	γ-BHC	58-89-9	14.14	20.00
12	Heptachlor	76-44-8	18.34	21.16
13	Aldrin	309-00-2	20.37	22.78
14	Alachlor	15972-60-8	18.58	24.18
15	Chlorothalonil	1897-45-6	15.81	24.42
14	Alachlor	15972-60-8	18.58	24.18
16	ß-BHC	319-85-7	13.80	25.04
17	Isodrin	465-73-6	22.08	25.29
18	DCPA	1861-32-1	21.38	26.11
19	δ-BHC	319-86-8	15.49	26.37
20	Heptachlor epoxide	1024-57-3	22.83	27.31
21	Endosulfan-I	959-98-8	25.00	28.88
22	γ-Chlordane	5103-74-2	24.29	29.32
23	α-Chlordane	5103-71-9	25.25	29.82
24	*trans*-Nonachlor	39765-80-5	25.58	30.01
25	4,4'-DDE	72-55-9	26.80	30.40
26	Dieldrin	60-57-1	26.60	31.20
27	Captan	133-06-2	23.29	31.47
28	Perthane	72-56-0	28.45	32.18
29	Endrin	72-20-8	27.86	32.44
30	Chloropropylate	99516-95-7	28.92	34.14
31	Chlorobenzilate	510-15-6	28.92	34.42
32	Nitrofen	1836-75-5	27.86	34.42
33	4,4'-DDD	72-54-8	29.32	35.32
34	Endosulfan II	33213-65-9	28.45	35.51
35	4,4'-DDT	50-29-3	31.62	36.30
36	Endrin aldehyde	7421-93-4	29.63	38.08
37	Mirex	2385-85-5	37.15	38.79
38	Endosulfan sulfate	1031-07-8	31.62	40.05

continued

TABLE 5
(Continued)

Compound No.	Compound	CAS No.	DB-5 RT(min)	DB-1701 RT(min)
39	Methoxychlor	72-43-5	35.33	40.31
40	Captafol	2425-06-1	32.65	41.42
41	Endrin ketone	53494-70-5	33.79	42.26
42	*trans*-Permethrin	51877-74-8	41.50	45.81
43	Kepone	143-50-0	31.10	b
44	Dicofol	115-32-2	35.33	b
45	Dichlone	117-80-6	15.17	b
IS	α,α´-Dibromo-m-xylene		9.17	11.51
SU	2-Bromobiphenyl		8.54	12.49

[a]The GC operating conditions were as follows: 30-m x 0.53-mm ID DB-5 (0.83- m film thickness) and 30-m x 0.53-mm ID DB-1701 (1.0-µm film thickness) connected to an 8-in injection tee (Supelco Inc.). Temperature program: 140°C (2-min hold) to 270°C (1-min hold) at 2.8°C/min; injector temperature 250°C; detector temperature 320°C; helium carrier gas 6 mL/min; nitrogen makeup gas 20 mL/min.
[b]Not detected at 2 ng per injection.

TABLE 6
GC OPERATING CONDITIONS FOR ORGANOCHLORINE PESTICIDES
FOR DUAL COLUMN METHOD OF ANALYSIS
LOW TEMPERATURE, THIN FILM

Column 1:

Type: DB-1701 (J&W) or equivalent
Dimensions: 30 m x 0.53 mm ID
Film Thickness (µm): 1.0

Column 2:

Type: DB-5 (J&W) or equivalent
Dimensions: 30 m x 0.53 mm ID
Film Thickness (µm): 0.83

Carrier gas flowrate (mL/min): 6 (Helium)

Makeup gas flowrate (mL/min): 20 (Nitrogen)

Temperature program: 140°C (2 min hold) to 270°C (1 min hold) at 2.8°C/min

Injector temperature: 250°C

Detector temperature: 320°C

Injection volume: 2 µL

Solvent: Hexane

Type of injector: Flash vaporization

Detector type: Dual ECD

Range: 10

Attenuation: 64 (DB-1701)/32 (DB-5)

Type of splitter: Supelco 8 in injection tee

TABLE 7
GC OPERATING CONDITIONS FOR ORGANOCHLORINE PESTICIDES
FOR THE DUAL COLUMN METHOD OF ANALYSIS
HIGH TEMPERATURE, THICK FILM

Column 1:

Type: DB-1701 (J&W) or equivalent
Dimensions: 30 m x 0.53 mm ID
Film Thickness (µm): 1.0

Column 2:

Type: DB-5 (J&W) or equivalent
Dimensions: 30 m x 0.53 mm ID
Film Thickness (µm): 1.5

Carrier gas flowrate (mL/min): 6 (Helium)

Makeup gas flowrate (mL/min): 20 (Nitrogen)

Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Injector temperature: 250°C

Detector temperature: 320°C

Injection volume: 2 µL

Solvent: Hexane

Type of injector: Flash vaporization

Detector type: Dual ECD

Range: 10

Attenuation: 64 (DB-1701)/64 (DB-5)

Type of splitter: J&W Scientific press-fit Y-shaped inlet splitter

TABLE 8 SUMMARY OF RETENTION TIMES (MIN) OF AROCLORS ON THE DB-5 COLUMN[a] DUAL SYSTEM OF ANALYSIS

Peak No.[b]	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Pesticide eluting at same retention time
1		5.85	5.85					
2		7.63	7.64	7.57				
3	8.41	8.43	8.43	8.37				
4	8.77	8.77	8.78	8.73				
5	8.98	8.99	9.00	8.94	8.95			
6	9.71			9.66				
7	10.49	10.50	10.50	10.44	10.45			
8	10.58	10.59	10.59	10.53				
9	10.90		10.91	10.86	10.85			
10	11.23	11.24	11.24	11.18	11.18			Chlorothalonil (11.18)
11	11.88		11.90	11.84	11.85			
12	11.99		12.00	11.95				
13	12.27	12.29	12.29	12.24	12.24			
14	12.66	12.68	12.69	12.64	12.64			
15	12.98	12.99	13.00	12.95	12.95			
16	13.18		13.19	13.14	13.15			
17	13.61		13.63	13.58	13.58	13.59	13.59	
18	13.80		13.82	13.77	13.77	13.78		
19	13.96		13.97	13.93	13.93	13.90		
20	14.48		14.50	14.46	14.45	14.46		
21	14.63		14.64	14.60	14.60			
22	14.99		15.02	14.98	14.97	14.98		
23	15.35		15.36	15.32	15.31	15.32		
24	16.01			15.96				
25			16.14	16.08	16.08	16.10		
26	16.27		16.29	16.26	16.24	16.25	16.26	Captan (16.21)
27						16.53		
28			17.04		16.99	16.96	16.97	gamma-Chlordane (16.95)
29			17.22	17.19	17.19	17.19	17.21	
30			17.46	17.43	17.43	17.44		
31					17.69	17.69		
32				17.92	17.91	17.91		
33				18.16	18.14	18.14		
34			18.41	18.37	18.36	18.36	18.37	4,4'-DDE (18.38)
35			18.58	18.56	18.55	18.55		Dieldrin (18.59)
36							18.68	
37			18.83	18.80	18.78	18.78	18.79	
38			19.33	19.30	19.29	19.29	19.29	
39						19.48	19.48	
40						19.81	19.80	
41			20.03	19.97	19.92	19.92		Chloropropylate (19.91) Endosulfan II (19.91)
42						20.28	20.28	
43				20.46	20.45			
44						20.57	20.57	
45				20.85	20.83	20.83	20.83	
46			21.18	21.14	21.12	20.98		Kepone (20.99)
47					21.36	21.38	21.38	
48						21.78	21.78	4,4'-DDT (21.75) Endosulfan sulfate (21.75)
49				22.08	22.05	22.04	22.03	
50						22.38	22.37	
51						22.74	22.73	Captafol (22.71)
52						22.96	22.95	
53						23.23	23.23	
54							23.42	
55						23.75	23.73	Endrin ketone (23.73)

(continued)

[a]The GC operating conditions are given in Table 7.

TABLE 8 CONTINUED

Peak No.	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Pesticide eluting at same retention time
56						23.99	23.97	
57							24.16	
58						24.27		Methoxychlor (24.29) Dicofol (24.29)
59							24.45	
60						24.61	24.62	
61						24.93	24.91	
62							25.44	
63						26.22	26.19	Mirex (26.19)
64							26.52	
65							26.75	
66							27.41	
67							28.07	
68							28.35	
69							29.00	

[a]The GC operating conditions are given in Table 7.
[b]These are sequentially numbered from elution order and are not isomer numbers

TABLE 9 SUMMARY OF RETENTION TIMES (MIN) OF AROCLORS ON THE DB-1701 COLUMN[a] DUAL SYSTEM OF ANALYSIS

Peak No.[b]	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Pesticide eluting at same retention time
1		4.45	4.45					
2		5.38						
3		5.78						
4		5.86	5.86					
5	6.33	6.34	6.34	6.28				
6	6.78	6.78	6.79	6.72				
7	6.96	6.96	6.96	6.90	6.91			Trifluralin (6.96)
8	7.64			7.59				
9	8.23	8.23	8.23	8.15	8.16			
10	8.62	8.63	8.63	8.57				
11	8.88		8.89	8.83	8.83			
12	9.05	9.06	9.06	8.99	8.99			
13	9.46		9.47	9.40	9.41			
14	9.77	9.79	9.78	9.71	9.71			
15	10.27	10.29	10.29	10.21	10.21			
16	10.64	10.65	10.66	10.59	10.59			
17				10.96	10.95	10.95		
18	11.01		11.02	11.02	11.03			
19	11.09		11.10					
20	11.98		11.99	11.94	11.93	11.93		
21	12.39		12.39	12.33	12.33	12.33		
22			12.77	12.71	12.69			
23	12.92			12.94	12.93			
24	12.99		13.00	13.09	13.09	13.10		
25	13.14		13.16					
26						13.24		
27	13.49		13.49	13.44	13.44			
28	13.58		13.61	13.54	13.54	13.51	13.52	
29				13.67		13.68		
30			14.08	14.03	14.03	14.03	14.02	
31			14.30	14.26	14.24	14.24	14.25	
32					14.39	14.36		
33			14.49	14.46	14.46			
34						14.56	14.56	
35					15.10	15.10		
36			15.38	15.33	15.32	15.32		Chlordane (15.32)
37			15.65	15.62	15.62	15.61	16.61	4,4'-DDE (15.67)
38			15.78	15.74	15.74	15.74	15.79	
39			16.13	16.10	16.10	16.08		
40							16.19	
41						16.34	16.34	
42						16.44	16.45	
43						16.55		
44			16.77	16.73	16.74	16.77	16.77	Perthane (16.71)
45			17.13	17.09	17.07	17.07	17.08	
46						17.29	17.31	
47				17.46	17.44	17.43	17.43	
48				17.69	17.69	17.68	17.68	
49					18.19	18.17	18.18	
50				18.48	18.49	18.42	18.40	
51						18.59		
52						18.86	18.86	
53				19.13	19.13	19.10	19.09	Endosulfan II (19.05)
54						19.42	19.43	

(continued)

[a]The GC operating conditions are given in Table 7.

TABLE 9 CONTINUED

Peak No.	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Pesticide eluting at same retention time
55						19.55	19.59	4,4'-DDT (19.54)
56						20.20	20.21	
57						20.34		
58							20.43	
59					20.57	20.55		
60						20.62	20.66	Endrin aldehyde (20.69)
61						20.88	20.87	
62							21.03	
63						21.53	21.53	
64						21.83	21.81	
65						23.31	23.27	
66							23.85	
67							24.11	
68							24.46	
69							24.59	
70							24.87	
71							25.85	
72							27.05	
73							27.72	

[a]The GC operating conditions are given in Table 7.
[b]These are sequentially numbered from elution order and are not isomer numbers

TABLE 10
PEAKS DIAGNOSTIC OF PCBs OBSERVED IN 0.53 mm ID COLUMN
SINGLE COLUMN ANALYSIS

Peak No.[c]	RT on DB 608[a]	RT on DB 1701[a]	Aroclor[b]	Retention Window
I	4.90	4.66	1221	Before TCmX
II	7.15	6.96	1221, 1232, 1248	Before α-BHC
III	7.89	7.65	1061, 1221, 1232, 1242,	Before α-BHC
IV	9.38	9.00	1016, 1232, 1242, 1248,	just after α-BHC on DB 1701;just before γ-BHC on DB 608
V	10.69	10.54	1016, 1232, 1242,	1248 α-BHC and heptachlor on DB 1701; just after heptachlor on DB 608
VI	14.24	14.12	1248, 1254	γ-BHC and heptachlor epoxide on DB 1701; heptachlor epoxide and γ- Chlordane on DB 608
VII	14.81	14.77	1254	Heptachlor epoxide and γ-Chlordane on DB 1701; α- and γ-Chlordane on DB 608
VIII	16.71	16.38	1254	DDE and Dieldrin on DB 1701; Dieldrin and Endrin on DB 608
IX	19.27	18.95	1254, 1260	Endosulfan II on DB 1701; DDT on DB 608

Continued

TABLE 10 (Continued)
PEAKS DIAGNOSTIC OF PCBs OBSERVED IN 0.53 mm ID COLUMN
SINGLE COLUMN ANALYSIS

Peak No.	RT on DB 608[a]	RT on DB 1701[a]	Aroclor[b]	Retention Window
X	21.22	21.23	1260	Endrin aldehyde and Endosulfan sulfate on DB 1701; Endosulfan sulfate and Methoxychlor on on DB 608
XI	22.89	22.46	1260	Just before endrin ketone on DB 1701; after endrin ketone on DB 608

[a] Using oven temperature program: T_i = 150°C, hold 30 seconds; increase temperature at 5°C/minutes to 275°C.

[b] Underlined Aroclor indicates the largest peak in the pattern.

[c] These are sequentially numbered from elution order and are not isomer numbers

TABLE 11 SPECIFIC PCB CONGENERS IN AROCLORS

Congener	IUPAC number	Aroclor 1016	1221	1232	1242	1248	1254	1260
Biphenyl	--		X					
2CB	1	X	X	X	X			
23DCB	5	X	X	X	X	X		
34DCB	12	X		X	X	X		
244'TCB	28*	X		X	X	X	X	
22'35'TCB	44			X	X	X	X	
23'44'TCB	66*					X	X	X
233'4'6PCB	110						X	
23'44'5PCB	118*						X	X
22'44'55'HCB	153							X
22'344'5'HCB	138							X
22'344'55'HpCB	180							X
22'33'44'5HpCB	170							X

*apparent co-elution of two major peaks:

28 with 31 (2,4',5 trichloro)
66 with 95 (2,2',3,5',6 pentachloro)
118 with 149 (2,2',3,4',5',6 hexachloro)

TABLE 12 ANALYTE RECOVERY FROM SEWAGE SLUDGE

Compound	Sonication		Soxhlet	
	Recovery%	%RSD	Recovery	%RSD
Hexachloroethane	80	7	79	1
2-Chloronapthalene	50	56	67	8
4-Bromodiphenyl ether	118	14	nd	
a-BHC	88	25	265	18
g-BHC	55	9	155	29
Heptachlor	60	13	469	294
Aldrin	92	33	875	734
b-BHC	351	71	150	260
d-BHC	51	11	57	2
Heptachlor epoxide	54	11	70	3
Endosulfan I	52	11	70	4
g-Chlordane	50	9	65	1
a-Chlordane	49	8	66	0
DDE	52	11	74	1
Dieldrin	89	19	327	7
Endrin	56	10	92	15
Endosulfan II	52	10	88	11
DDT	57	10	95	17
Endrin aldehyde	45	6	42	10
DDD	57	11	99	8
Tetrachloro-m-xylene	71	19	82	1
Decachlorobiphenyl	26	23	28	48

Concentration spiked in the sample: 500-1000 ng/g
Three replicates/sample

Extraction solvent, Method 3540 - methylene chloride
Extraction solvent, Method 3550 - methylene chloride/acetone (1:1)

Cleanup - Method 3640

GC column - DB-608, 30M X 0.53 mm id

TABLE 13 ANALYTE RECOVERY FROM DCE STILL BOTTOMS

Compound	Sonication		Soxhlet	
	Recovery%	%RSD	Recovery	%RSD
Hexachloroethane	70	2	50	30
2-Chloronapthalene	59	3	35	35
4-Bromodiphenyl ether	159	14	128	137
a-BHC	55	7	47	25
g-BHC	43	6	30	30
Heptachlor	48	6	55	18
Aldrin	48	5	200	258
b-BHC	51	7	75	42
d-BHC	43	4	119	129
Heptachlor epoxide	47	6	66	34
Endosulfan I	47	4	41	18
g-Chlordane	48	5	47	13
a-Chlordane	45	5	37	21
DDE	45	4	70	40
Dieldrin	45	5	58	24
Endrin	50	6	41	23
Endosulfan II	49	5	46	17
DDT	49	4	40	29
Endrin aldehyde	40	4	29	20
DDD	48	5	35	21
Tetrachloro-m-xylene	49	2	176	211
Decachlorobiphenyl	17	29	104	93

Concentration spiked in the sample: 500-1000 ng/g
Three replicates/sample

Extraction solvent, Method 3540 - methylene chloride
Extraction solvent, Method 3550 - methylene chloride/acetone (1:1)

Cleanup - Method 3640

GC column - DB-608, 30M X 0.53 mm id

TABLE 14
SINGLE LABORATORY ACCURACY DATA FOR THE EXTRACTION OF ORGANOCHLORINE PESTICIDES FROM SPIKED CLAY SOIL BY METHOD 3541 (AUTOMATED SOXHLET)[a]

Compound Name	Spike Level	% Recovery	
	µg/kg	DB-5	DB-1701
alpha-BHC	500	89	94
delta-BHC	500	86	b
Heptachlor	500	94	95
Aldrin	500	b	92
Heptachlor epoxide	500	97	97
trans-Chlordane	500	94	95
Endosulfan I	500	92	92
Dieldrin	500	b	113
Endrin	500	111	104
Endosulfan II	500	104	104
4,4'-DDT	500	b	b
Mirex	500	108	102

a The operating conditions for the automated Soxhlet were as follows: immersion time 45 min; extraction time 45 min; the sample size was 10 g clay soil, extraction solvent, 1:1 acetone/hexane. No equilibration time following spiking.

b Not able to determine because of interference.

Data taken from Reference 14.

TABLE 15
Single Laboratory Recovery Data for Extraction of
PCBs from Clay and Soil by Method 3541[a] (Automated Soxhlet)

Matrix	Compound	Spike Level (ppm)	Trial	Percent Recovery[b]
Clay	Aroclor-1254	5	1	87.0
			2	92.7
			3	93.8
			4	98.6
			5	79.4
			6	28.3
Clay	Aroclor-1254	50	1	65.3
			2	72.6
			3	97.2
			4	79.6
			5	49.8
			6	59.1
Clay	Aroclor-1260	5	1	87.3
			2	74.6
			3	60.8
			4	93.8
			5	96.9
			6	113.1
Clay	Aroclor-1260	50	1	73.5
			2	70.1
			3	92.4
			4	88.9
			5	90.2
			6	67.3
Soil	Aroclor-1254	5	1	69.7
			2	89.1
			3	91.8
			4	83.2
			5	62.5
Soil	Aroclor-1254	50	1	84.0
			2	77.5
			3	91.8
			4	66.5
			5	82.3
			6	61.6

(continued)

TABLE 15
(continued)

Matrix	Compound	Spike Level (ppm)	Trial	Percent Recovery[b]
Soil	Aroclor-1260	5	1	83.9
			2	82.8
			3	81.6
			4	96.2
			5	93.7
			6	93.8
			7	97.5
Soil	Aroclor-1260	50	1	76.9
			2	69.4
			3	92.6
			4	81.6
			5	83.1
			6	76.0

a The operating conditions for the automated Soxhlet were as follows: immersion time 60 min; reflux time 60 min.

b Multiple results from two different extractors.

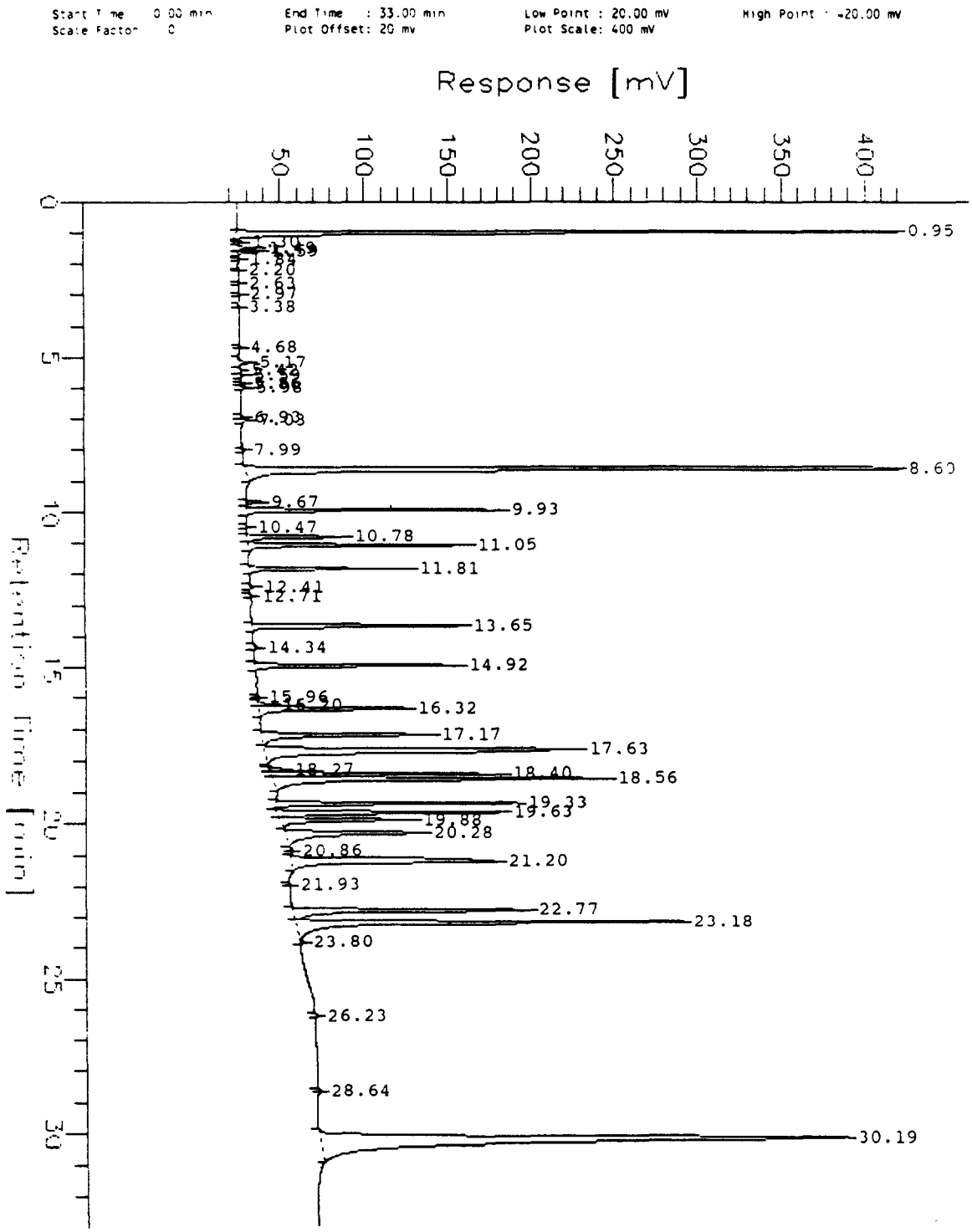
Data from Reference 15.

Table 16. Multi-Laboratory Precision and Accuracy Data for the Extraction of PCBs from Spiked Soil by Method 3541 (Automated Soxhlet)

PCB Percent Recovery (%)		Aroclor						All Levels
		1254			1260			
		PCB Level			PCB Level			
Laboratory		5	50	500	5	50	500	
Lab 1	Num	3.0	3.0		3.0	3.0		12.0
	Average	101.2	74.0		83.9	78.5		84.4
	St Dev	34.9	41.8		7.4	7.4		26.0
Lab 2	Num		6.0	6.0		6.0	6.0	24.0
	Average		56.5	66.9		70.1	74.5	67.0
	St Dev		7.0	15.4		14.5	10.3	13.3
Lab 3	Num	3.0	3.0		3.0	3.0		12.0
	Average	72.8	63.3		70.6	57.2		66.0
	St Dev	10.8	8.3		2.5	5.6		9.1
Lab 4	Num	6.0	6.0		6.0	6.0		24.0
	Average	112.6	144.3		100.3	84.8		110.5
	St Dev	18.2	30.4		13.3	3.8		28.5
Lab 5	Num		3.0	3.0		3.0	3.0	12.0
	Average		97.1	80.1		79.5	77.0	83.5
	St Dev		8.7	5.1		3.1	9.4	10.3
Lab 6	Num	2.0	3.0		3.0	4.0		12.0
	Average	140.9	127.7		138.7	105.9		125.4
	St Dev	4.3	15.5		15.5	7.9		18.4
Lab 7	Num	3.0	3.0		3.0	3.0		12.0
	Average	100.1	123.4		82.1	94.1		99.9
	St Dev	17.9	14.6		7.9	5.2		19.0
Lab 8	Num	3.0	3.0		3.0	3.0		12.0
	Average	65.0	38.3		92.8	51.9		62.0
	St Dev	16.0	21.9		36.5	12.8		29.1
All Laboratories	Num	20.0	30.0	9.0	21.0	31.0	9.0	120.0
	Average	98.8	92.5	71.3	95.5	78.6	75.3	87.6
	St Dev	28.7	42.9	14.1	25.3	18.0	9.5	29.7

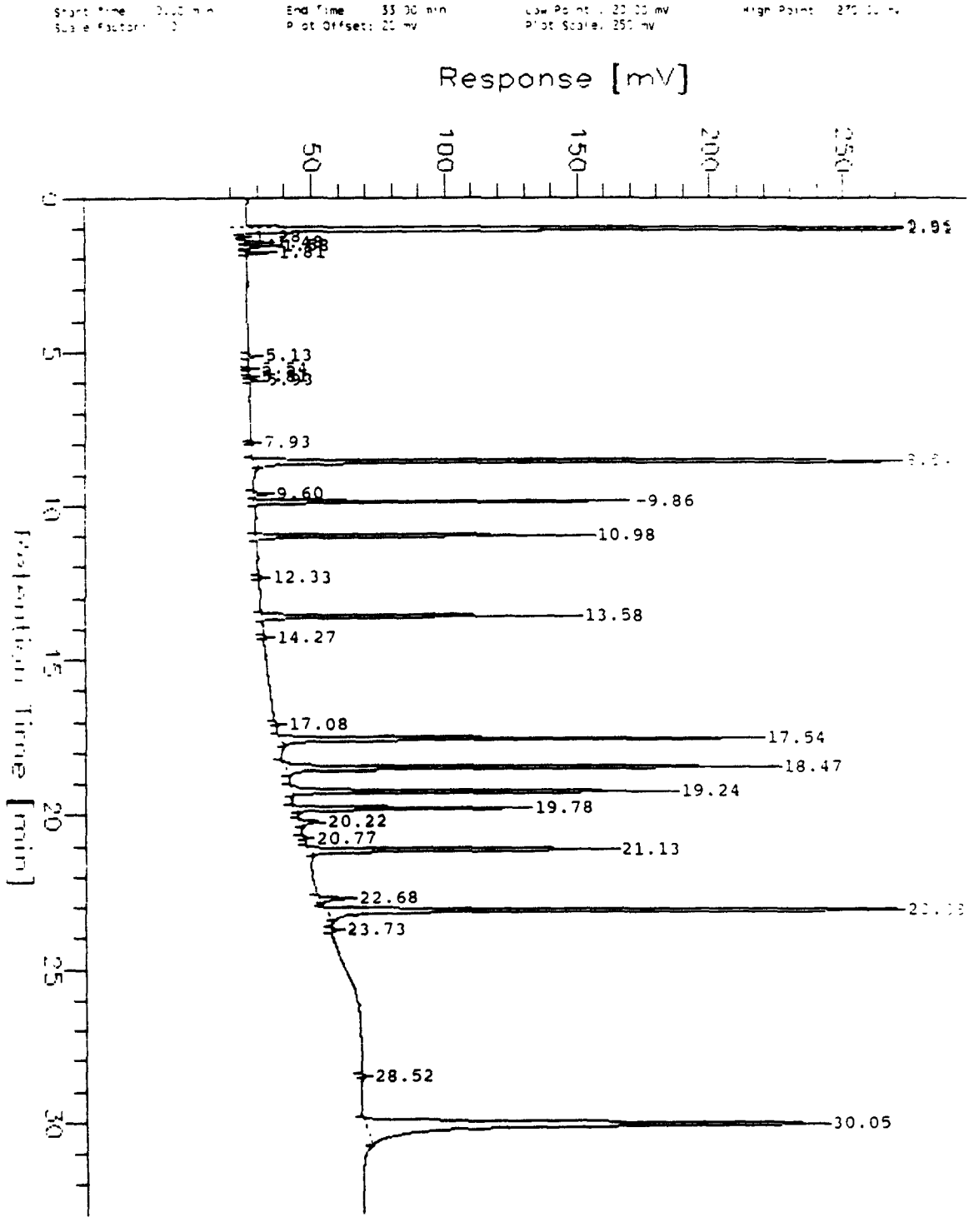
Data from Reference 13.

FIGURE 1.
GAS CHROMATOGRAM OF THE MIXED ORGANOCHLORINE PESTICIDE STANDARD



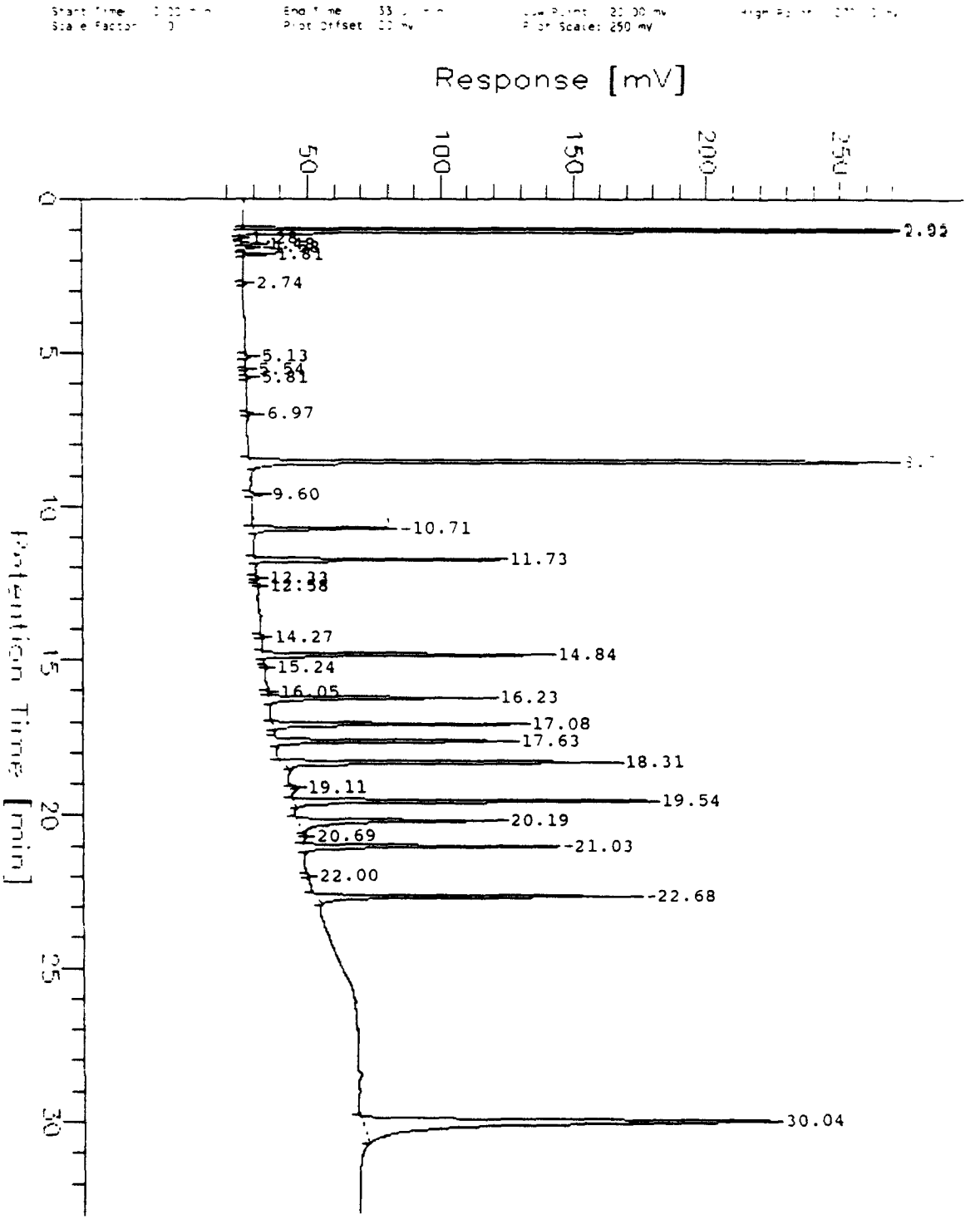
Column: 30 m x 0.25 mm ID, DB 5
Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

FIGURE 2.
GAS CHROMATOGRAM OF INDIVIDUAL ORGANOCHLORINE PESTICIDE STANDARD MIX A



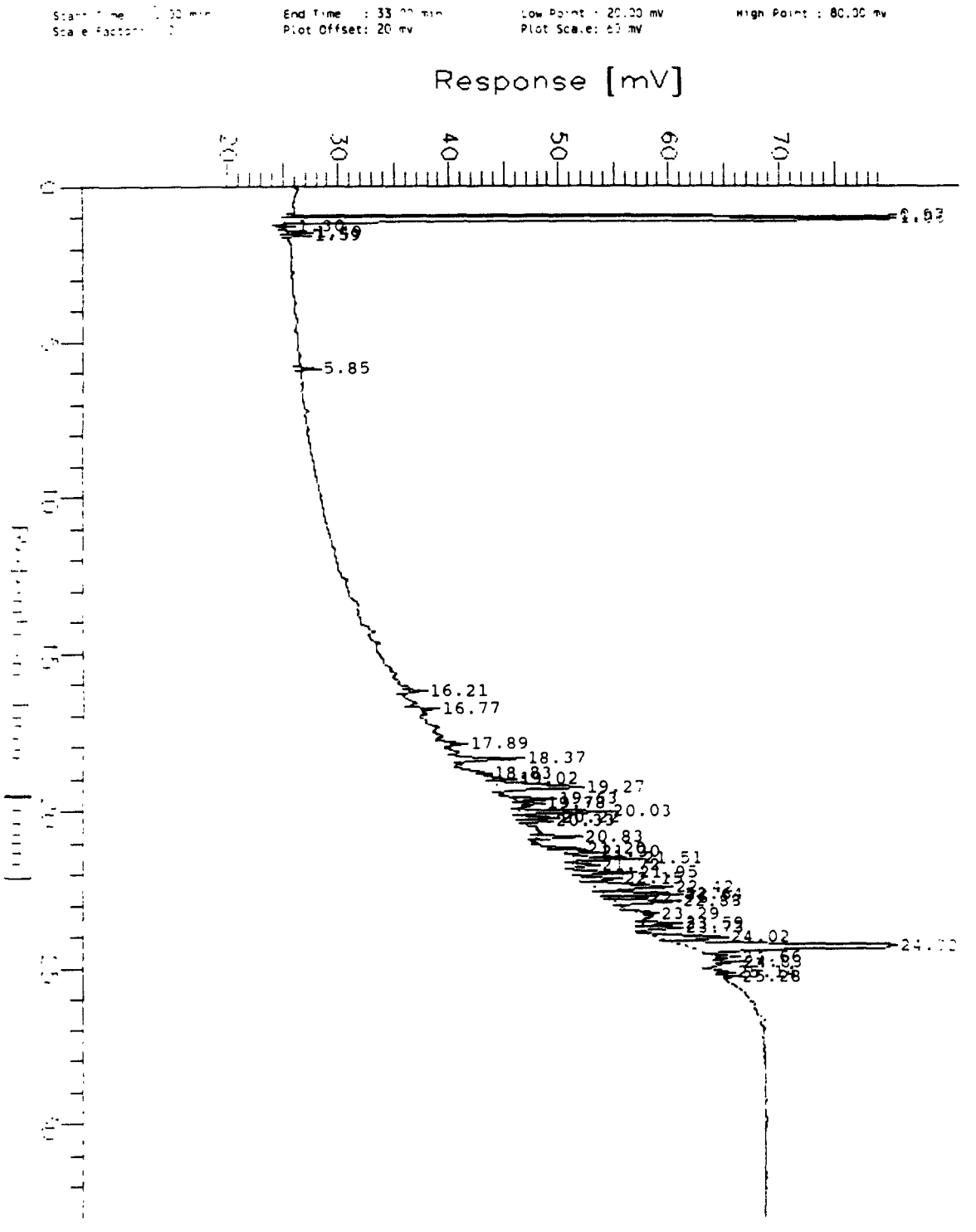
Column: 30 m x 0.25 mm ID, DB 5
Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

FIGURE 3
GAS CHROMATOGRAM OF INDIVIDUAL ORGANOCHLORINE PESTICIDE STANDARD MIX B



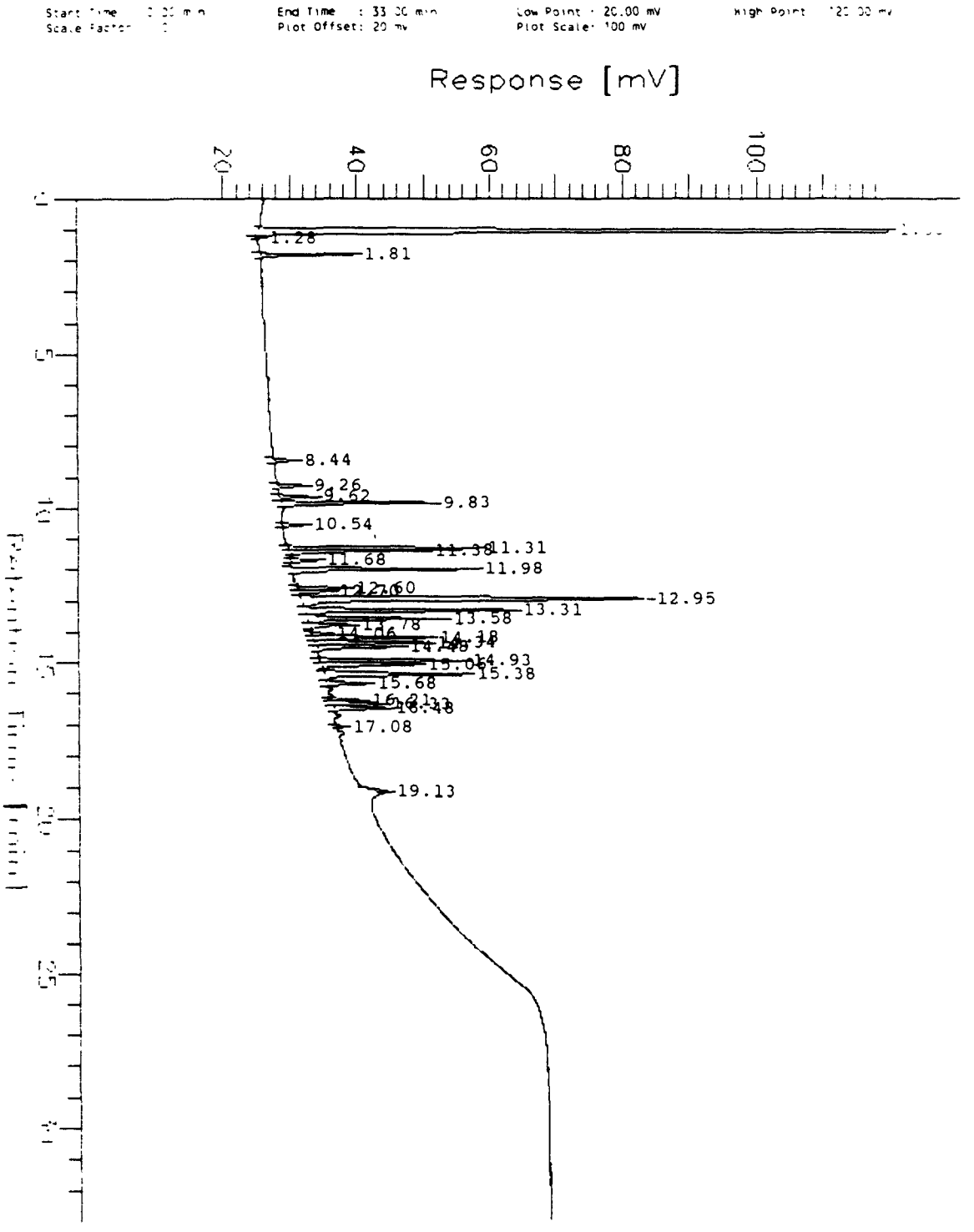
Column: 30 m x 0.25 mm ID, DB 5
Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

FIGURE 4.
GAS CHROMATOGRAM OF THE TOXAPHENE STANDARD



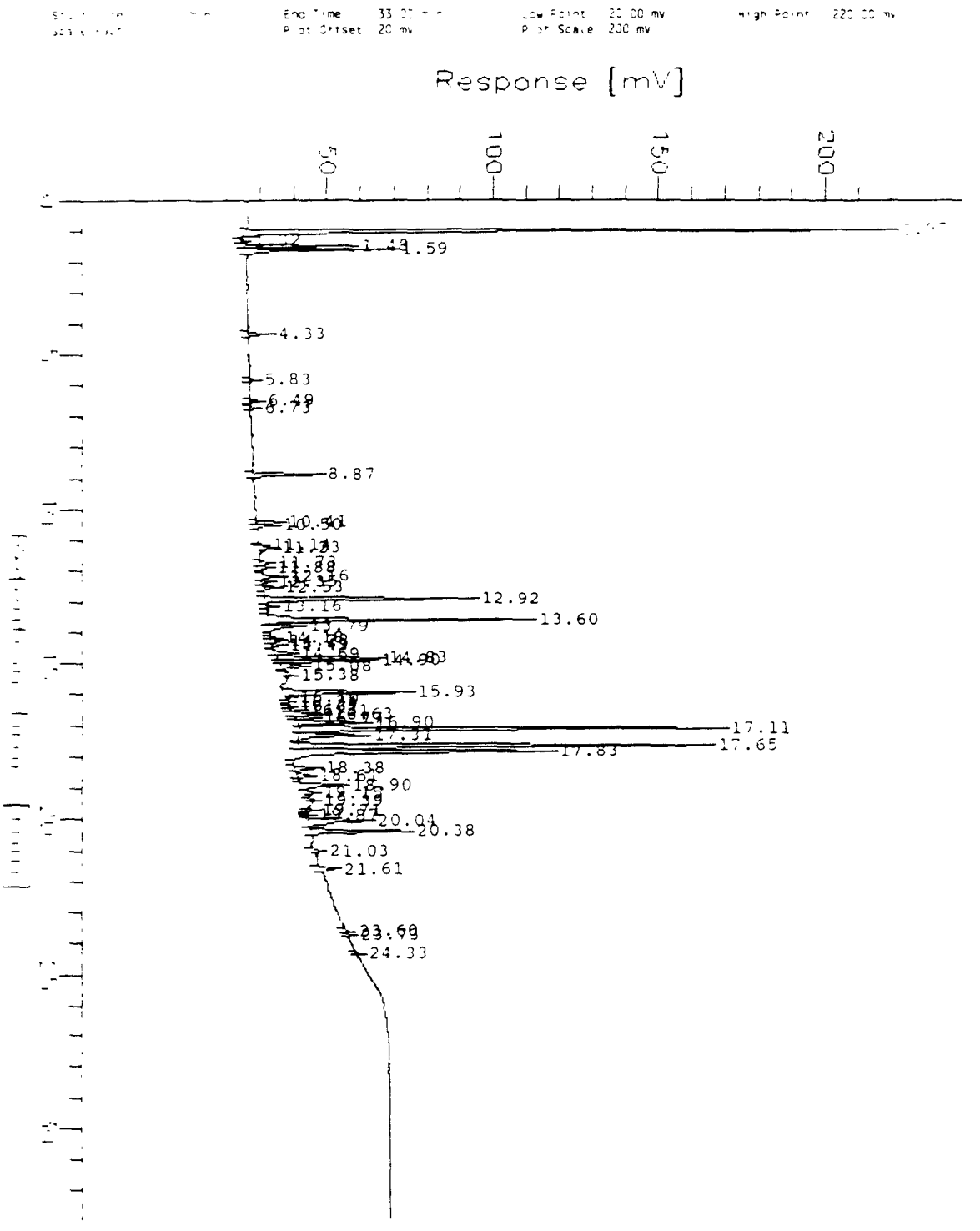
Column: 30 m x 0.25 mm ID, DB 5
Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

FIGURE 5.
GAS CHROMATOGRAM OF THE AROCLOR-1016 STANDARD



Column: 30 m x 0.25 mm ID DB 5 fused silica capillary.
Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

FIGURE 6.
GAS CHROMATOGRAM OF THE TECHNICAL CHLORDANE STANDARD



Column: 30 m x 0.25 mm ID DB 5 fused silica capillary.
Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

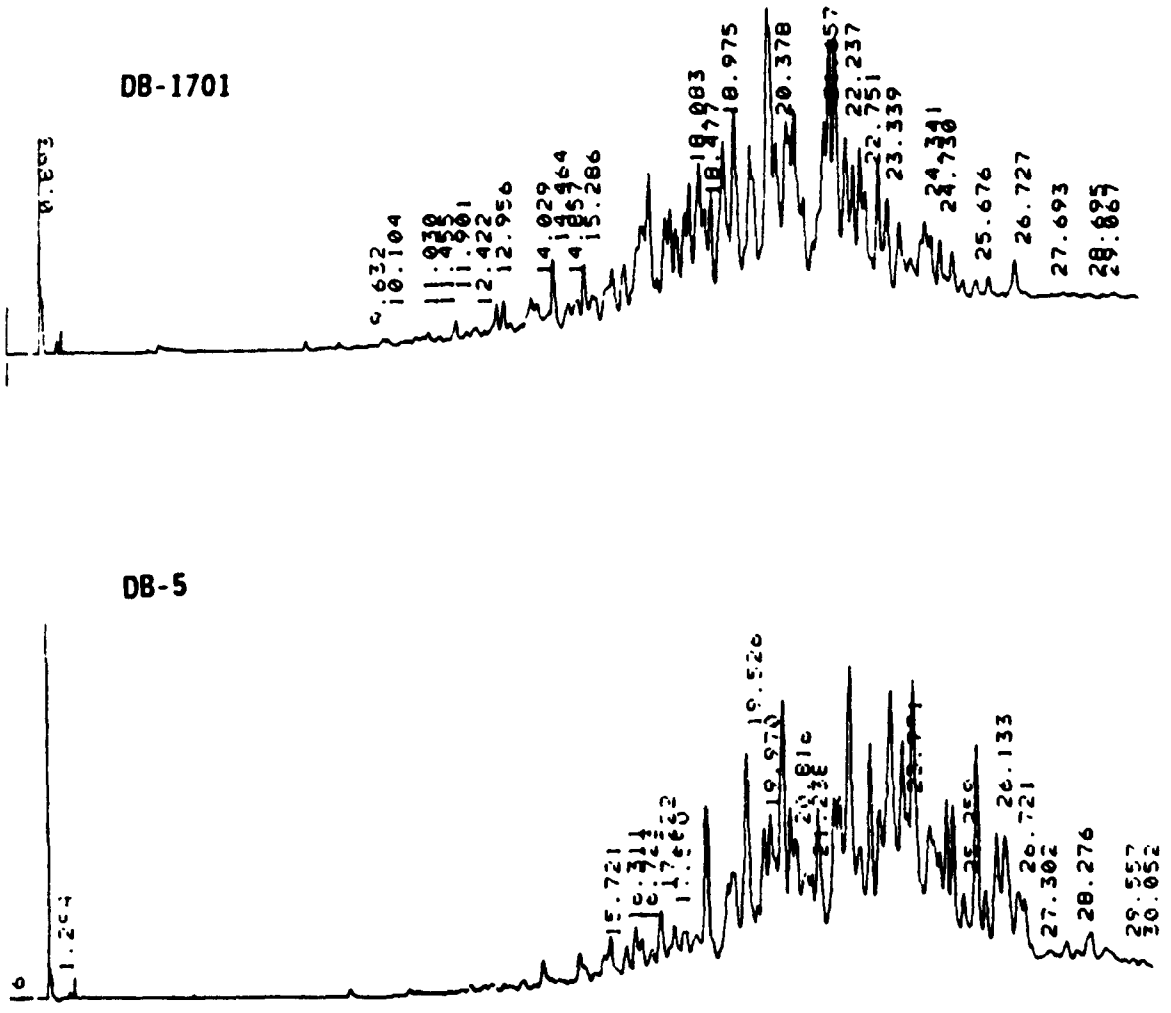


Figure 7. GC/ECD chromatogram of Toxaphene analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

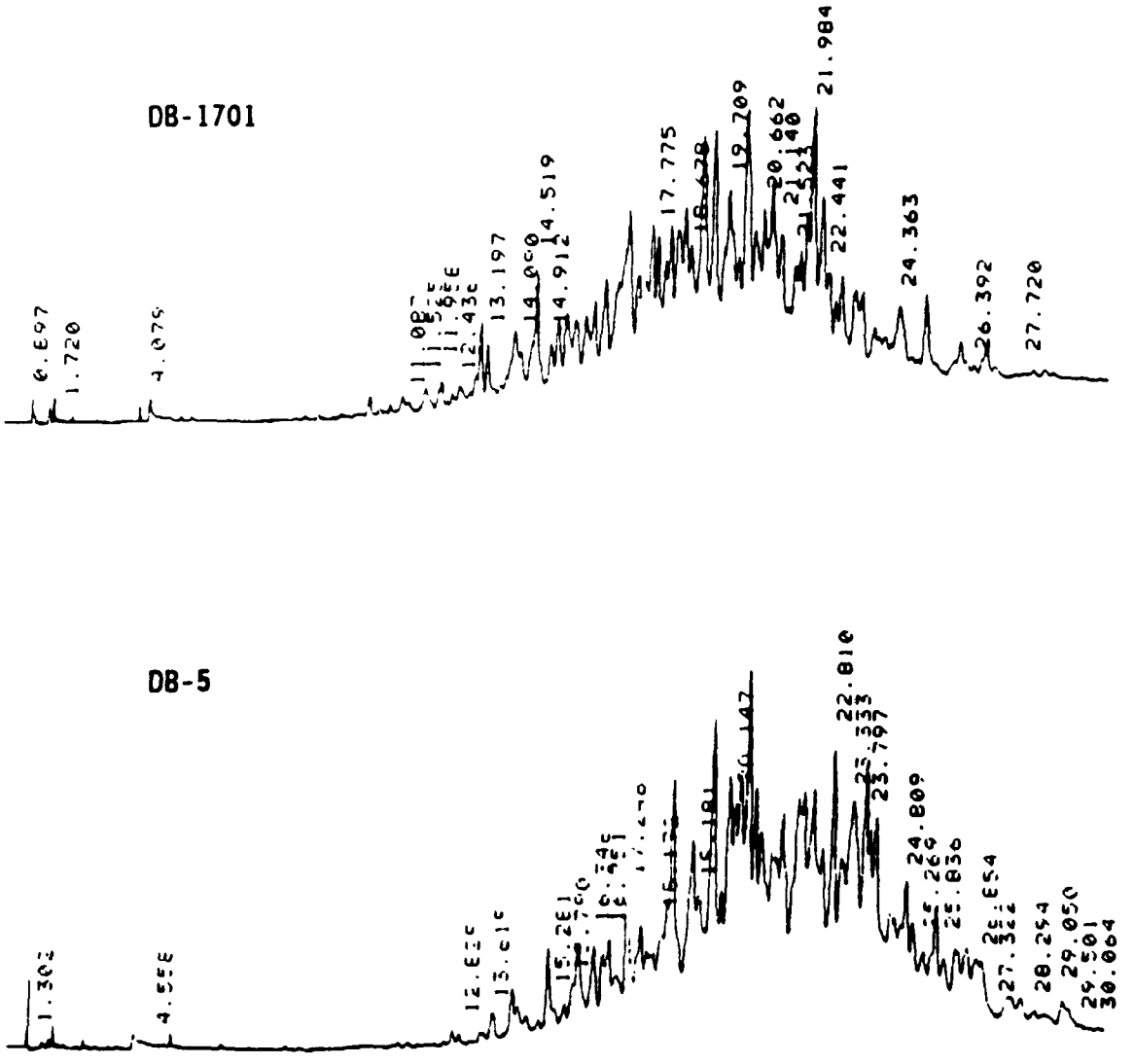


Figure 8. GC/ECD chromatogram of Strobane analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

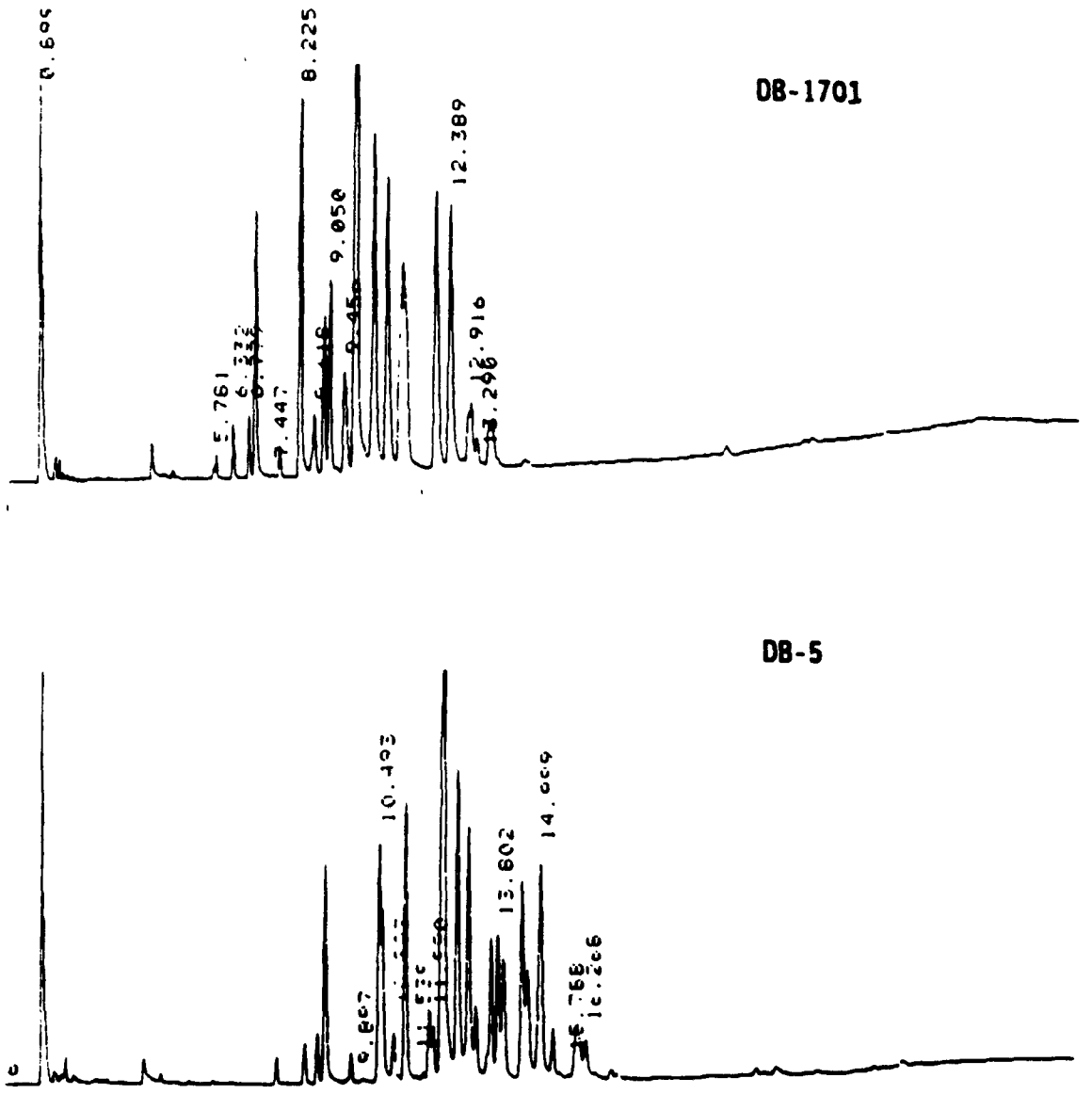


Figure 9. GC/ECD chromatogram of Aroclor 1016 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

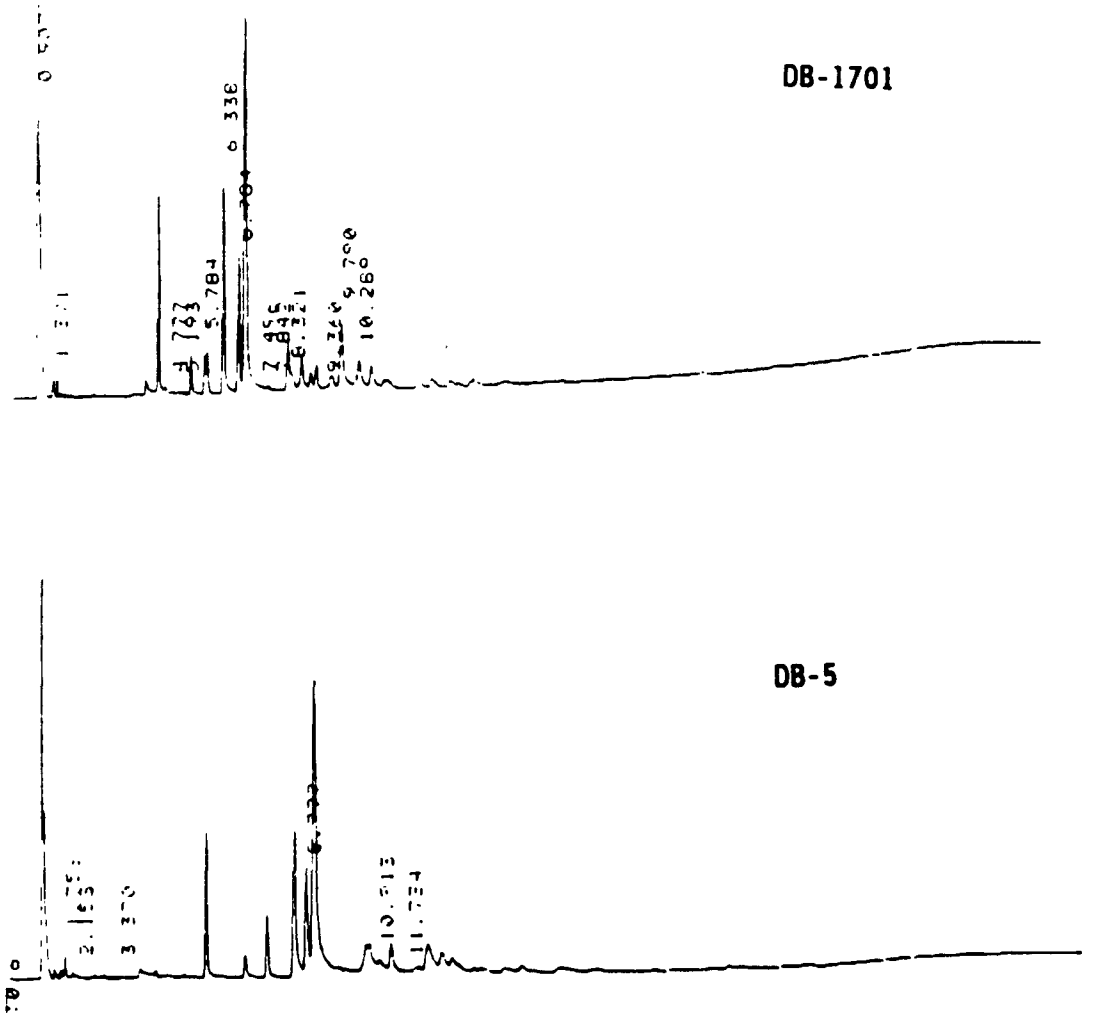


Figure 10. GC/ECD chromatogram of Aroclor 1221 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

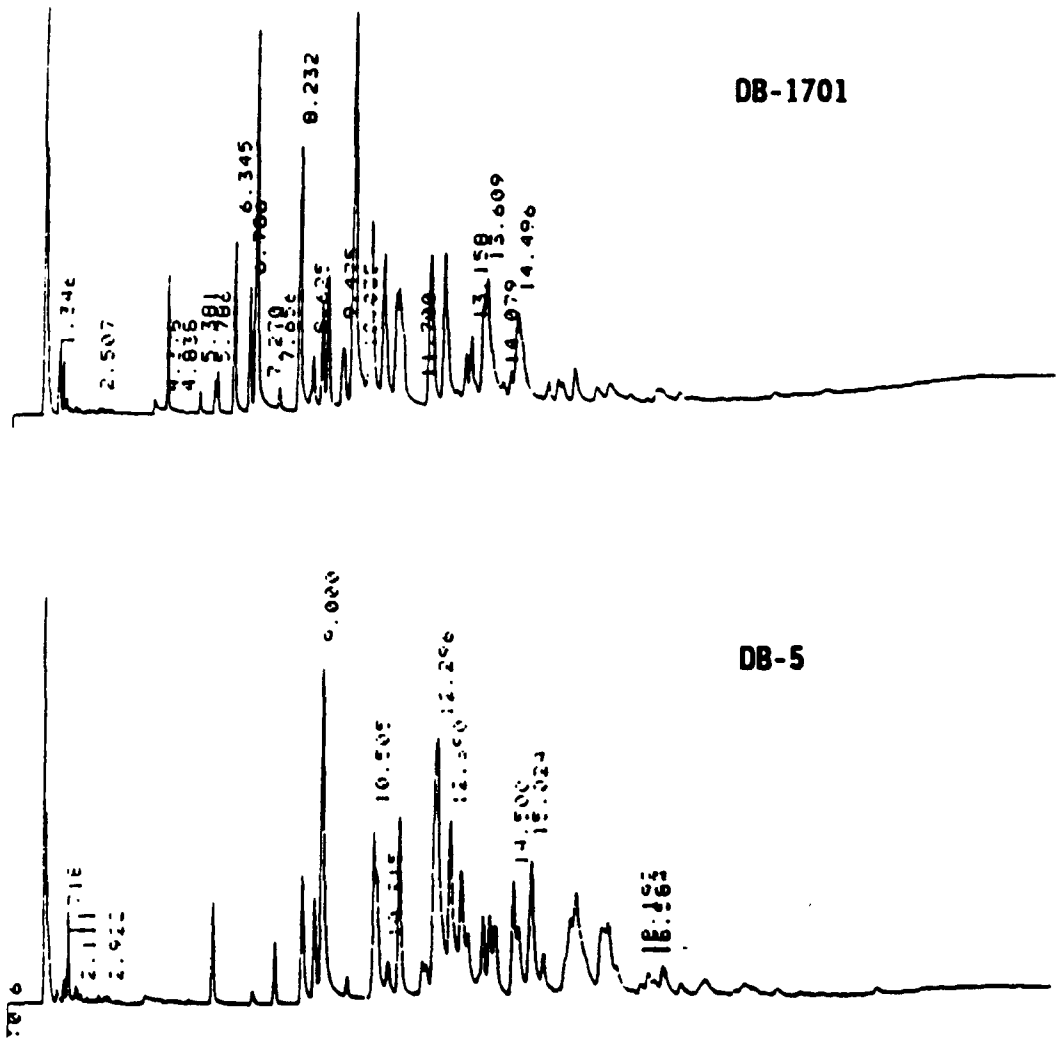


Figure 11. GC/ECD chromatogram of Aroclor 1232 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

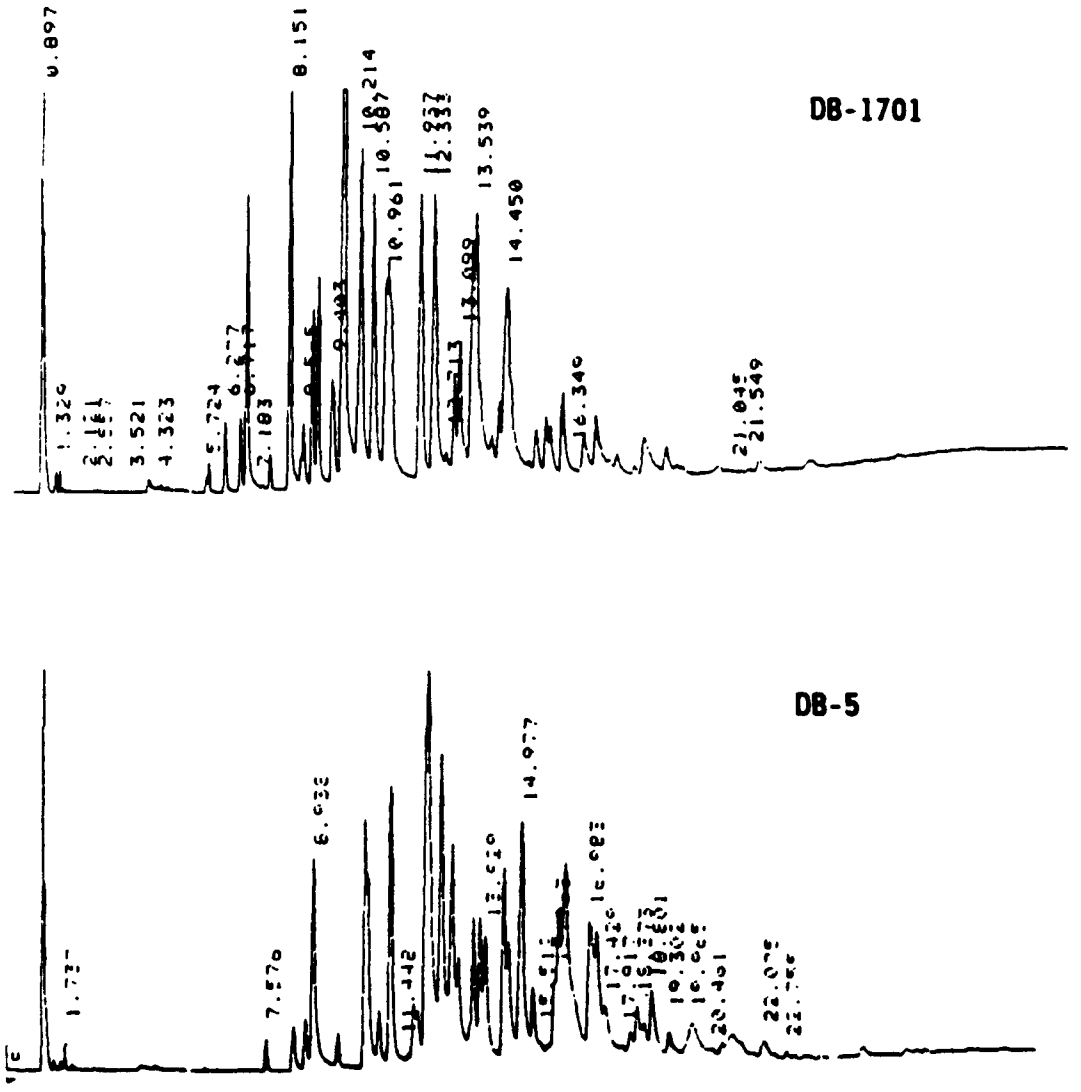


Figure 12. GC/ECD chromatogram of Aroclor 1242 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

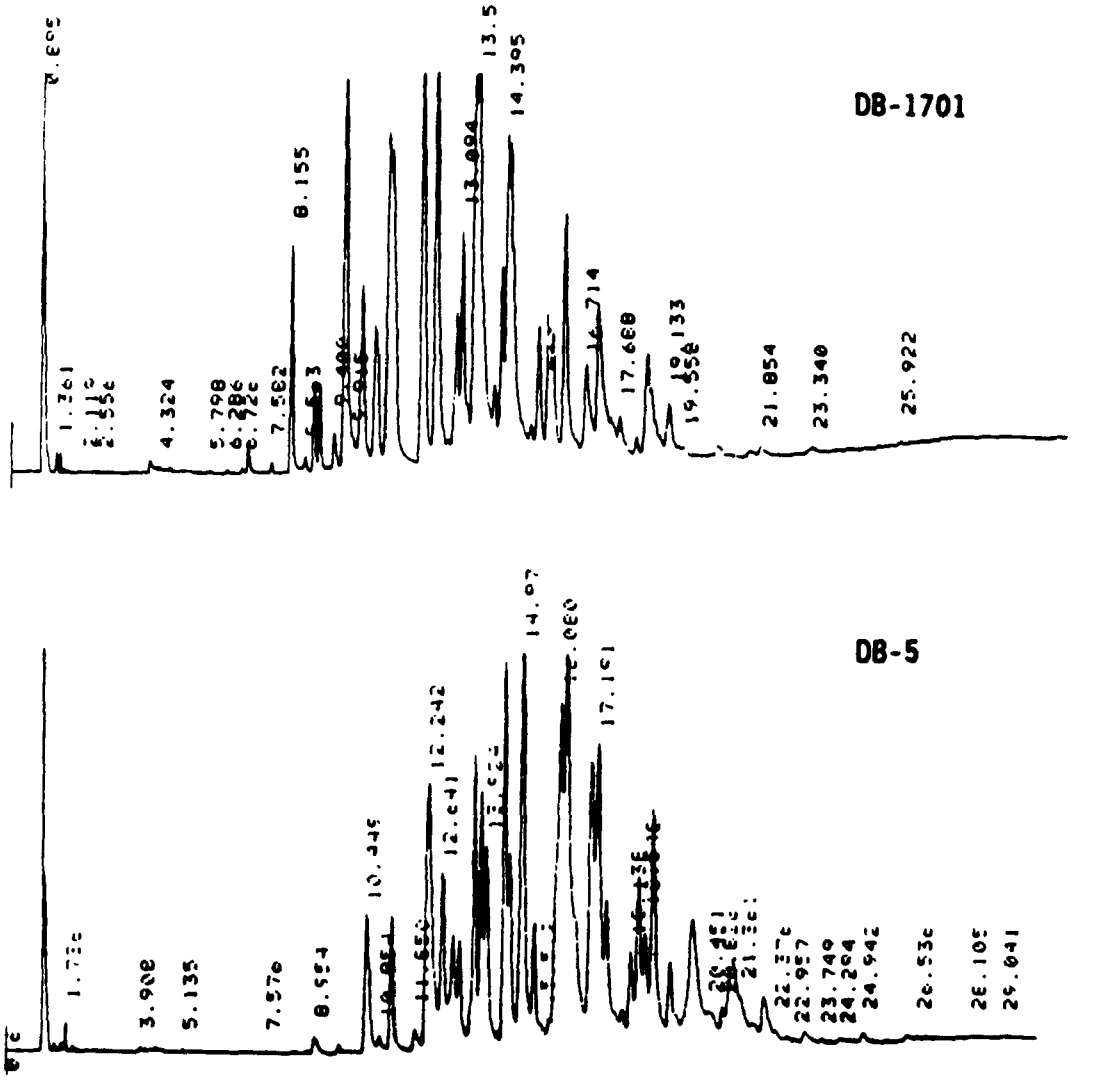


Figure 13. GC/ECD chromatogram of Aroclor 1248 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

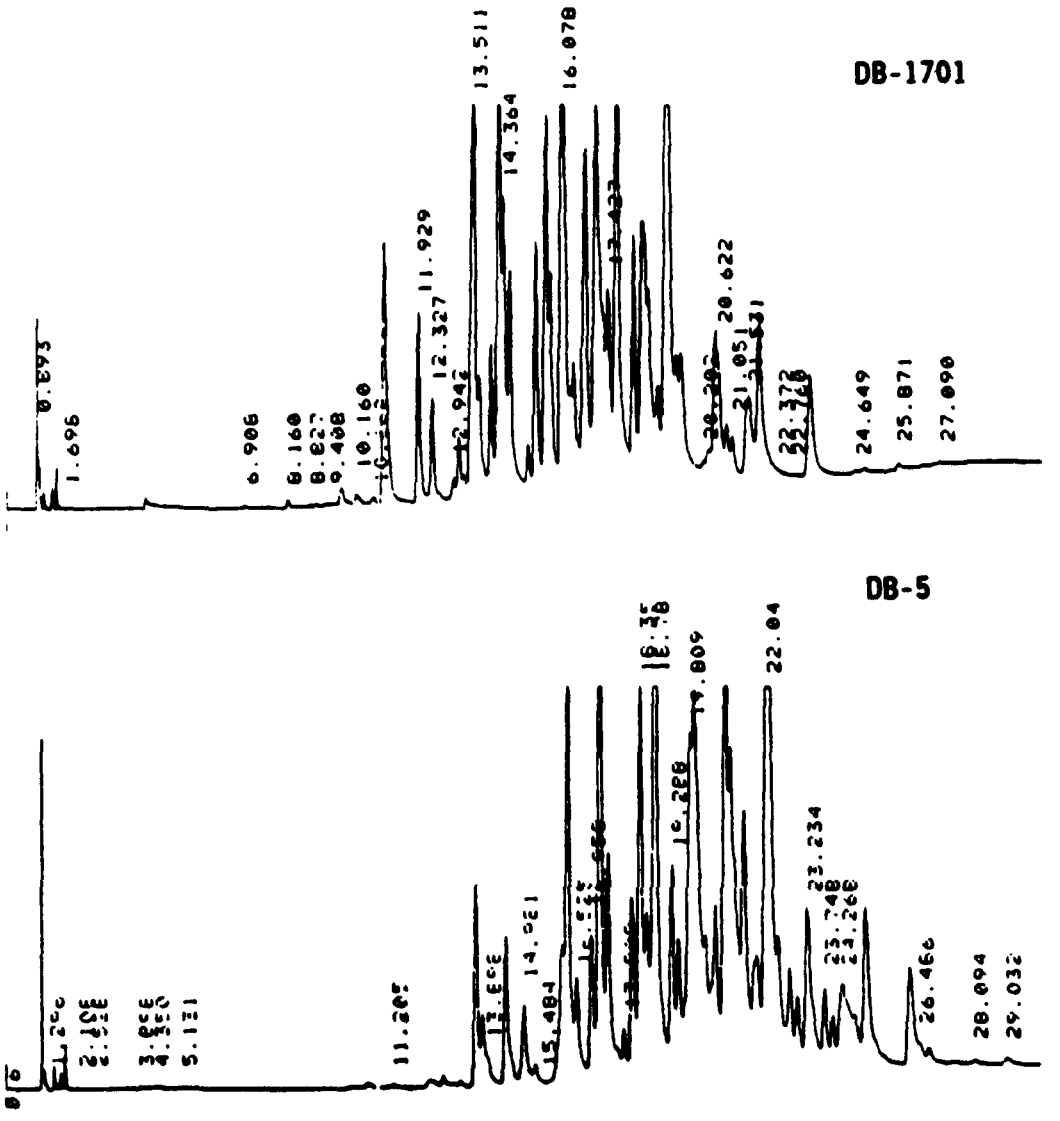


Figure 14. GC/ECD chromatogram of Aroclor 1254 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

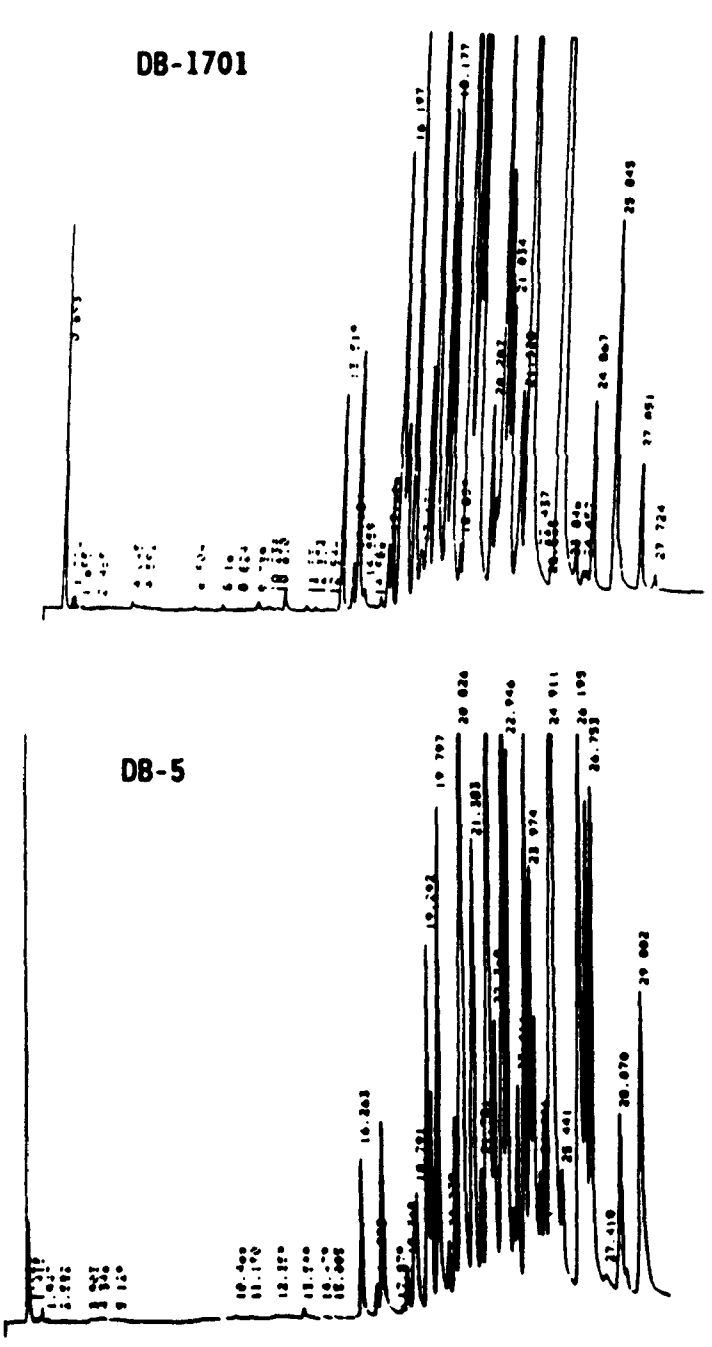


Figure 15. GC/ECD chromatogram of Aroclor 1260 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

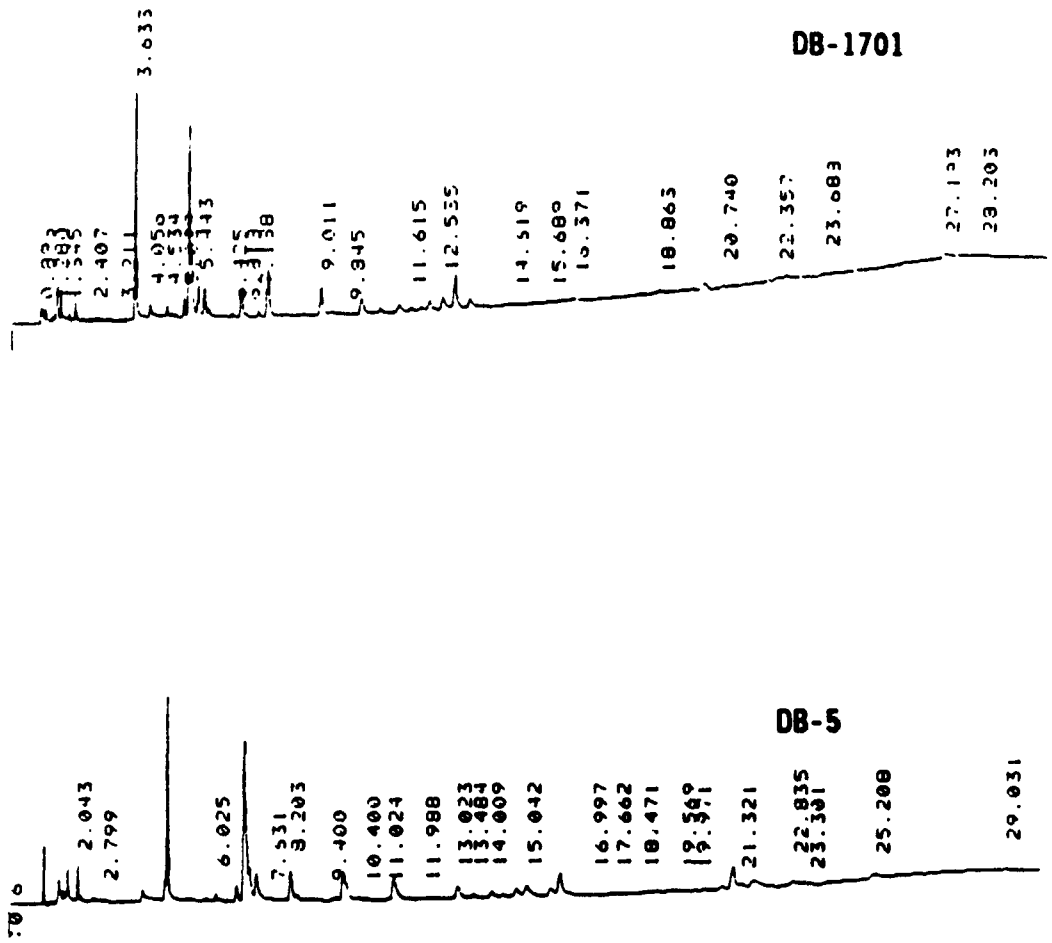


Figure 16. GC/ECD chromatogram of Halowax 1000 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

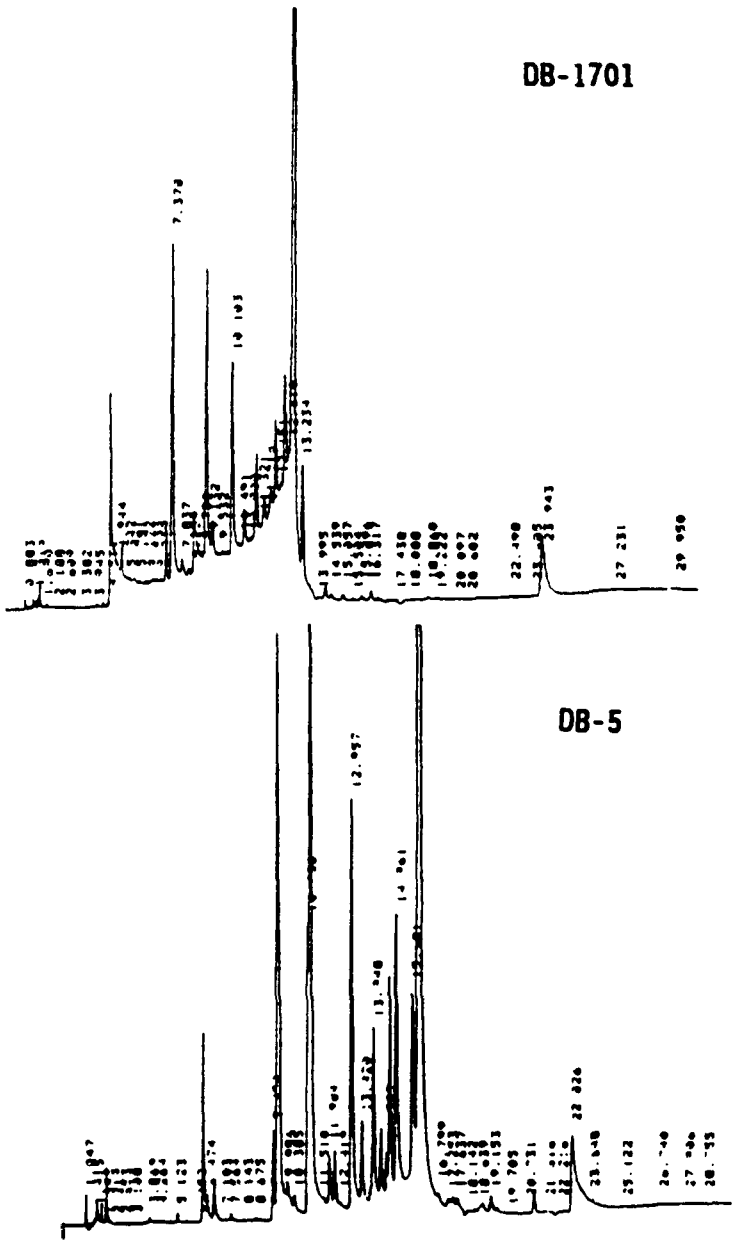


Figure 17. GC/ECD chromatogram of Halowax 1001 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

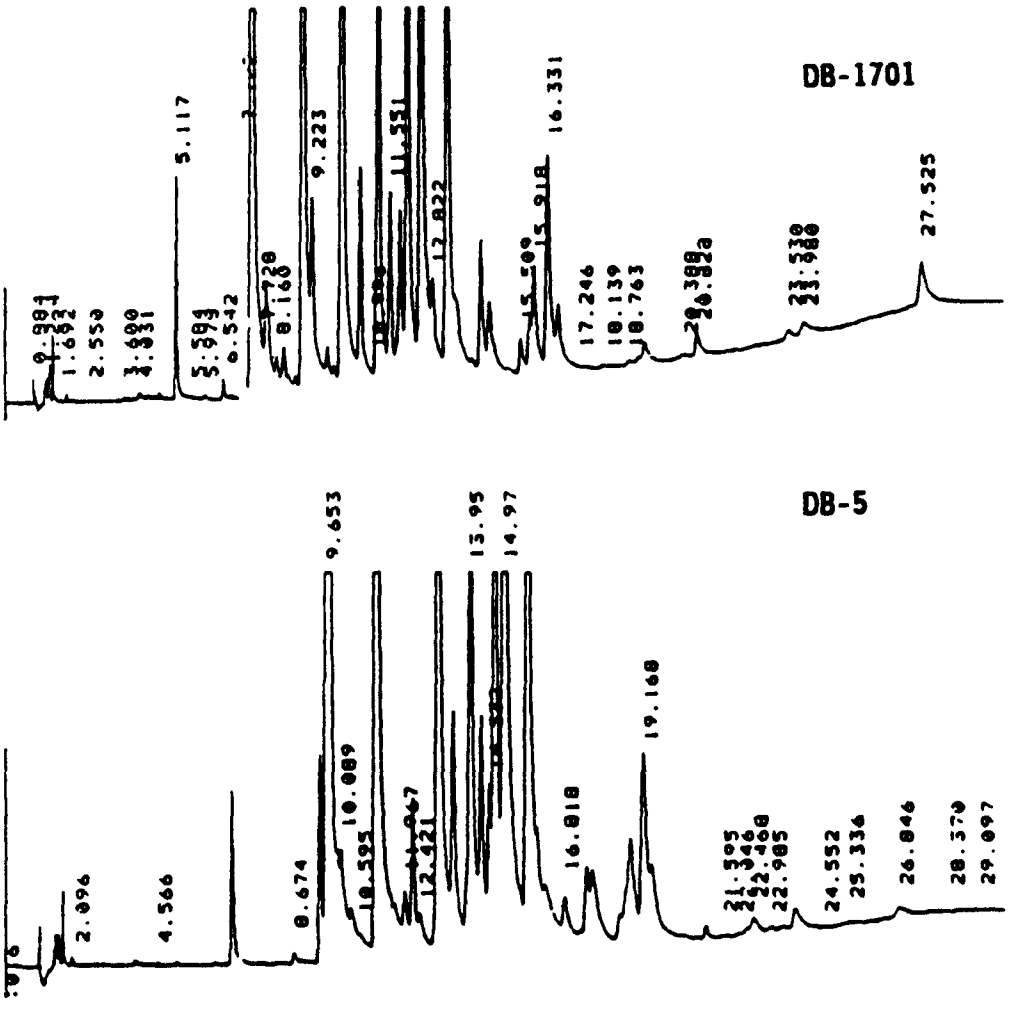


Figure 18. GC/ECD chromatogram of Halowax 1099 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

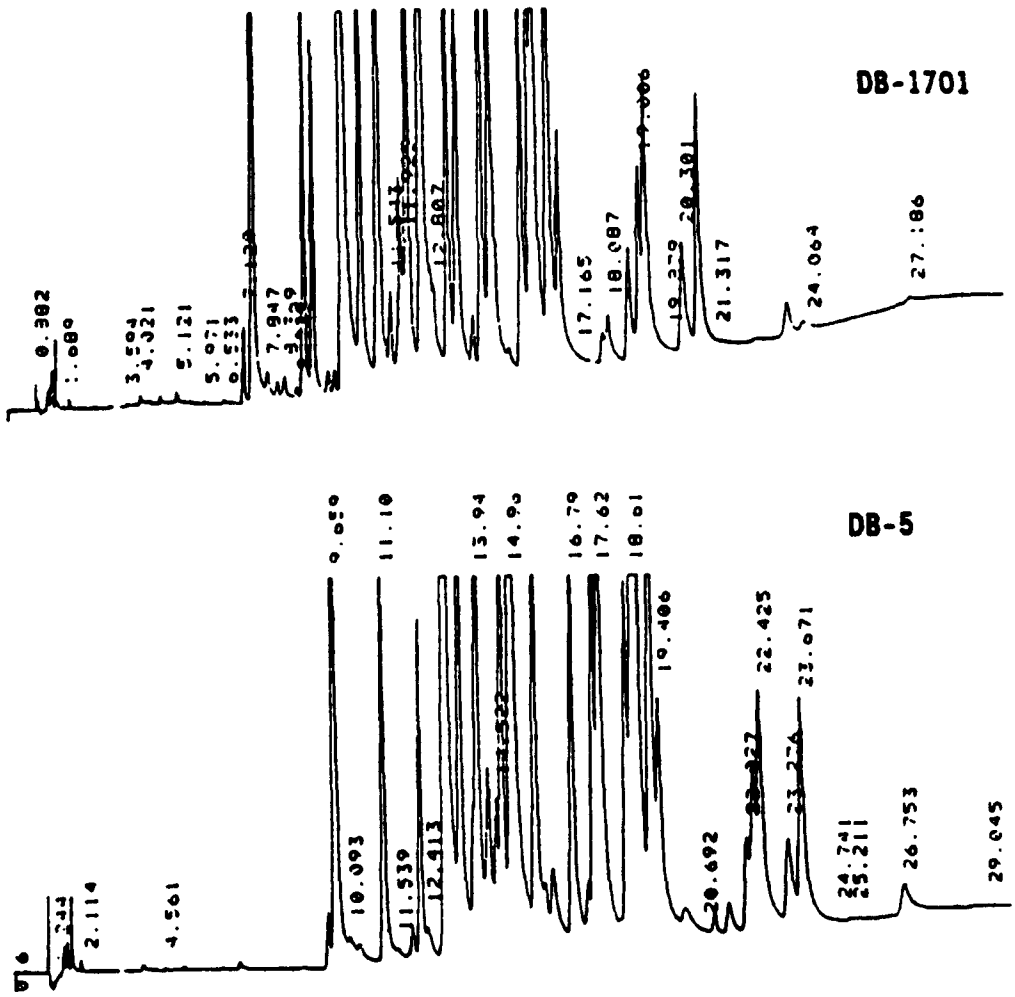


Figure 19. GC/ECD chromatogram of Halowax 1013 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

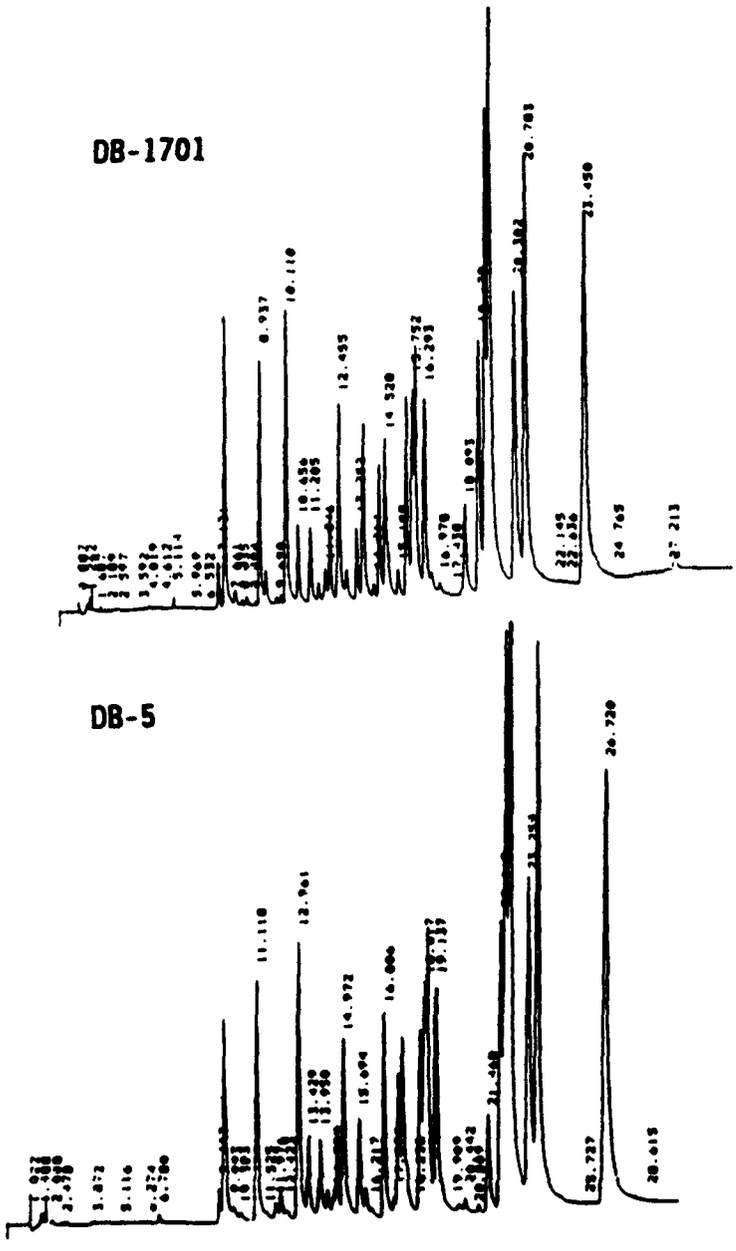


Figure 20. GC/ECD chromatogram of Halowax 1014 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

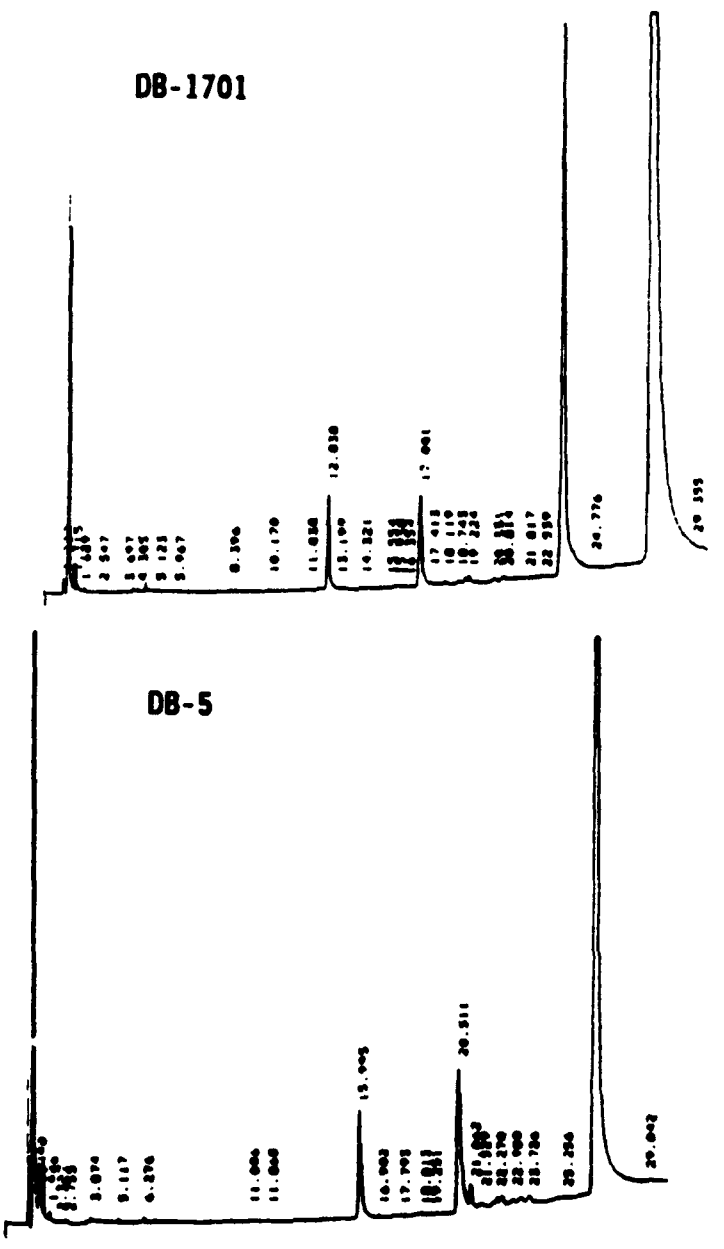


Figure 21. GC/ECD chromatogram of Halowax 1051 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

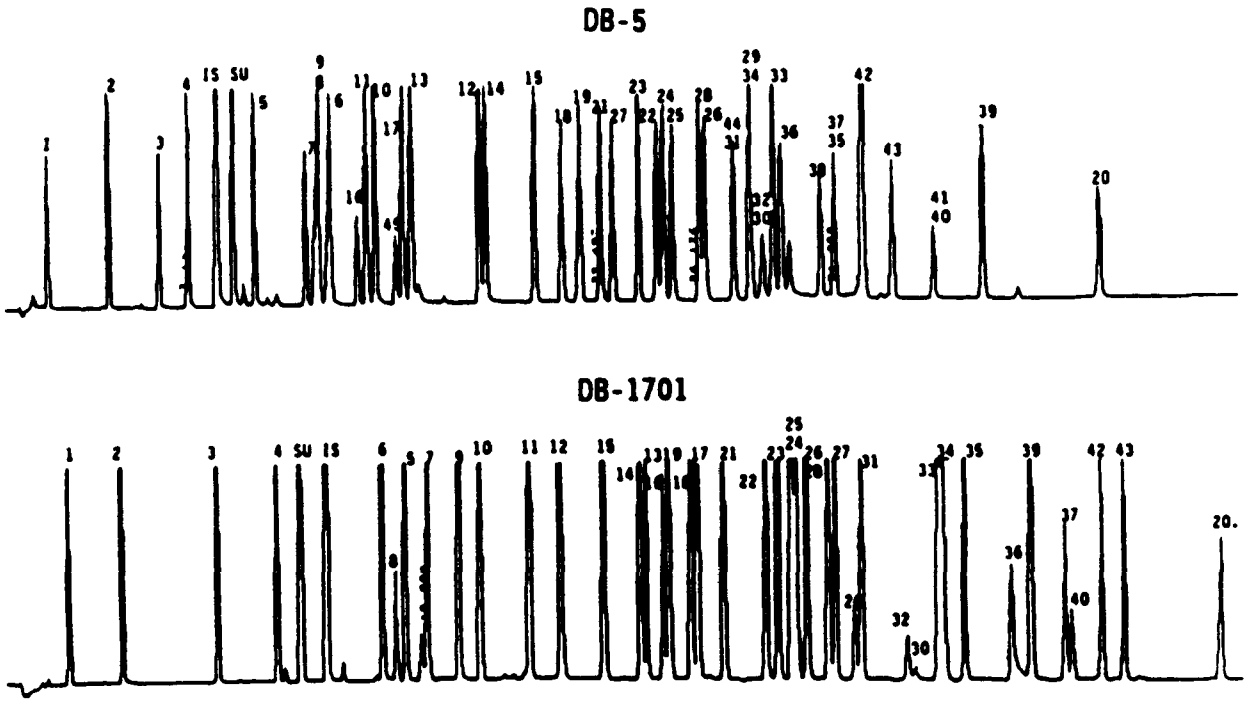


Figure 22. GC/ECD chromatogram of the organochlorine pesticides analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (0.83-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to an 8 in injection tee (Supelco Inc.). Temperature program: 140°C (2 min hold) to 270°C (1 min hold) at 2.8°C/min.

ORGANOCHLORINE PESTICIDES, HALOWAXES AND PCBs AS AROCLORS BY GAS CHROMATOGRAPHY: CAPILLARY COLUMN TECHNIQUE

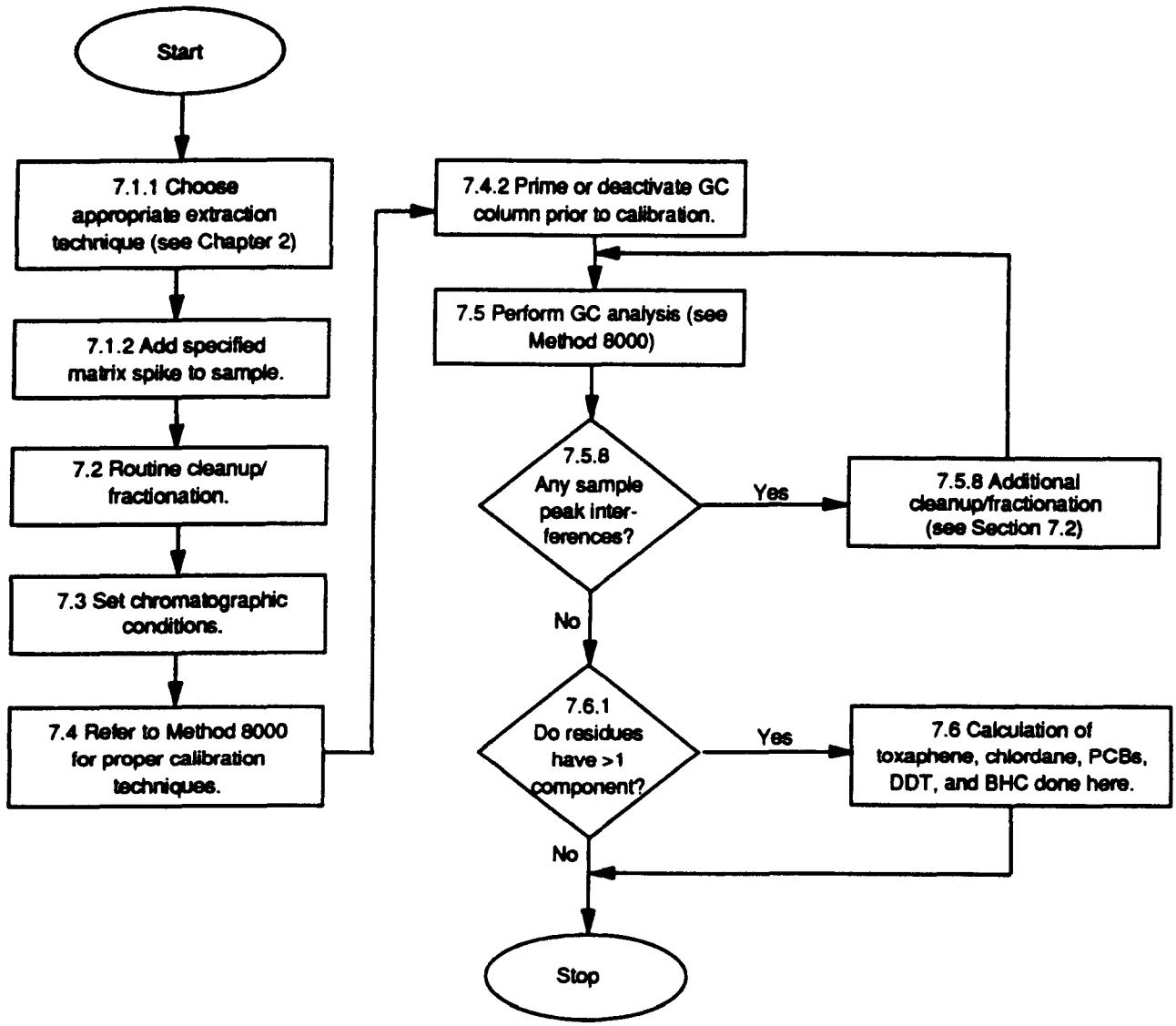


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Figure 2. GC of Individual Organochlorine Pesticide Standard Mix A. The GC operating conditions were as follows: 30 m x 0.25 mm ID DB-5 column. Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

Figure 3. GC of Individual Organochlorine Pesticide Standard Mix B. The GC operating conditions were as follows: 30 m x 0.25 mm ID DB-5 column. Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

Figure 4. GC of the Toxaphene Standard. The GC operating conditions were as follows: 30 m x 0.25 mm ID DB-5 column. Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

Figure 5. GC of the Aroclor-1016 Standard. The GC operating conditions were as follows: 30 m x 0.25 mm ID DB-5 fused silica capillary column. Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

Figure 6. GC of the Technical Chlordane Standard. The GC operating conditions were as follows: 30 m x 0.25 mm ID DB-5 fused silica capillary column. Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

Figure 7. GC/ECD chromatogram of Toxaphene analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 8. GC/ECD chromatogram of Strobane analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 9. GC/ECD chromatogram of Aroclor 1016 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W

Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 10. GC/ECD chromatogram of Aroclor 1221 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 11. GC/ECD chromatogram of Aroclor 1232 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 12. GC/ECD chromatogram of Aroclor 1242 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 13. GC/ECD chromatogram of Aroclor 1248 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 14. GC/ECD chromatogram of Aroclor 1254 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 15. GC/ECD chromatogram of Aroclor 1260 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 16. GC/ECD chromatogram of Halowax 1000 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions

were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 17. GC/ECD chromatogram of Halowax 1001 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 18. GC/ECD chromatogram of Halowax 1099 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 19. GC/ECD chromatogram of Halowax 1013 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 20. GC/ECD chromatogram of Halowax 1014 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 21. GC/ECD chromatogram of Halowax 1051 analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (1.5-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150°C (0.5 min hold) to 190°C (2 min hold) at 12°C/min then to 275°C (10 min hold) at 4°C/min.

Figure 22. GC/ECD chromatogram of the organochlorine pesticides analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (0.83-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0-µm film thickness) connected to an 8 in injection tee (Supelco Inc.). Temperature program: 140°C (2 min hold) to 270°C (1 min hold) at 2.8°C/min.

METHOD 8110

HALOETHERS

1.0 SCOPE AND APPLICATION

1.1 This method covers the determination of certain haloethers. The following parameters can be determined by this method:

Parameter	CAS No.
Bis(2-chloroethoxy) methane	111-91-1
Bis(2-chloroethyl) ether	111-44-4
Bis(2-chloroisopropyl) ether	108-60-1
4-Bromophenyl phenyl ether	101-55-3
4-Chlorophenyl phenyl ether	7005-72-3

1.2 This is a gas chromatographic (GC) method applicable to the determination of the compounds listed above in municipal and industrial discharges. When this method is used to analyze unfamiliar samples for any or all of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions of a second GC column that can be used to confirm measurements made with the primary column. Method 8270 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for all of the parameters listed above, using the extract from this method.

1.3 The method detection limit (MDL, defined in Step 9.1) for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from that listed, depending upon the nature of interferences in the sample matrix.

1.4 Any modification of this method, beyond those expressly permitted, shall be considered as major modifications subject to application and approval of alternate test procedures.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Step 8.2.

1.6 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical

analysis. Additional references to laboratory safety are available and have been identified.

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample, approximately one-liter, is solvent extracted with methylene chloride using a separatory funnel. The methylene chloride extract is dried and exchanged to hexane during concentration to a volume of 10 mL or less. GC conditions are described which permit the separation and measurement of the compounds in the extract using a halide specific detector.

2.2 Method 8110 provides gas chromatographic conditions for the detection of ppb levels of haloethers. Prior to use of this method, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2- to 5-uL aliquot of the extract is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by a halide-specific detector (HSD).

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. The cleanup procedures in Step 7.3 can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDL listed in Table 1.

3.3 Dichlorobenzenes are known to coelute with haloethers under some gas chromatographic conditions. If these materials are present in a sample, it may be necessary to analyze the extract with two different column packings to completely resolve all of the compounds.

3.4 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by analyzing calibration and reagent blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

4.0 APPARATUS AND MATERIALS

4.1 Kuderna-Danish (K-D) apparatus

4.1.1 Concentrator tube - 10-mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

4.1.2 Evaporative flask - 500 mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

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

4.2 Vials - Amber glass, 10- to 15- mL capacity, with Teflon lined screw-cap.

4.3 Boiling chips - Approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride.

4.4 Water bath - Heated, with concentric ring cover, capable of temperature control (± 2°C). The bath should be used in a hood.

4.5 Balance - Analytical, capable of accurately weighing 0.0001 g.

4.6 Gas chromatograph - An analytical system complete with temperature programmable gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

4.6.1 Column 1 - 1.8 m x 2 mm i.d. pyrex glass, packed with Supelcoport, (100/120 mesh) coated with 3% SP-1000 or equivalent. This column was used to develop the method performance statements in Section 9.0. Guidelines for the use of alternate column packings are provided in Step 7.3.1.

4.6.2 Column 2 - 1.8 m x 2 mm i.d. pyrex glass, packed with Tenax-GC (60/80 mesh) or equivalent.

4.6.3 Detector - Halide specific: electrolytic conductivity or microcoulometric. These detectors have proven effective in the analysis of wastewaters for the parameters listed in the scope of this method. The Hall conductivity detector was used to develop the method performance statements in Section 9.0. Guidelines for the use of alternate detectors are provided in Step 7.3.1. Although less selective, an electron capture detector is an acceptable alternative.

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 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Acetone, CH_3COCH_3. Pesticide quality or equivalent.

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

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

5.5.1 Prepare stock standard solutions by accurately weighing 0.1000 ± 0.0010 g of pure material. Dissolve the material in pesticide quality acetone and dilute to volume in a 100-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.5.2 Transfer the stock standard solutions into Teflon lined screw-cap bottles. 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.

5.5.3 Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicate a problem.

5.6 Calibration standards - Calibration standards at a minimum of five concentration levels should be prepared through dilution of the stock standards with isooctane. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.7 Internal standards (if internal standard calibration is used) - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.7.1 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest as described in Step 5.6.

5.7.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane.

5.7.3 Analyze each calibration standard according to Section 7.0.

5.8 Surrogate standards - The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent blank with one or two surrogates (e.g.

haloethers that are not expected to be in the sample) recommended to encompass the range of the temperature program used in this method. Method 3500, Step 5.3.1.1, details instructions on the preparation of base/ neutral surrogates. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1. Extracts must be stored at 4°C and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral, or as is, pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550.

NOTE: Some of the haloethers are very volatile and significant losses will occur in concentration steps if care is not exercised. It is important to maintain a constant gentle evaporation rate and not to allow the liquid volume to fall below 1 to 2 mL before removing the K-D apparatus from the hot water bath.

7.1.2 Prior to gas chromatographic analysis, the extraction solvent must be exchanged to hexane. The exchange is performed during the K-D procedures listed in all of the extraction methods. The exchange is performed as follows.

7.1.2.1 Following K-D of the methylene chloride extract to 1 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 minutes.

7.1.2.2 Momentarily remove the Snyder column, add 50 mL of hexane, a new boiling chip, and reattach the macro-Snyder column. Concentrate the extract using 1 mL of hexane to prewet the Snyder column. Place the K-D apparatus on the 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 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 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. The extract will be handled differently at this point, depending on whether or not cleanup is needed. If cleanup is not required, proceed to Step 7.1.2.3. If cleanup is needed, proceed to Step 7.1.2.4.

7.1.2.3 If cleanup of the extract is not required, remove the Snyder column and rinse the flask and its lower joint into the

concentrator tube with 1-2 mL of hexane. A 5-mL syringe is recommended for this operation. Adjust the extract volume to 10.0 mL. Stopper the concentrator tube and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon lined screw-cap vial. Proceed with gas chromatographic analysis.

7.1.2.4 If cleanup of the extract is required, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with a minimum amount of hexane. A 5-mL syringe is recommended for this operation. Add a clean boiling chip to the concentrator tube and attach a two ball micro-Snyder column. Prewet the column by adding about 0.5 mL of hexane to the top. Place the micro-K-D apparatus on the water bath (80°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 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 and allow it to drain and cool for at least 10 minutes.

7.1.2.5 Remove the micro-Snyder column and rinse the flask and its lower joint into the concentrator tube with 0.2 mL of hexane. Adjust the extract volume to 2.0 mL and proceed with either Method 3610 or 3620.

7.2 Cleanup

7.2.1 Proceed with either Method 3610 or 3620, using the 2-mL hexane extracts obtained from Step 7.1.2.5.

7.2.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous paragraphs and in Method 8000.

7.3 Gas Chromatography Conditions

7.3.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. This table includes retention times and MDLs that were obtained under these conditions. Examples of the parameter separations achieved by these columns are shown in Figures 1 and 2. Other packed columns, chromatographic conditions, or detectors may be used if the requirements of Step 8.2 are met. Capillary (open-tubular) columns may also be used if the relative standard deviations of responses for replicate injections are demonstrated to be less than 6% and the requirements of Step 8.2 are met.

7.4 Calibration - Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.4.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.4.2 If cleanup is performed on the samples, the analyst should process a series of standards through the cleanup procedure and then analyze the samples by GC. This will confirm elution patterns and the absence of interferents from the reagents.

7.5 Gas chromatographic analysis

7.5.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 uL of internal standard to the sample prior to injection.

7.5.2 Follow Step 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level check standard after each group of 10 samples in the analysis sequence.

7.5.3 Examples of GC/HSD chromatograms for haloethers are shown in Figures 1 and 2.

7.5.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.5.5 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each analyte peak in the sample chromatogram. See Step 7.8 of Method 8000 for calculation equations.

7.5.6 If peak detection and identification are prevented due to interferences, the hexane extract may undergo cleanup using either Method 3610 or 3620.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000, Step 8.6.

8.2.1 The quality control (QC) reference sample concentrate (Method 8000, Step 8.6) should contain each analyte of interest at 20 ug/mL.

8.2.2 Table 1 indicates the recommended operating conditions, retention times, and MDLs that were obtained under these conditions. Table 2 gives method accuracy and precision for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Step 8.10).

8.3.1 If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

9.0 METHOD PERFORMANCE

9.1 This method has been tested for linearity of recovery from spiked water and has been demonstrated to be applicable for the concentration range from 4 x MDL to 1000 x MDL.

9.2 In a single laboratory (Monsanto Research Center), using spiked wastewater samples, the average recoveries presented in Table 2 were obtained. Each spiked sample was analyzed in triplicate on three separate occasions. The standard deviation of the percent recovery is also included in Table 2.

9.3 The U.S. Environmental Protection Agency is in the process of conducting an interlaboratory method study to fully define the performance of this method.

10.0 REFERENCES

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8. ASTM Annual Book of Standards, Part 31; "Standard Practice for Sampling Water"; ASTM: Philadelphia, PA, p. 76, 1980; D3370.

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11. "EPA Method Validation Study 21 Methods 611 (Halothers)," Report for EPA Contract 68-03-2633.

12. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

13. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

14. "Determination of Haloethers in Industrial and Municipal Wastewaters"; Report for EPA Contract 68-03-2633 (In preparation).

TABLE 1.
CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Parameter	Retention Time (minutes) Column 1	Column 2	Method Detection Limit (ug/L)
Bis(2-chloroisopropyl) ether	8.4	9.7	0.8
Bis(2-chloroethyl) ether	9.4	9.1	0.3
Bis(2-chloroethoxy)methane	13.1	10.0	0.5
4-Chlorophenyl phenyl ether	19.4	15.0	3.9
4-Bromophenyl phenyl ether	21.2	16.2	2.3

Column 1 conditions: Supelcoport (100/120 mesh) coated with 3% SP-1000 packed in a 1.8 m x 2 mm i.d. glass column with helium carrier gas at a flow rate of 40 mL/min. Column temperature: 60°C for 2 minutes after injection then program at 8°C/min to 230°C and hold for 4 minutes. Under these conditions the retention time for aldrin is 22.6 minutes.

Column 2 conditions: Tenax-GC (60/80 mesh) packed in a 1.8 m x 2 mm i.d. glass column with helium carrier gas at 40 mL/min flow rate. Column temperature: 150°C for 4 minutes after injection then program at 16°C/min to 310°C. Under these conditions the retention time for aldrin is 18.4 minutes.

TABLE 2.
SINGLE OPERATOR ACCURACY AND PRECISION

Parameter	Average Percent Recovery	Standard Deviation %	Spike Range (ug/L)	Number of Analyses	Matrix Types
Bis(2-chloroethoxy) methane	62	5.3	138	27	3
Bis(2-chloroethyl) ether	59	4.5	97	27	3
Bis(2-chloroisopropyl) ether	67	4.0	54	27	3
4-Bromophenyl phenyl ether	78	3.5	14	27	3
4-Chlorophenyl phenyl ether	73	4.5	30	27	3

FIGURE 1.
GAS CHROMATOGRAM OF HALOTHERS

Column: 3% SP-1000 on Supelcoport
Program. 60°C.-2 minutes 8°/minute to 230°C.
Detector: Hall electrolytic conductivity

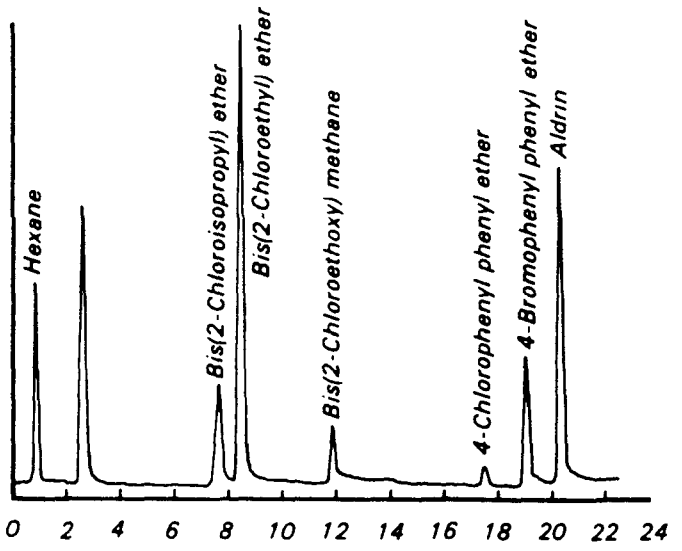
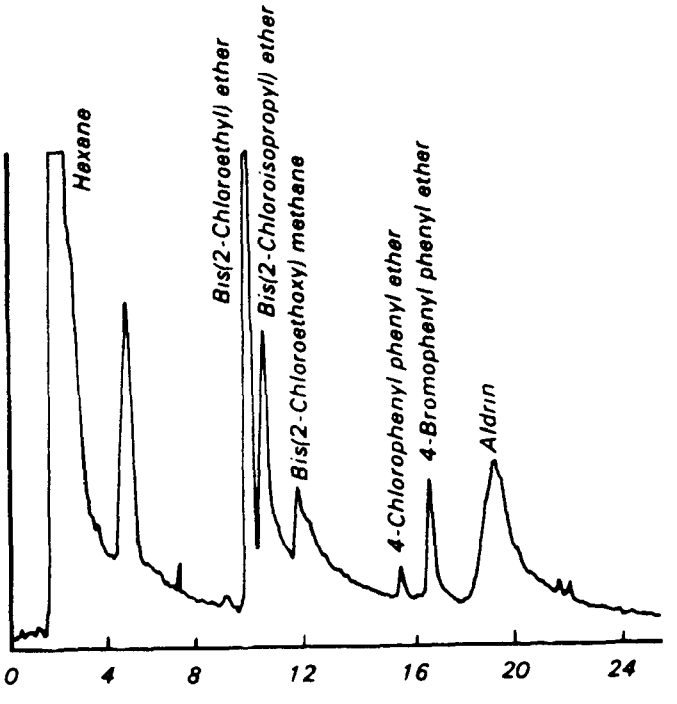
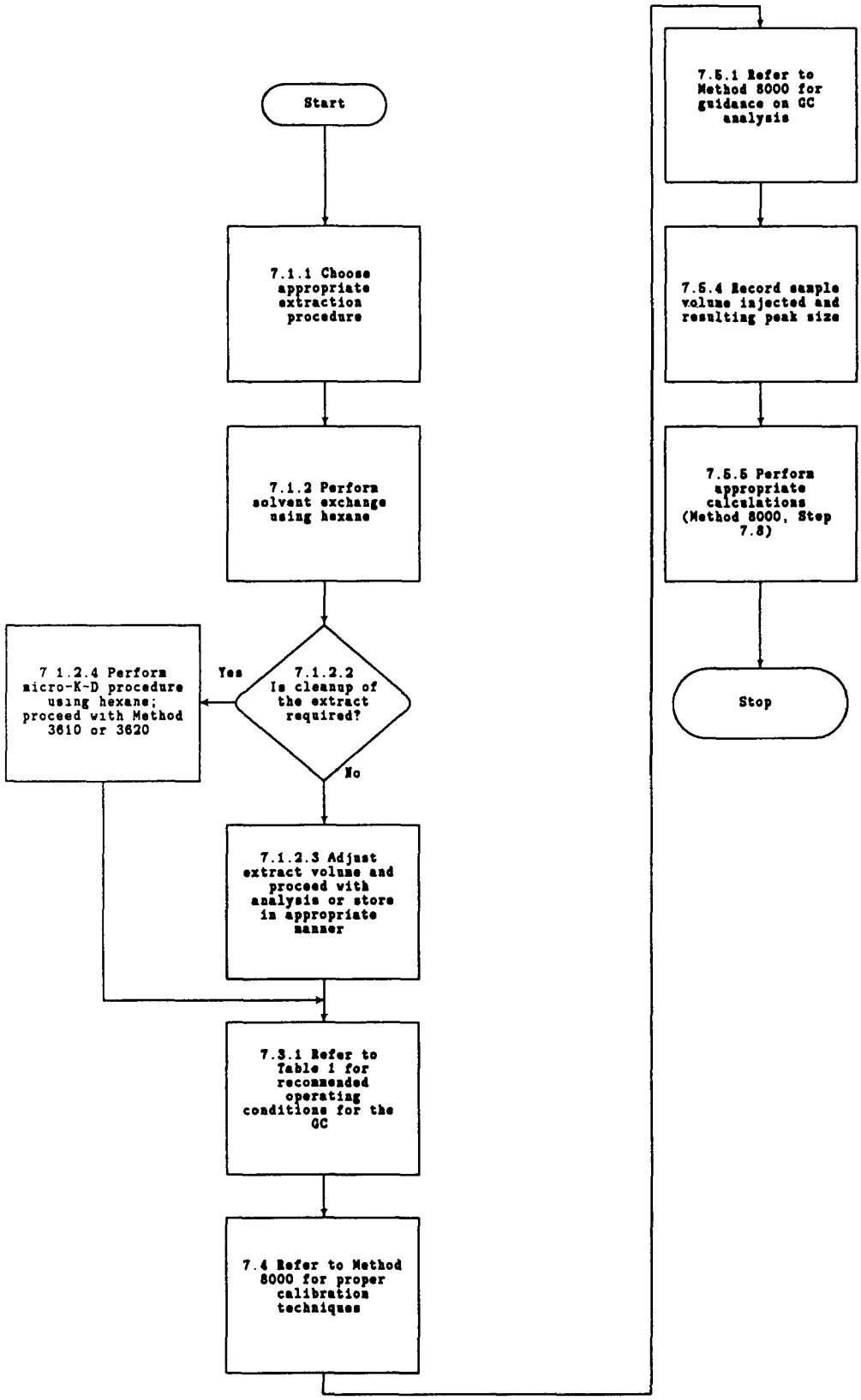


FIGURE 2.
GAS CHROMATOGRAM OF HALOETHERS

Column: Tenax GC
Program: 150°C.-4 minutes 16°/minute to 310°C.
Detector: Hall electrolytic conductivity




Start
7.1.1 Choose appropriate extraction procedure
7.1.2 Perform solvent exchange using hexane
7.1.2.2 Is cleanup of the extract required?
Yes
7.1.2.4 Perform micro-K-D procedure using hexane; proceed with Method 3610 or 3620
No
7.1.2.3 Adjust extract volume and proceed with analysis or store in appropriate manner
7.3.1 Refer to Table 1 for recommended operating conditions for the GC
7.4 Refer to Method 8000 for proper calibration techniques
7.5.1 Refer to Method 8000 for guidance on GC analysis
7.5.4 Record sample volume injected and resulting peak size
7.5.5 Perform appropriate calculations (Method 8000, Step 7.8)
Stop

METHOD 8120A

CHLORINATED HYDROCARBONS BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8120 is used to determine the concentration of certain chlorinated hydrocarbons. The following compounds can be determined by this method:

		Appropriate Preparation Techniques				
Compounds	CAS No[a]	3510	3520	3540	3550	3580
2-Chloronaphthalene	91-58-7	X	X	X	X	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
Hexachlorobenzene	118-74-1	X	X	X	X	X
Hexachlorobutadiene	87-68-3	X	X	X	X	X
Hexachlorocyclohexane	608-73-1	X	X	X	X	X
Hexachlorocyclopentadiene	77-47-4	X	X	X	X	X
Hexachloroethane	67-72-1	X	X	X	X	X
Pentachlorohexane		X	X	X	X	X
Tetrachlorobenzenes		X	ND	ND	ND	X
1,2,4-Trichlorobenzene	120-82-1	X	X	X	X	X

a Chemical Abstract Services Registry Number.
x Greater than 70 percent recovery by this technique
ND Not determined.

1.2 Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in organic-free reagent water. Table 2 lists the estimated quantitation limit (EQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8120 provides gas chromatographic conditions for the detection of ppb concentrations of certain chlorinated hydrocarbons. Prior to use of this method, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2 to 5 µL aliquot of the extract is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by an electron capture detector (ECD).

2.2 If interferences are encountered in the analysis, Method 8120 may also be performed on extracts that have undergone cleanup using Method 3620.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all glass systems may be required.

3.3 Interferences coextracted from samples will vary considerably from source to source, depending upon the waste being sampled. Although general cleanup techniques are recommended as part of this method, unique samples may require additional cleanup.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

4.1.1 Gas chromatograph - Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak areas and/or peak heights is recommended.

4.1.2 Columns

4.1.2.1 Column 1 - 1.8 m x 2 mm ID glass column packed with 1% SP-1000 on Supelcoport (100/120 mesh) or equivalent.

4.1.2.2 Column 2 - 1.8 m x 2 mm ID glass column packed with 1.5% OV-1/2.4% OV-225 on Supelcoport (80/100 mesh) or equivalent.

4.1.3 Detector - Electron capture (ECD).

4.2 Kuderna-Danish (K-D) apparatus

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

4.2.2 Evaporation flask - 500 mL (Kontes K-570001-500 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 K-569001-0219 or equivalent).

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

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

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

4.5 Volumetric flasks - 10, 50, and 100 mL, with ground glass stoppers.

4.6 Microsyringe - 10 μL.

4.7 Syringe - 5 mL.

4.8 Vials - Glass, 2, 10, and 20 mL capacity 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 Solvents

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

5.3.2 Acetone, CH_3COCH_3. Pesticide quality or equivalent.

5.3.3 Isooctane, C_8H_{18}. Pesticide quality or equivalent.

5.4 Stock standard solutions

5.4.1 Prepare stock standard solutions at a concentration of 1000 mg/L by dissolving 0.0100 g of assayed reference material in isooctane or hexane and diluting 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 can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

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

5.4.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.5 Calibration standards - Calibration standards at a minimum of five concentrations should be prepared through dilution of the stock standards with isooctane or hexane. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.6 Internal standards (if internal standard calibration is used) - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.6.1 Prepare calibration standards at a minimum of five concentrations for each analyte of interest as described in Section 5.5.

5.6.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane or hexane.

5.6.3 Analyze each calibration standard according to Section 7.0.

5.7 Surrogate standards - The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and organic-free reagent water blank with one or two surrogates (e.g. chlorinated hydrocarbons that are not expected to be in the sample) recommended to encompass the range of the temperature program used in this method. Method 3500 details instructions on the preparation of base/neutral surrogates. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

6.2 Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a

neutral, or as is, pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550.

7.1.2 Prior to gas chromatographic analysis, the extraction solvent must be exchanged to hexane. The exchange is performed during the K-D procedures listed in all of the extraction methods. The exchange is performed as follows.

7.1.2.1 Following K-D of the methylene chloride extract to 1 mL using the macro Snyder column, allow the apparatus to cool and drain for at least 10 minutes.

7.1.2.2 Momentarily remove the Snyder column, add 50 mL of hexane, a new boiling chip, and reattach the macro Snyder column. Concentrate the extract using 1 mL of hexane to prewet the Snyder column. Place the K-D apparatus on the 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 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 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. The extract will be handled differently at this point, depending on whether or not cleanup is needed. If cleanup is not required, proceed to Section 7.1.2.3. If cleanup is needed, proceed to Section 7.1.2.4.

7.1.2.3 If cleanup of the extract is not required, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane. A 5 mL syringe is recommended for this operation. Adjust the extract volume to 10.0 mL. Stopper the concentrator tube and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a vial with a Teflon lined screw cap or crimp top. Proceed with gas chromatographic analysis.

7.1.2.4 If cleanup of the extract is required, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with a minimum amount of hexane. A 5 mL syringe is recommended for this operation. Add a clean boiling chip to the concentrator tube and attach a two ball micro Snyder column. Prewet the column by adding about 0.5 mL of hexane to the top. Place the micro K-D apparatus on the water bath (80°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 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 and allow it to drain and cool for at least 10 minutes.

7.1.2.5 Remove the micro Snyder column and rinse the flask and its lower joint into the concentrator tube with 0.2 mL of

hexane. Adjust the extract volume to 2.0 mL and proceed with Method 3620.

7.2 Gas chromatographic conditions (Recommended)

7.2.1 Column 1

Carrier gas (5% methane/95% argon) flow rate = 25 mL/min
Column temperature = 65°C isothermal, unless otherwise specified (see Table 1).

7.2.2 Column 2

Carrier gas (5% methane/95% argon) flow rate = 25 mL/min
Column temperature = 75°C isothermal, unless otherwise specified (see Table 1).

7.3 Calibration - Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.3.2 If cleanup is performed on the samples, the analyst should process a series of standards through the cleanup procedure and then analyze the samples by GC. This will validate elution patterns and the absence of interferents from the reagents.

7.4 Gas chromatographic analysis

7.4.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 µL of internal standard to the sample prior to injecting.

7.4.2 Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

7.4.3 Examples of GC/ECD chromatograms for certain chlorinated hydrocarbons are shown in Figures 1 and 2.

7.4.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.5 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes. See Method 8000 for calculation equations.

7.4.6 If peak detection and identification are prevented due to interferences, the hexane extract may undergo cleanup using Method 3620.

7.5 Cleanup: If required, the samples may be cleaned up using the Methods presented in Chapter 4.

7.5.1 Proceed with Method 3620 using the 2 mL hexane extracts obtained from Section 7.1.2.5.

7.5.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous paragraphs and in Method 8000.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000.

8.2.1 The quality control check sample concentrate (Method 8000) should contain each parameter of interest at the following concentrations in acetone: hexachloro-substituted hydrocarbon, 10 mg/L; and any other chlorinated hydrocarbon, 100 mg/L.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000).

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

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration".

9.0 METHOD PERFORMANCE

9.1 The method was tested by 20 laboratories using organic-free reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 1.0 to 356 µg/L. Single operator precision,

overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships for a flame ionization detector are presented in Table 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample preparation technique, and calibration procedures used.

10.0 REFERENCES

1. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 3 - Chlorinated Hydrocarbons, and Category 8 - Phenols," Report for EPA Contract 68-03-2625 (in preparation).

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

3. "EPA Method Validation Study 22, Method 612 (Chlorinated Hydrocarbons)," Report for EPA Contract 68-03-2625 (in preparation).

4. "Method Performance for Hexachlorocyclopentadiene by Method 612," Memorandum from R. Slater, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, December 7, 1983.

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.

6. "Determination of Chlorinated Hydrocarbons in Industrial and Municipal Wastewaters," Report for EPA Contract 68-03-2625 (in preparation).

TABLE 1.
GAS CHROMATOGRAPHY OF CHLORINATED HYDROCARBONS

Compound	Retention time (min) Col. 1	Col. 2	Method Detection limit (µg/L)
2-Chloronaphthalene	2.7[a]	3.6[b]	0.94
1,2-Dichlorobenzene	6.6	9.3	1.14
1,3-Dichlorobenzene	4.5	6.8	1.19
1,4-Dichlorobenzene	5.2	7.6	1.34
Hexachlorobenzene	5.6[a]	10.1[b]	0.05
Hexachlorobutadiene	7.7	20.0	0.34
Hexachlorocyclohexane			
Hexachlorocyclopentadiene	ND	16.5[c]	0.40
Hexachloroethane	4.9	8.3	0.03
Pentachlorohexane			
Tetrachlorobenzenes			
1,2,4-Trichlorobenzene	15.5	22.3	0.05

ND = Not determined.

[a]150°C column temperature.

[b]165°C column temperature.

[c]100°C column temperature.

TABLE 2.
DETERMINATION OF ESTIMATED QUANTITATION
LIMITS (EQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-concentration soil by ultrasonic extraction with GPC cleanup	670
High-concentration soil and sludges by ultrasonic extraction	10,000
Non-water miscible waste	100,000

a Sample EQLs are highly matrix dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

b EQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet weight basis.

TABLE 3.
QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (μg/L)	Limit for s (μg/L)	Range for $\bar{x}$ (μg/L)	Range P, P_s (%)
2-Chloronaphthalene	100	37.3	29.5-126.9	9-148
1,2-Dichlorobenzene	100	28.3	23.5-145.1	9-160
1,3-Dichlorobenzene	100	26.4	7.2-138.6	D-150
1,4-Dichlorobenzene	100	20.8	22.7-126.9	13-137
Hexachlorobenzene	10	2.4	2.6-14.8	15-159
Hexachlorobutadiene	10	2.2	D-12.7	D-139
Hexachlorocyclopentadiene	10	2.5	D-10.4	D-111
Hexachloroethane	10	3.3	2.4-12.3	8-139
1,2,4-Trichlorobenzene	100	31.6	20.2-133.7	5-149

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 612. These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 4.

TABLE 4.
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Parameter	Accuracy, as recovery, x' (μg/L)	Single analyst precision, s_r' (μg/L)	Overall precision, S' (μg/L)
Chloronaphthalene	0.75C+3.21	0.28$\bar{x}$-1.17	0.38$\bar{x}$-1.39
1,2-Dichlorobenzene	0.85C-0.70	0.22$\bar{x}$-2.95	0.41$\bar{x}$-3.92
1,3-Dichlorobenzene	0.72C+0.87	0.21$\bar{x}$-1.03	0.49$\bar{x}$-3.98
1,4-Dichlorobenzene	0.72C+2.80	0.16$\bar{x}$-0.48	0.35$\bar{x}$-0.57
Hexachlorobenzene	0.87C-0.02	0.14$\bar{x}$+0.07	0.36$\bar{x}$-0.19
Hexachlorobutadiene	0.61C+0.03	0.18$\bar{x}$+0.08	0.53$\bar{x}$-0.12
Hexachlorocyclopentadiene[a]	0.47C	0.24$\bar{x}$	0.50$\bar{x}$
Hexachloroethane	0.74C-0.02	0.23$\bar{x}$+0.07	0.36$\bar{x}$-0.00
1,2,4-Trichlorobenzene	0.76C+0.98	0.23$\bar{x}$-0.44	0.40$\bar{x}$-1.37

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.

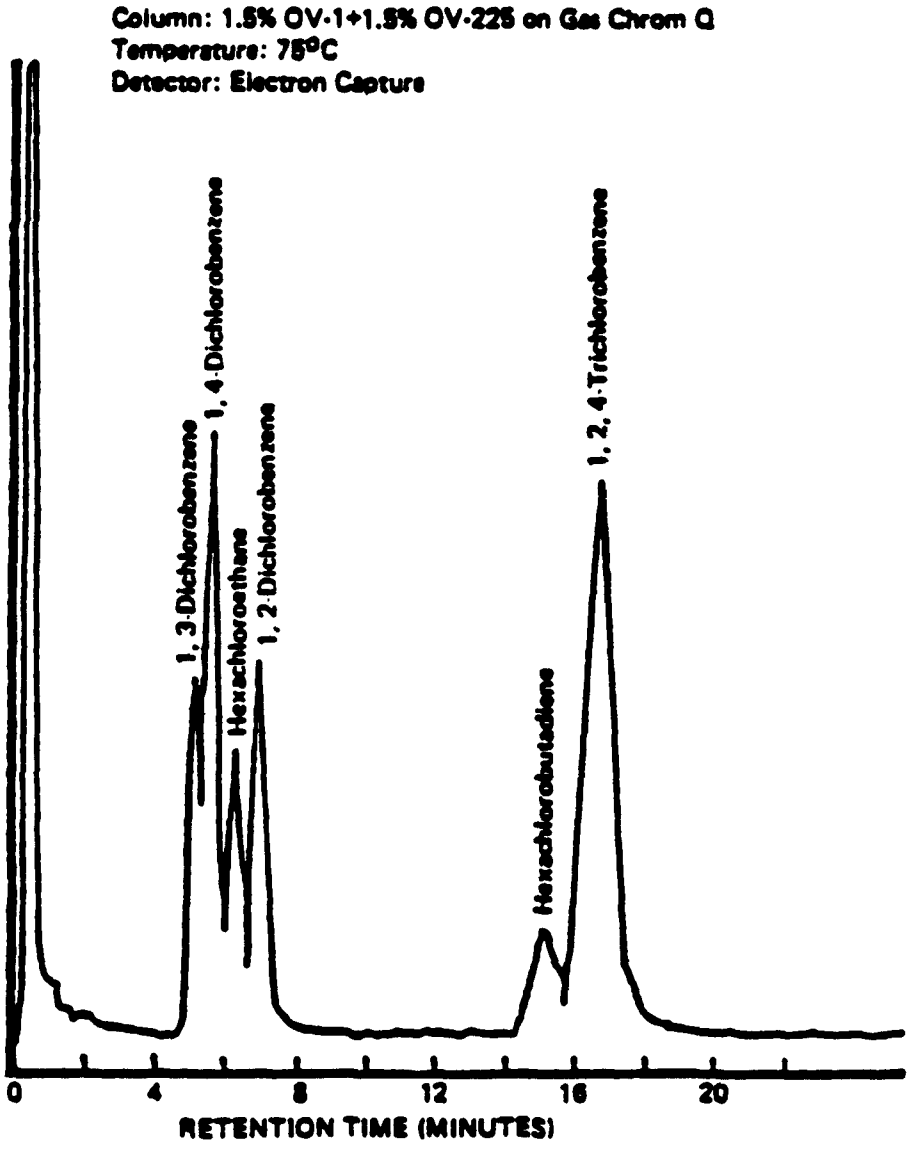
S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{x}$, in μg/L.

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.

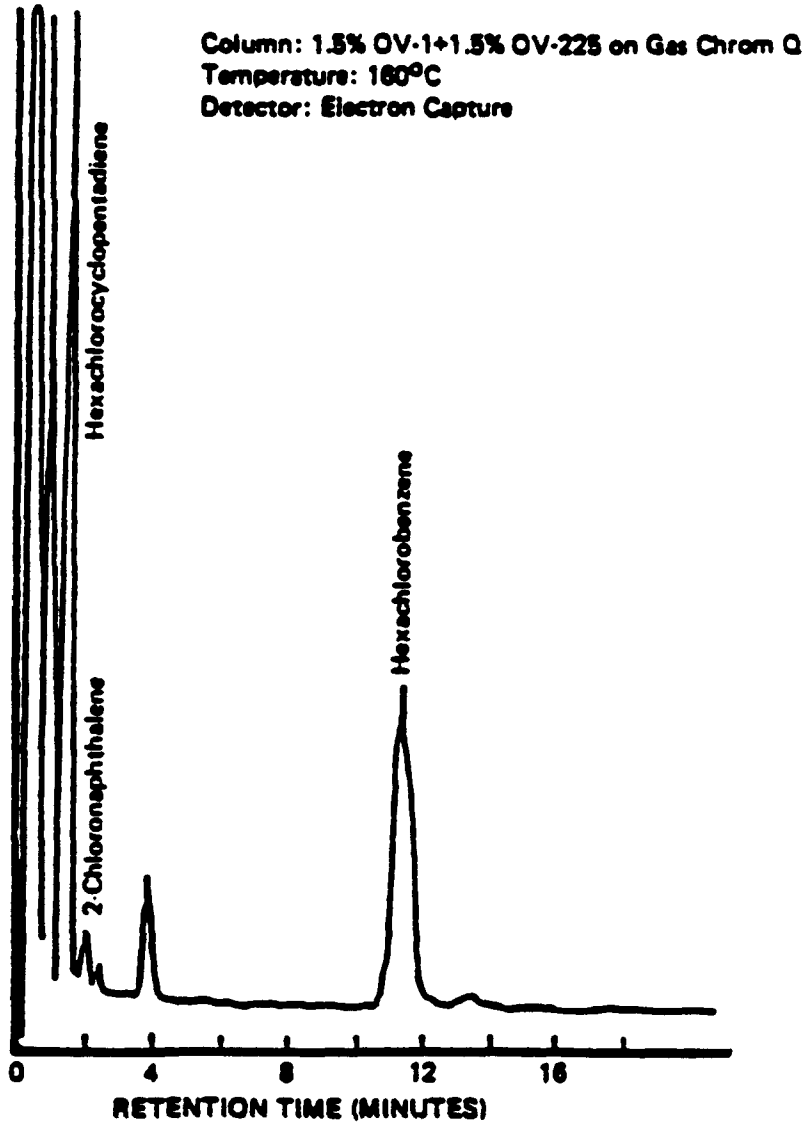
a Estimates based upon the performance in a single laboratory.

FIGURE 1

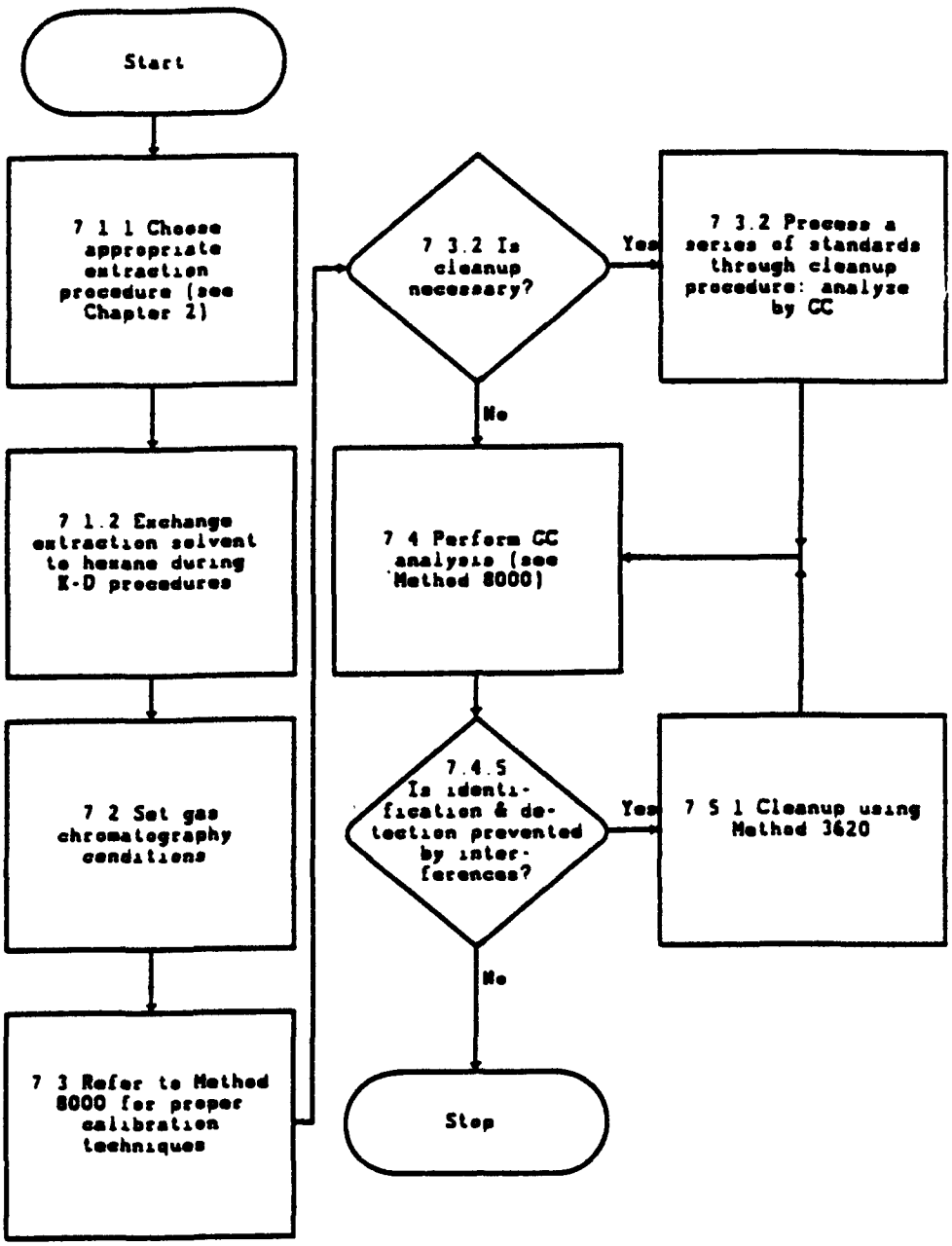


Gas chromatogram of chlorinated hydrocarbons (low molecular weight compounds).

FIGURE 2



Gas chromatogram of chlorinated hydrocarbons (high molecular weight compounds).


Start
7 1 1 Choose appropriate extraction procedure (see Chapter 2)
7 1 2 Exchange extraction solvent to hexane during K-D procedures
7 2 Set gas chromatography conditions
7 3 Refer to Method 8000 for proper calibration techniques
7 3.2 Is cleanup necessary?
Yes
7 3.2 Process a series of standards through cleanup procedure: analyze by GC
No
7 4 Perform GC analysis (see Method 8000)
7.4.5 Is identification & detection prevented by interferences?
Yes
7 5 1 Cleanup using Method 3620
No
Stop

CHLORINATED HYDROCARBONS BY GAS CHROMATOGRAPHY: CAPILLARY COLUMN TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 Method 8121 describes the determination of chlorinated hydrocarbons in extracts prepared from environmental samples and RCRA wastes. It describes wide-bore open-tubular, capillary column gas chromatography procedures using both single column/single detector and dual-column/dual-detector approaches. The following compounds can be determined by this method:

Compound Name	CAS Registry No.[a]
Benzal chloride	98-87-3
Benzotrichloride	98-07-7
Benzyl chloride	100-44-7
2-Chloronaphthalene	91-58-7
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-1
Hexachlorobenzene	118-74-1
Hexachlorobutadiene	87-68-3
α-Hexachlorocyclohexane (α-BHC)	319-84-6
ß-Hexachlorocyclohexane (ß-BHC)	319-85-7
γ-Hexachlorocyclohexane (γ-BHC)	58-89-9
δ-Hexachlorocyclohexane (δ-BHC)	319-86-8
Hexachlorocyclopentadiene	77-47-4
Hexachloroethane	67-72-1
Pentachlorobenzene	608-93-5
1,2,3,4-Tetrachlorobenzene	634-66-2
1,2,4,5-Tetrachlorobenzene	95-94-2
1,2,3,5-Tetrachlorobenzene	634-90-2
1,2,4-Trichlorobenzene	120-82-1
1,2,3-Trichlorobenzene	87-61-6
1,3,5-Trichlorobenzene	108-70-3

[a] Chemical Abstract Services Registry Number.

1.2 The dual-column/dual-detector approach involves the use of two 30 m x 0.53 mm ID fused-silica open-tubular columns of different polarities, thus different selectivities towards the target compounds. The columns are connected to an injection tee and two identical detectors. When compared to the packed columns, the megabore fused-silica open-tubular columns offer improved resolution, better selectivity, increased sensitivity, and faster analysis.

1.3 Table 1 lists method detection limits (MDL) for each compound in an organic-free reagent water matrix. The MDLs for the compounds of a specific sample may differ from those listed in Table 1 because they are dependent upon the nature of interferences in the sample matrix. Table 2 lists the estimated quantitation limits (EQL) for other matrices.

1.4 Table 3 lists the compounds that have been determined by this method and their retention times using the single column technique. Table 4 lists dual column/dual detector retention time data. Figures 1 and 2 are chromatograms showing the single column technique. Figure 3 shows a chromatogram of the target analytes eluted from a pair of DB-5/DB-1701 columns and detected with electron capture detectors (ECD) under the prescribed GC conditions listed in Table 2.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph and in the interpretation of gas chromatograms.

2.0 SUMMARY OF METHOD

2.1 Method 8121 provides gas chromatographic conditions for the detection of ppb concentrations of chlorinated hydrocarbons in water and soil or ppm concentrations in waste samples. Prior to use of this method, appropriate sample extraction techniques must be used for environmental samples (refer to Chapt. 2). Both neat and diluted organic liquids (Method 3580) may be analyzed by direct injection. Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. Analysis is accomplished by gas chromatography utilizing an instrument equipped with wide bore capillary columns and single or dual electron capture detectors.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 The electron capture detector responds to all electronegative compounds. Therefore, interferences are possible by other halogenated compounds, as well as phthalates and other oxygenated compounds, and, organonitrogen, organosulfur and organophosphorus compounds. Second column confirmation or GC/MS confirmation are necessary to ensure proper analyte identification unless previous characterization of the sample source will ensure proper identification.

3.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the syringe used for injection must be rinsed out between samples with solvent. Whenever an extract concentration exceeds that of the highest calibration standard, it should be followed by the analysis of a solvent blank to check for cross-contamination. Additional solvent blanks interspersed with the sample extracts should be considered whenever the analysis of a solvent blank indicates cross-contamination problems.

3.4 Phthalate esters, if present in a sample, will interfere only with the BHC isomers because they elute in Fraction 2 of the Florisil procedure described in Method 3620. The presence of phthalate esters can usually be minimized by avoiding contact with any plastic materials and by following standard decontamination procedures of reagents and glassware.

3.5 The presence of elemental sulfur will result in large peaks, and can often mask the region of compounds eluting after 1,2,4,5-tetrachlorobenzene. The

tetrabutylammonium (TBA)-sulfite procedure (Method 3660) works well for the removal of elemental sulfur.

3.6 In certain cases some compounds coelute on either one or both columns. In these cases the compounds must be reported as coeluting. The mixture can be reanalyzed by GC/MS techniques, see Section 8.7 and Method 8270.

3.6.1 Using the dual column system of analysis the following compounds coeluted:

DB 5	1,4-dichlorobenzene/benzyl chloride 1,2,3,5-tetrachlorobenzene/1,2,4,5-tetrachlorobenzene 1,2,3,4-tetrachlorobenzene/2-chloronaphthalene
DB 1701	benzyl chloride/1,2-dichlorobenzene/hexachloroethane benzal chloride/1,2,4-trichlorobenzene/ hexachlorobutadiene

Some of the injections showed a separation of 1,2,4-trichlorobenzene from the other two compounds, however, this is not always the case, so the compounds are listed as coeluting.

3.7 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All these materials must be demonstrated to be free from interferences under the conditions of the analysis, by analyzing reagent blanks.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph: An analytical system complete with a gas chromatograph suitable for on-column and split-splitless injection, and all required accessories, including syringes, analytical columns, gases, and two electron capture detectors. A data system for measuring peak areas, and dual display of chromatograms is recommended. A GC equipped with a single GC column and detector are acceptable, however, second column confirmation is obviously more time consuming. Following are the single and dual column configurations used for developing the retention time data presented in the method. The columns listed in the dual column configuration may also be used for single column analysis.

4.1.1 Single Column Analysis:

4.1.1.1 Column 1 - 30 m x 0.53 mm ID fused-silica capillary column chemically bonded with trifluoropropyl methyl silicone (DB-210 or equivalent).

4.1.1.2 Column 2 - 30 m x 0.53 mm ID fused-silica capillary column chemically bonded with polyethylene glycol (DB-WAX or equivalent).

4.1.2 Dual Column Analysis:

4.1.2.1 Column 1 - 30 m x 0.53 mm ID fused-silica open-tubular column, crosslinked and chemically bonded with 95 percent dimethyl and 5 percent diphenyl-polysiloxane (DB-5, RT_x-5, SPB-5, or equivalent), 0.83 µm or 1.5 µm film thickness.

4.1.2.2 Column 2 - 30 m x 0.53 mm ID fused-silica open-tubular column crosslinked and chemically bonded with 14 percent cyanopropylphenyl and 86 percent dimethyl-polysiloxane (DB-1701, RT_x-1701, or equivalent), 1.0 µm film thickness.

4.1.3 Splitter: If the splitter approach to dual column injection is chosen, following are three suggested splitters. An equivalent splitter is acceptable. See Section 7.5.1 for a caution on the use of splitters.

4.1.3.1 Splitter 1 - J&W Scientific press-fit Y-shaped glass 3-way union splitter (J&W Scientific, Catalog no. 705-0733).

4.1.3.2 Splitter 2 - Supelco 8 in. glass injection tee, deactivated (Supelco, Catalog no. 2-3665M).

4.1.3.3 Splitter 3 - Restek Y-shaped fused-silica connector (Restek, Catalog no. 20405).

4.1.4 Column rinsing kit (optional): Bonded-phase column rinse kit (J&W Scientific, Catalog no. 430-3000 or equivalent).

4.1.5 Microsyringes - 100 µL, 50 µL, 10 µL (Hamilton 701 N or equivalent), and 50 µL (Blunted, Hamilton 705SNR or equivalent).

4.1.6 Balances - Analytical, 0.0001 g.

4.1.7 Volumetric flasks, Class A - 10 mL to 1000 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 chemicals are of sufficiently high purity to permit their use without affecting the accuracy of the determinations.

NOTE: Store the standard solutions (stock, composite, calibration, internal, and surrogate) at 4°C in Teflon-sealed containers in the dark. All standard solutions must be replaced after six months or sooner if routine QC (Section 8) indicates a problem.

5.2 Solvents

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

5.2.2 Acetone, CH_3COCH_3 - Pesticide quality or equivalent.

5.2.3 Isooctane, $(CH_3)_3CCH_2CH(CH_3)_2$ - Pesticide quality or equivalent.

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

5.3.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure compound. Dissolve the compound in isooctane or hexane and dilute to volume in a 10 mL volumetric flask. If compound purity is 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard solution. Commercially prepared stock standard solutions can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.2 For those compounds which are not adequately soluble in hexane or isooctane, mixtures of acetone and hexane are recommended.

5.4 Composite stock standard: Can be prepared from individual stock solutions. For composite stock standards containing less than 25 components, take exactly 1 mL of each individual stock solution at 1000 mg/L, add solvent, and mix the solutions in a 25 mL volumetric flask. For example, for a composite containing 20 individual standards, the resulting concentration of each component in the mixture, after the volume is adjusted to 25 mL, will be 40 mg/L. This composite solution can be further diluted to obtain the desired concentrations.

5.5 Calibration standards should be prepared at a minimum of five concentrations by dilution of the composite stock standard with isooctane or hexane. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector. A suggested list of calibration solution standards is found in Table 7.

5.6 Recommended internal standard: Make a solution of 1000 mg/L of 1,3,5-tribromobenzene. (Two other internal standards, 2,5-dibromotoluene and alpha,alpha'-dibromo-m-xylene, are suggested if matrix interferences are a problem.) For spiking, dilute this solution to 50 ng/µL. Use a spiking volume of 10 µL/mL of extract. The spiking concentration of the internal standards should be kept constant for all samples and calibration standards. Store the internal standard spiking solutions at 4°C in Teflon-sealed containers in the dark.

5.7 Recommended surrogate standards: Monitor the performance of the method using surrogate compounds. Surrogate standards are added to all samples, method blanks, matrix spikes, and calibration standards. Make a solution of 1000 mg/L of 1,4-dichloronaphthalene and dilute it to 100 ng/µL. Use a spiking volume of 100 µL for a 1 L aqueous sample. If matrix interferences are a problem, two alternative surrogates are: alpha, 2,6-trichlorotoluene or 2,3,4,5,6-pentachlorotoluene.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

6.2 Extracts must be stored at 4 °C and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction and Cleanup:

7.1.1 Refer to Chapter Two and Method 3500 for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral, or as is, pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550 with methylene chloride/acetone (1:1) as the extraction solvent.

7.1.2 If required, the samples may be cleaned up using Method 3620 (Florisil) and/or Method 3640 (Gel Permeation Chromatography). See Chapter Two, Section 2.3.2 and Method 3600 for general guidance on cleanup and method selection. Method 3660 is used for sulfur removal.

7.1.3 Prior to gas chromatographic analysis, the extraction solvent must exchanged into hexane using the Kuderna-Danish concentration step found in any of the extraction methods. Any methylene chloride remaining in the extract will cause a very broad solvent peak.

7.2 Gas Chromatographic Conditions:

7.2.1 Retention time information for each of the analytes is presented in Tables 3 and 4. The recommended GC operating conditions are provided in Tables 5 and 6. Figures 1, 2 and 3 illustrate typical chromatography of the method analytes for both the single column approach and the dual column approach when operated at the conditions specified in Tables 5 and 6.

7.3 Calibration:

7.3.1 Prepare calibration standards using the procedures in Section 5.0. Refer to Method 8000 for proper calibration procedures. The procedure for internal or external calibration may be used.

7.3.2 Refer to Method 8000 for the establishment of retention time windows.

7.4 Gas chromatographic analysis:

7.4.1 Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria.

7.4.2 Automatic injections of 1 µL are recommended. Hand injections of no more than 2 µL may be used if the analyst demonstrates quantitation precision of $\leq$ 10 percent relative standard deviation. The solvent flush technique may be used if the amount of solvent is kept at a minimum. If the internal standard calibration technique is used, add 10 µL of the internal standard to each mL of sample extract prior to injection.

7.4.3 Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window.

7.4.4 Validation of gas chromatographic system qualitative performance: Use the midconcentration standards interspersed throughout the analysis sequence (Section 7.3) to evaluate this criterion. If any of the standards fall outside their daily retention time windows, the system is out of control. Determine the cause of the problem and correct it (see Section 7.5).

7.4.5 Record the volume injected to the nearest 0.05 µL and the resulting peak size in peak height or area units. Using either the internal or the external calibration procedure (Method 8000), determine the identity and the quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes. See Method 8000 for calculation equations.

7.4.6 If the responses exceed the linear range of the system, dilute the extract and reanalyze. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

7.4.7 If partially overlapping or coeluting peaks are found, change columns or try a GC/MS technique (see Section 8.7 and Method 8270). Interferences that prevent analyte identification and/or quantitation may be removed by the cleanup techniques mentioned above.

7.4.8 If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The analyst should consult with the source of the sample to determine whether further concentration of the sample is warranted.

7.5 Instrument Maintenance:

7.5.1 Injection of sample extracts from waste sites often leaves a high boiling residue in: the injection port area, splitters when used, and the injection port end of the chromatographic column. This residue effects chromatography in many ways (i.e., peak tailing, retention time shifts, analyte degradation, etc.) and, therefore, instrument maintenance is very important. Residue buildup in a splitter may limit flow through one leg and therefore change the split ratios. If this occurs during an analytical run, the quantitative data may be incorrect. Proper cleanup techniques will minimize the problem and instrument QC will indicate when instrument maintenance is required.

7.5.2 Suggested chromatograph maintenance: Corrective measures may require any one or more of the following remedial actions. Also see Section 7 in Method 8000 for additional guidance on corrective action for capillary columns and the injection port.

7.5.2.1 Splitter connections: For dual columns which are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector, clean and deactivate the splitter or replace with a cleaned and deactivated splitter. Break off the first few inches (up to one foot) of the injection port side of the column. Remove the columns and solvent backflush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the columns.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Quality control required to evaluate the GC system operation is found in Method 8000, Section 8.3.

8.3 Calculate surrogate standard recoveries for all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Section 8). If the recovery is not within limits, the following are required:

8.3.1 Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.

8.3.2 Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

8.3.3 Reextract and reanalyze the sample if none of the above are a problem, or flag the data as "estimated concentrations".

8.4 Data from systems that automatically identify target analytes on the basis of retention time or retention time indices should be reviewed by an experienced analyst before they are reported.

8.5 When using the internal standard calibration technique, an internal standard peak area check must be performed on all samples. The internal standard must be evaluated for acceptance by determining whether the measured area for the internal standard deviates by more than 50 percent from the average area for the internal standard in the calibration standards. When the internal standard peak area is outside that limit, all samples that fall outside the QC criteria must be reanalyzed.

8.6 Include a mid-concentration calibration standard after each group of 20 samples in the analysis sequence. The response factors for the mid-concentration calibration must be within ± 15 percent of the average values for the multiconcentration calibration. When the response factors fall outside that limit, all samples analyzed after that mid-concentration calibration standard must be reanalyzed after performing instrument maintenance to correct the usual source of the problem. If this fails to correct the problem, a new calibration curve must be established.

8.7 GC/MS confirmation:

8.7.1 GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. Follow the GC/MS operating requirements specified in Method 8270. Ensure that there is sufficient concentration of the analyte(s) to be confirmed, in the extract for GC/MS analysis.

8.7.2 When available, chemical ionization mass spectra may be employed to aid in the qualitative identification process.

8.7.3 To confirm an identification of a compound, the background corrected mass spectrum of the compound must be obtained from the sample extract and must be compared with a mass spectrum from a stock or calibration standard analyzed under the same chromatographic conditions. At least 25 ng of material should be injected into the GC/MS. The identification criteria specified in Method 8270 must be met for qualitative confirmation.

8.7.3.1 Should the MS procedure fail to provide satisfactory results, additional steps may be taken before reanalysis. These steps may include the use of alternate packed or capillary GC columns or additional sample cleanup.

9.0 METHOD PERFORMANCE

9.1 The MDL is defined in Chapter One. The MDLs listed in Table 1 were obtained by using organic-free reagent water. Details on how to determine MDLs are given in Chapter One. The MDLs actually achieved in a given analysis will vary since they depend on instrument sensitivity and matrix effects.

9.2 This method has been tested in a single laboratory by using organic-free reagent water, sandy loam samples and extracts which were spiked with the test compounds at one concentration. Single-operator precision and method accuracy were found to be related to the concentration of compound and the type of matrix.

9.3 Single laboratory accuracy data were obtained for chlorinated hydrocarbons in a clay soil. The spiking concentrations ranged from 500 to 5000 µg/kg, depending on the sensitivity of the analyte to the electron capture detector. The spiking solution was mixed into the soil during addition and then immediatly transferred to the extraction device and immersed in the extraction solvent. The spiked sample was then extracted by Method 3541 (Automated

Soxhlet). The data represents a single determination. Analysis was by capillary column gas chromatography/electron capture detector following Method 8121 for the chlorinated hydrocarbons. These data are listed in Table 9 and were taken from Reference 4.

10.0 REFERENCES

1. Lopez-Avila, V., N.S. Dodhiwala, and J. Milanes, "Single Laboratory Evaluation of Method 8120, Chlorinated Hydrocarbons", 1988, EPA Contract Numbers 68-03-3226 and 68-03-3511.

2. Glazer, J.A., G.D. Foerst, G.D. McKee, S.A. Quave, and W.L. Budde, "Trace Analyses for Wastewaters," Environ. Sci. and Technol. 15:1426-1431, 1981.

3. Lopez-Avila, V.; Baldin, E.; Benedicto, J; Milanes, J.; Beckert, W. F. "Application of Open-Tubular Columns to SW 846 GC Methods"; final report to the U.S. Environmental Protection Agency on Contract 68-03-3511; Mid-Pacific Environmental Laboratory, Mountain View, CA, 1990.

4. Lopez-Avila, V. (Beckert, W., Project Officer), "Development of a Soxtec Extraction Procedure for Extracting Organic Compounds from Soils and Sediments", EPA 600/X-91/140, US EPA, Environmental Monitoring Systems Laboratory-Las Vegas, October 1991.

Table 1
METHOD DETECTION LIMITS FOR CHLORINATED HYDROCARBONS
SINGLE COLUMN METHOD OF ANALYSIS

Compound name	CAS Reg. No.	MDL[a] (ng/L)
Benzal chloride	98-87-3	2-5[b]
Benzotrichloride	98-07-7	6.0
Benzyl chloride	100-44-7	180
2-Chloronaphthalene	91-58-7	1,300
1,2-Dichlorobenzene	95-50-1	270
1,3-Dichlorobenzene	541-73-1	250
1,4-Dichlorobenzene	106-46-1	890
Hexachlorobenzene	118-74-1	5.6
Hexachlorobutadiene	87-68-3	1.4
α-Hexachlorocyclohexane (α-BHC)	319-84-6	11
ß-Hexachlorocyclohexane (ß-BHC)	319-85-7	31
γ-Hexachlorocyclohexane (γ-BHC)	58-89-9	23
δ-Hexachlorocyclohexane (δ-BHC)	319-86-8	20
Hexachlorocyclopentadiene	77-47-4	240
Hexachloroethane	67-72-1	1.6
Pentachlorobenzene	608-93-5	38
1,2,3,4-Tetrachlorobenzene	634-66-2	11
1,2,4,5-Tetrachlorobenzene	95-94-2	9.5
1,2,3,5-Tetrachlorobenzene	634-90-2	8.1
1,2,4-Trichlorobenzene	120-82-1	130
1,2,3-Trichlorobenzene	87-61-6	39
1,3,5-Trichlorobenzene	108-70-3	12

[a] MDL is the method detection limit for organic-free reagent water. MDL was determined from the analysis of eight replicate aliquots processed through the entire analytical method (extraction, Florisil cartridge cleanup, and GC/ECD analysis).

$$MDL = t_{(n-1,0.99)} \times SD$$

where $t_{(n-1,0.99)}$ is the student's t value appropriate for a 99 percent confidence interval and a standard deviation with n-1 degrees of freedom, and SD is the standard deviation of the eight replicate measurements.

[b] Estimated from the instrument detection limit.

Table 2

ESTIMATED QUANTITATION LIMIT (EQL) FACTORS FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-concentration soil by ultrasonic extraction with GPC cleanup	670
High-concentration soil and sludges by ultrasonic extraction	10,000
Waste not miscible with water	100,000

[a] Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

[b] EQL = [Method detection limit (Table 1)] x [Factor (Table 2)]. For nonaqueous samples, the factor is on a wet-weight basis.

Table 3
GAS CHROMATOGRAPHIC RETENTION TIMES FOR CHLORINATED HYDROCARBONS: SINGLE COLUMN METHOD OF ANALYSIS

Compound Number	Compound name	Retention time (min) DB-210[a]	DB-WAX[b]
1	Benzal chloride	6.86	15.91
2	Benzotrichloride	7.85	15.44
3	Benzyl chloride	4.59	10.37
4	2-Chloronaphthalene	13.45	23.75
5	1,2-Dichlorobenzene	4.44	9.58
6	1,3-Dichlorobenzene	3.66	7.73
7	1,4-Dichlorobenzene	3.80	8.49
8	Hexachlorobenzene	19.23	29.16
9	Hexachlorobutadiene	5.77	9.98
10	α-BHC	25.54	33.84
12	γ-BHC	24.07	54.30
13	δ-BHC	26.16	33.79
14	Hexachlorocyclopentadiene	8.86	c
15	Hexachloroethane	3.35	8.13
16	Pentachlorobenzene	14.86	23.75
17	1,2,3,4-Tetrachlorobenzene	11.90	21.17
18	1,2,4,5-Tetrachlorobenzene	10.18	17.81
19	1,2,3,5-Tetrachlorobenzene	10.18	17.50
20	1,2,4-Trichlorobenzene	6.86	13.74
21	1,2,3-Trichlorobenzene	8.14	16.00
22	1,3,5-Trichlorobenzene	5.45	10.37
	Internal Standards		
	2,5-Dibromotoluene	9.55	18.55
	1,3,5-Tribromobenzene	11.68	22.60
	α,α'-Dibromo-meta-xylene	18.43	35.94
	Surrogates		
	α,2,6-Trichlorotoluene	12.96	22.53
	1,4-Dichloronaphthalene	17.43	26.83
	2,3,4,5,6-Pentachlorotoluene	18.96	27.91

[a] GC operating conditions: 30 m x 0.53 mm ID DB-210 fused-silica capillary column; 1 μm film thickness; carrier gas helium at 10 mL/min; makeup gas is nitrogen at 40 mL/min; temperature program from 65°C to 175°C (hold 20 minutes) at 4°C/min; injector temperature 220°C; detector temperature 250°C.

[b] GC operating conditions: 30 m x 0.53 mm ID DB-WAX fused-silica capillary column; 1 μm film thickness; carrier gas helium at 10 mL/min; makeup gas is nitrogen at 40 mL/min; temperature program from 60°C to 170°C (hold 30 minutes) at 4°C/min; injector temperature 200°C; detector temperature 230°C.

[c] Compound decomposes on-column.

TABLE 4
RETENTION TIMES OF THE CHLORINATED HYDROCARBONS[a]
DUAL COLUMN METHOD OF ANALYSIS

Compound No.	Compound	DB-5 RT(min)	DB-1701 RT(min)
1	1,3-Dichlorobenzene	5.82	7.22
2	1,4-Dichlorobenzene	6.00	7.53
3	Benzyl chloride	6.00	8.47
4	1,2-Dichlorobenzene	6.64	8.58
5	Hexachloroethane	7.91	8.58
6	1,3,5-Trichlorobenzene	10.07	11.55
7	Benzal chloride	10.27	14.41
8	1,2,4-Trichlorobenzene	11.97	14.54
9	1,2,3-Trichlorobenzene	13.58	16.93
10	Hexachlorobutadiene	13.88	14.41
11	Benzotrichloride	14.09	17.12
12	1,2,3,5-Tetrachlorobenzene	19.35	21.85
13	1,2,4,5-Tetrachlorobenzene	19.35	22.07
14	Hexachlorocyclopentadiene	19.85	21.17
15	1,2,3,4-Tetrachlorobenzene	21.97	25.71
16	2-Chloronaphthalene	21.77	26.60
17	Pentachlorobenzene	29.02	31.05
18	α-BHC	34.64	38.79
19	Hexachlorobenzene	34.98	36.52
20	ß-BHC	35.99	43.77
21	γ-BHC	36.25	40.59
22	δ-BHC	37.39	44.62
IS	1,3,5-Tribromobenzene	11.83	13.34
SU	1,4-Dichloronaphthalene	15.42	17.71

[a] The GC operating conditions were as follows: 30 m x 0.53 mm ID DB-5 (0.83-µm film thickness) and 30 m x 0.53 mm ID DB-1701 (1.0 µm film thickness) connected to an 8-in injection tee (Supelco Inc.). Temperature program: 80°C (1.5 min hold) to 125°C (1 min hold) at 2°C/min then to 240°C (2 min hold) at 5°C/min; injector temperature 250°C; detector temperature 320°C; helium carrier gas 6 mL/min; nitrogen makeup gas 20 mL/min.

Table 5
GC OPERATING CONDITIONS FOR CHLOROHYDROCARBONS
SINGLE COLUMN METHOD OF ANALYSIS

Column 1: DB 210 30 m x 0.53 mm ID fused-silica capillary column chemically bonded with trifluoropropyl methyl silicone

Carrier gas (He)	10 mL/min	
Column temperature:		
	Initial temperature	65°C
	Temperature program	65°C to 175°C at 4°C/min
	Final temperature	175°C, hold 20 minutes.
Injector temperature	220°C	
Detector temperature	250°C	
Injection volume	1-2 µL	

Column 2: DB WAX 30 m x 0.53 mm ID fused-silica capillary column chemically bonded with polyethylene glycol

Carrier gas (He)	10 mL/min	
Column temperature:		
	Initial temperature	60°C
	Temperature program	60°C to 170°C at 4°C/min
	Final temperature	170°C, hold 30 minutes.
Injector temperature	200°C	
Detector temperature	230°C	
Injection volume	1-2 µL	

TABLE 6
GC OPERATING CONDITIONS FOR CHLORINATED HYDROCARBONS
DUAL COLUMN METHOD OF ANALYSIS

Column 1:

Type: DB-1701 (J&W Scientific) or equivalent
Dimensions: 30 m x 0.53 mm ID
Film Thickness (µm): 1.0

Column 2:

Type: DB-5 (J&W Scientific) or equivalent
Dimensions: 30 m x 0.53 mm ID
Film Thickness (µm): 0.83

Carrier gas flowrate (mL/min): 6 (Helium)

Makeup gas flowrate (mL/min): 20 (Nitrogen)

Temperature program: 80°C (1.5 min hold) to 125°C (1 min hold) at 2°C/min then to 240°C (2 min hold) at 5°C/min.

Injector temperature: 250°C

Detector temperature: 320°C

Injection volume: 2 µL

Solvent: Hexane

Type of injector: Flash vaporization

Detector type: Dual ECD

Range: 10

Attenuation: 32 (DB-1701)/32 (DB-5)

Type of splitter: Supelco 8-in injection tee

Table 7

SUGGESTED CONCENTRATIONS FOR THE CALIBRATION SOLUTIONS[a]

	Concentration (ng/µL)				
Benzal chloride	0.1	0.2	0.5	0.8	1.0
Benzotrichloride	0.1	0.2	0.5	0.8	1.0
Benzyl chloride	0.1	0.2	0.5	0.8	1.0
2-Chloronaphthalene	2.0	4.0	10	16	20
1,2-Dichlorobenzene	1.0	2.0	5.0	8.0	10
1,3-Dichlorobenzene	1.0	2.0	5.0	8.0	10
1,4-Dichlorobenzene	1.0	2.0	5.0	8.0	10
Hexachlorobenzene	0.01	0.02	0.05	0.08	0.1
Hexachlorobutadiene	0.01	0.02	0.05	0.08	0.1
α-BHC	0.1	0.2	0.5	0.8	1.0
ß-BHC	0.1	0.2	0.5	0.8	1.0
γ-BHC	0.1	0.2	0.5	0.8	1.0
δ-BHC	0.1	0.2	0.5	0.8	1.0
Hexachlorocyclopentadiene	0.01	0.02	0.05	0.08	0.1
Hexachloroethane	0.01	0.02	0.05	0.08	0.1
Pentachlorobenzene	0.01	0.02	0.05	0.08	0.1
1,2,3,4-Tetrachlorobenzene	0.1	0.2	0.5	0.8	1.0
1,2,4,5-Tetrachlorobenzene	0.1	0.2	0.5	0.8	1.0
1,2,3,5-Tetrachlorobenzene	0.1	0.2	0.5	0.8	1.0
1,2,4-Trichlorobenzene	0.1	0.2	0.5	0.8	1.0
1,2,3-Trichlorobenzene	0.1	0.2	0.5	0.8	1.0
1,3,5-Trichlorobenzene	0.1	0.2	0.5	0.8	1.0
Surrogates					
α,2,6-Trichlorotoluene	0.02	0.05	0.1	0.15	0.2
1,4-Dichloronaphthalene	0.2	0.5	1.0	1.5	2.0
2,3,4,5,6-Pentachlorotoluene	0.02	0.05	0.1	0.15	0.2

[a] One or more internal standards should be spiked prior to GC/ECD analysis into all calibration solutions. The spike concentration of the internal standards should be kept constant for all calibration solutions.

Table 8

ELUTION PATTERNS OF CHLORINATED HYDROCARBONS
FROM THE FLORISIL COLUMN BY ELUTION WITH PETROLEUM ETHER (FRACTION 1)
AND 1:1 PETROLEUM ETHER/DIETHYL ETHER (FRACTION 2)

Compound	Amount (µg)	Recovery (percent)[a]	
		Fraction 1[b]	Fraction 2[c]
Benzal chloride[d]	10	0	0
Benzotrichloride	10	0	0
Benzyl chloride	100	82	16
2-Chloronaphthalene	200	115	
1,2-Dichlorobenzene	100	102	
1,3-Dichlorobenzene	100	103	
1,4-Dichlorobenzene	100	104	
Hexachlorobenzene	1.0	116	
Hexachlorobutadiene	1.0	101	
α-BHC	10		95
ß-BHC	10		108
γ-BHC	10		105
δ-BHC	10		71
Hexachlorocyclopentadiene	1.0	93	
Hexachloroethane	1.0	100	
Pentachlorobenzene	1.0	129	
1,2,3,4-Tetrachlorobenzene	10	104	
1,2,4,5-Tetrachlorobenzene[e]	10	102	
1,2,3,5-Tetrachlorobenzene[e]	10	102	
1,2,4-Trichlorobenzene	10	59	
1,2,3-Trichlorobenzene	10	96	
1,3,5-Trichlorobenzene	10	102	

[a] Values given represent average values of duplicate experiments.

[b] Fraction 1 was eluted with 200 mL petroleum ether.

[c] Fraction 2 was eluted with 200 mL petroleum ether/diethyl ether (1:1).

[d] This compound coelutes with 1,2,4-trichlorobenzene; separate experiments were performed with benzal chloride to verify that this compound is not recovered from the Florisil cleanup in either fraction.

[e] This pair cannot be resolved on the DB-210 fused-silica capillary columns.

TABLE 9
SINGLE LABORATORY ACCURACY DATA FOR THE EXTRACTION OF CHLORINATED HYDROCARBONS FROM SPIKED CLAY SOIL BY METHOD 3541 (AUTOMATED SOXHLET)[a]

Compound Name	Spike Level	% Recovery	
	µg/kg	DB-5	DB-1701
1,3-Dichlorobenzene	5000	b	39
1,2-Dichlorobenzene	5000	94	77
Benzal chloride	500	61	66
Benzotrichloride	500	48	53
Hexachlorocyclopentadiene	500	30	32
Pentachlorobenzene	500	76	73
alpha-BHC	500	89	94
delta-BHC	500	86	b
Hexachlorobenzene	500	84	88

a The operating conditions for the automated Soxhlet were as follows: immersion time 45 min; extraction time 45 min; the sample size was 10 g clay soil, extraction solvent, 1:1 acetone/hexane. No equilibration time following spiking.

b Not able to determine because of interference.

Data taken from Reference 4.

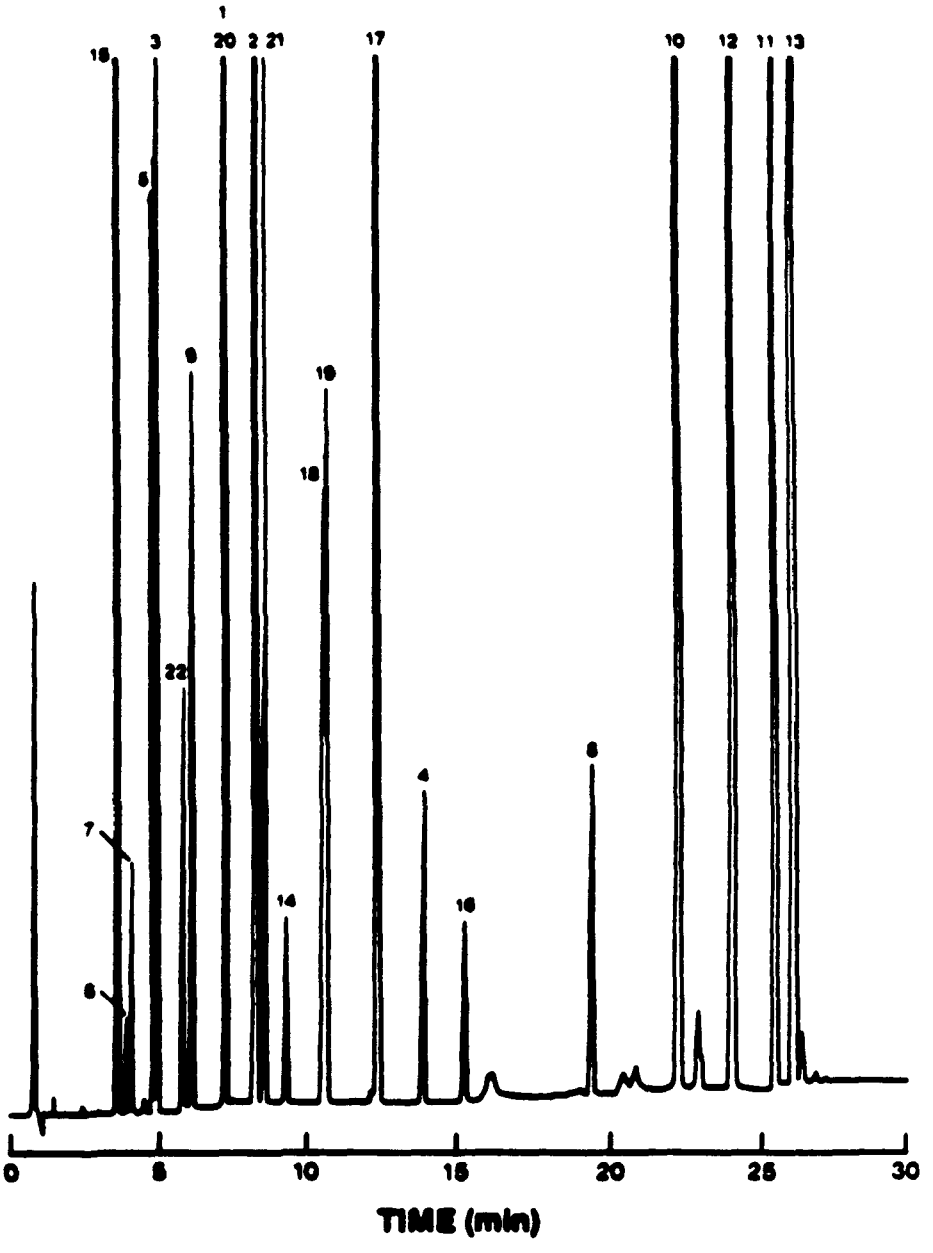


Figure 1. GC/ECD chromatogram of Method 8121 composite standard analyzed on a 30 m x 0.53 mm ID DB-210 fused-silica capillary column. GC operating conditions are given in Section 7.4. See Table 3 for compound identification.

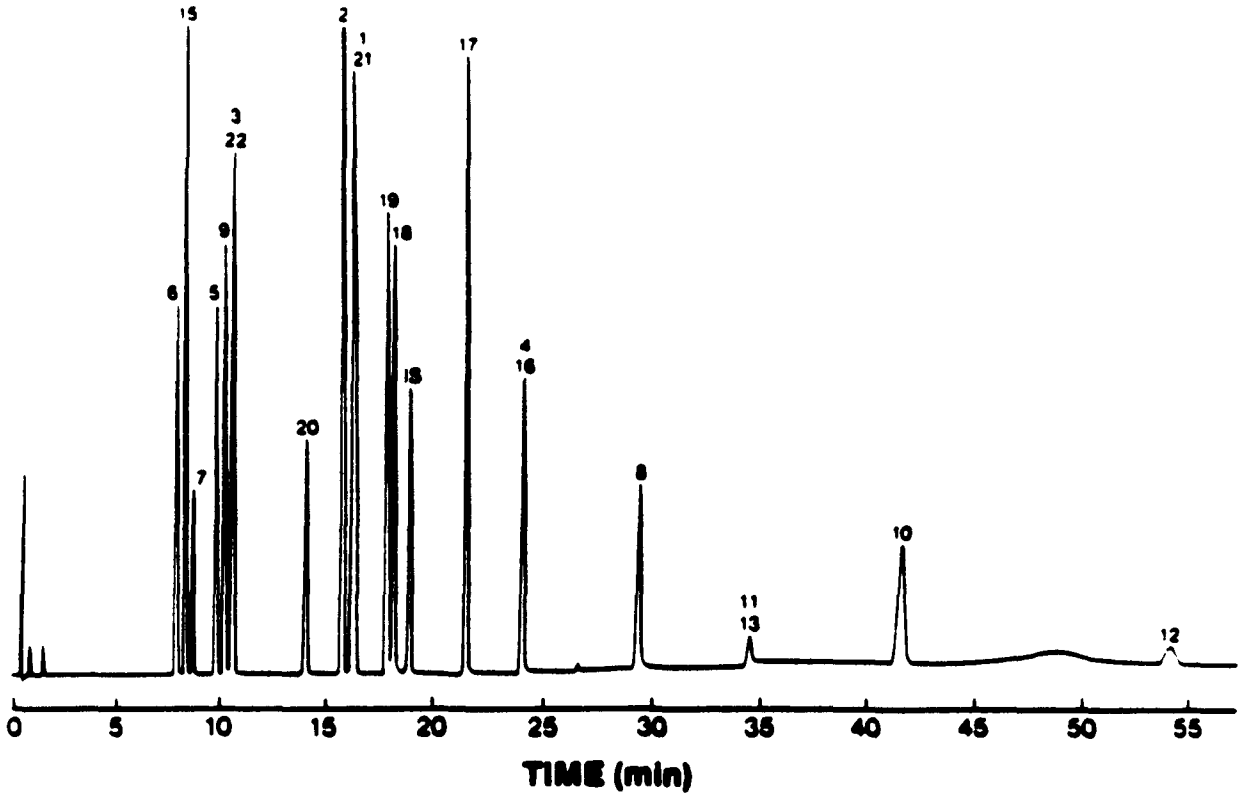


Figure 2. GC/ECD chromatogram of Method 8121 composite standard analyzed on a 30 m x 0.53 mm ID DB-WAX fused-silica capillary column. GC operating conditions are given in Section 7.4. See Table 3 for compound identification.

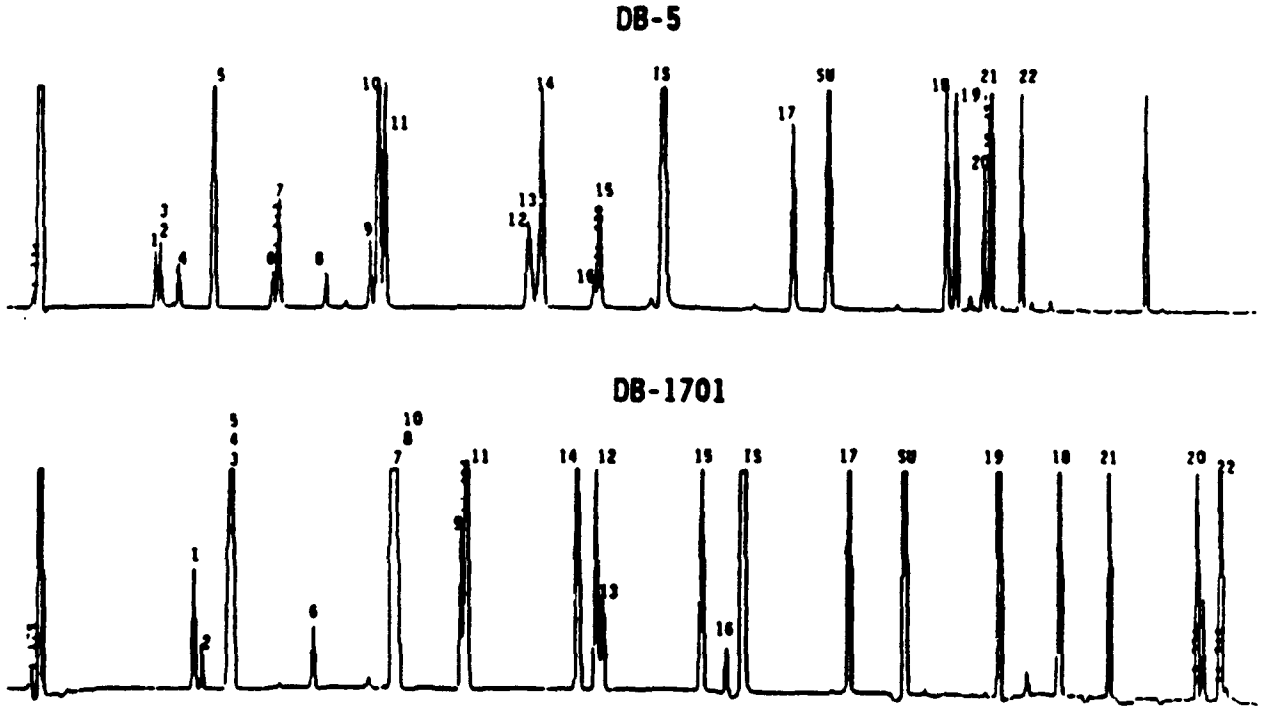
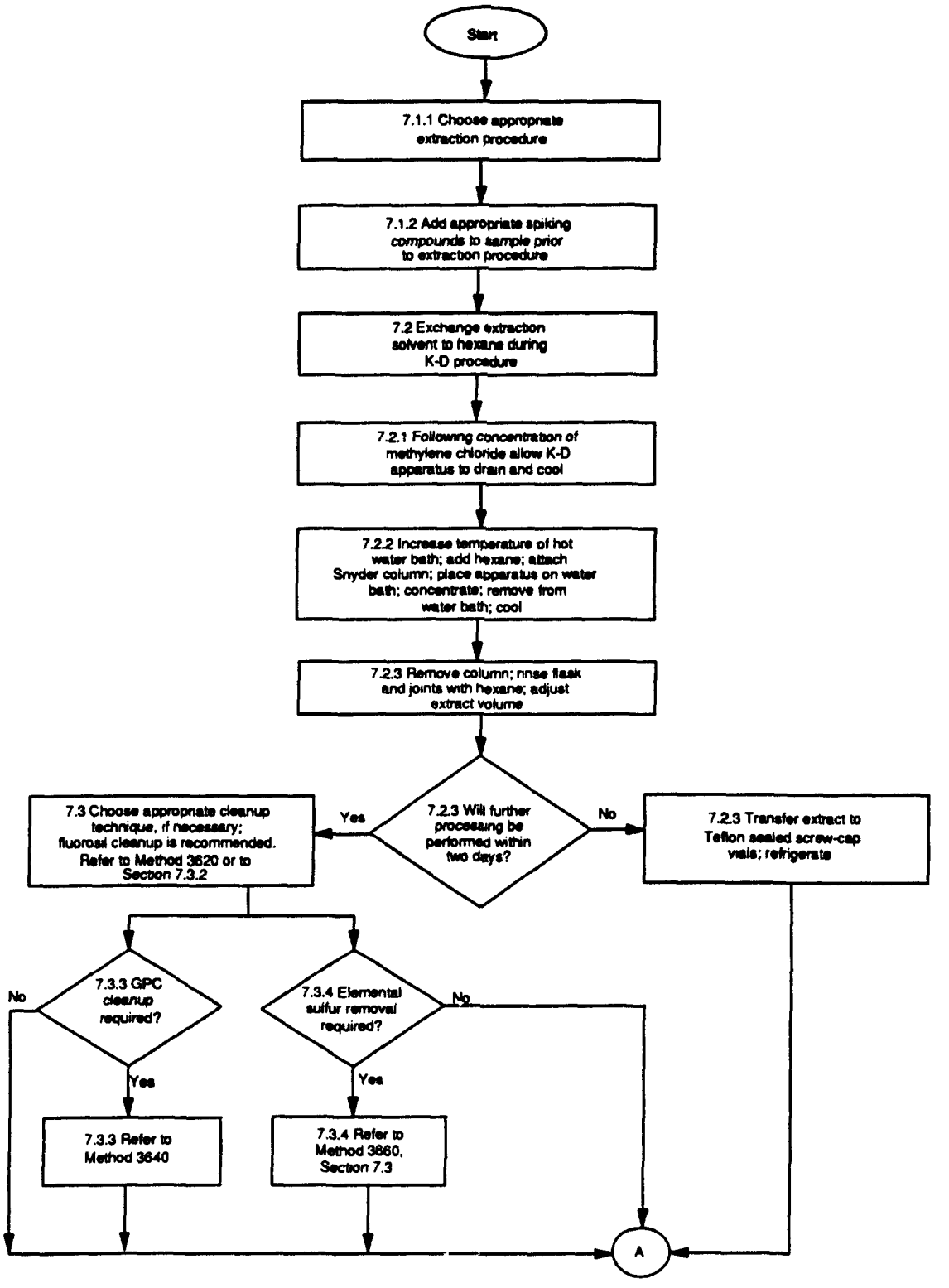
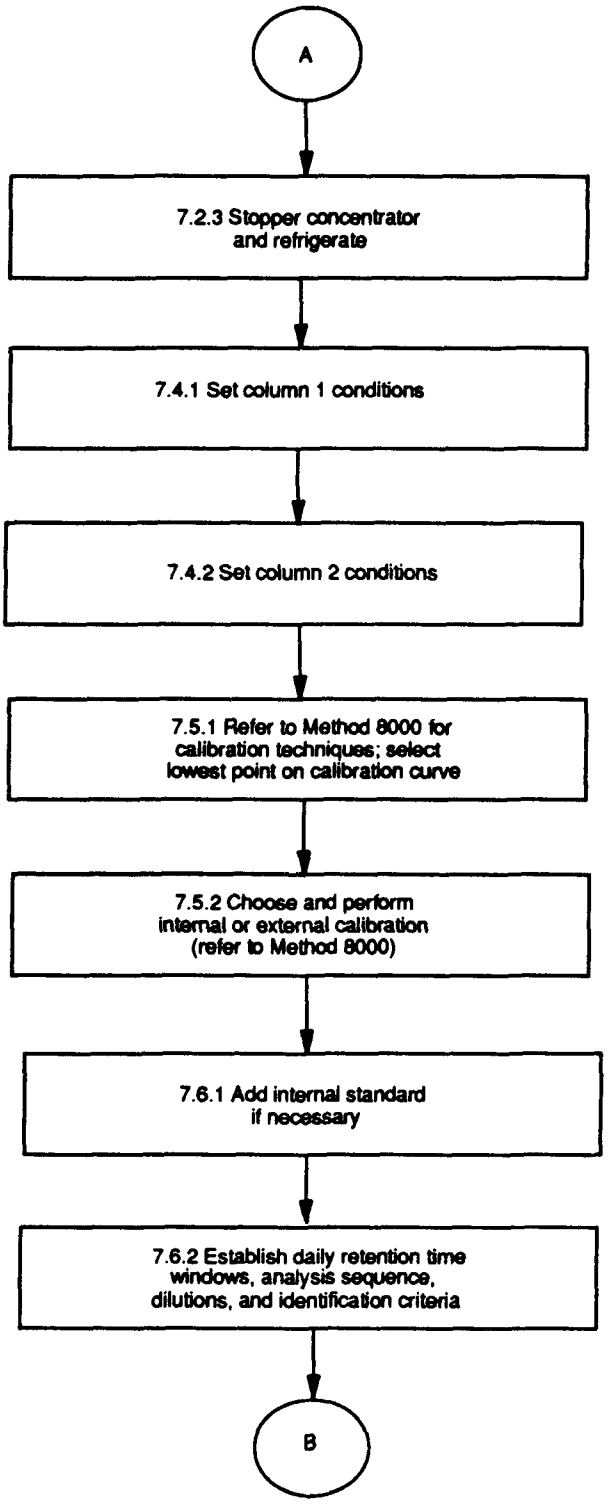
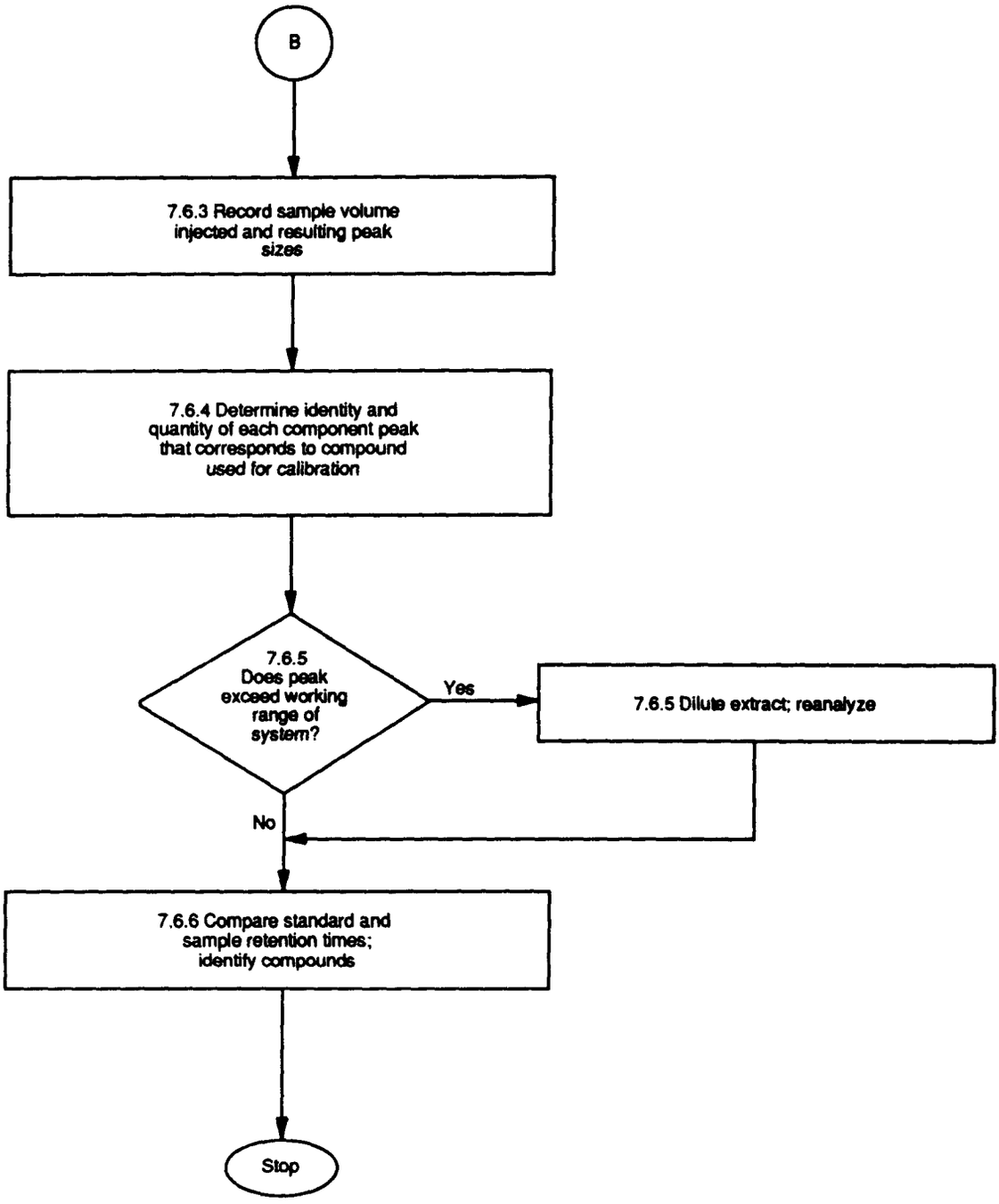


Figure 3. GC/ECD chromatogram of chlorinated hydrocarbons analyzed on a DB 5/DB 1701 fused-silica, open-tubular column pair. The GC operating conditions were as follows: 30 m x 0.53 mm ID DB 5 (0.83 µm film thickness) and 30 m x 0.53 mm ID DB 1701 (1.0 µm film thickness) connected to an 8 in injection tee (Supelco Inc.). Temperature program: 80°C (1.5 min hold) to 125°C (1 min hold) at 2°C/min, then to 240°C (2 min hold) at 5°C/min.

CHLORINATED HYDROCARBONS BY GAS CHROMATOGRAPHY: CAPILLARY COLUMN TECHNIQUE




A
7.2.3 Stopper concentrator and refrigerate
7.4.1 Set column 1 conditions
7.4.2 Set column 2 conditions
7.5.1 Refer to Method 8000 for calibration techniques; select lowest point on calibration curve
7.5.2 Choose and perform internal or external calibration (refer to Method 8000)
7.6.1 Add internal standard if necessary
7.6.2 Establish daily retention time windows, analysis sequence, dilutions, and identification criteria
B


B
7.6.3 Record sample volume injected and resulting peak sizes
7.6.4 Determine identity and quantity of each component peak that corresponds to compound used for calibration
7.6.5 Does peak exceed working range of system?
Yes
7.6.5 Dilute extract; reanalyze
No
7.6.6 Compare standard and sample retention times; identify compounds
Stop

METHOD 8141A

ORGANOPHOSPHORUS COMPOUNDS BY GAS CHROMATOGRAPHY:
CAPILLARY COLUMN TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 Method 8141 is a capillary gas chromatographic (GC) method used to determine the concentration of organophosphorus (OP) compounds. The fused-silica, open-tubular columns specified in this method offer improved resolution, better selectivity, increased sensitivity, and faster analysis than packed columns. The compounds listed in the table below can be determined by GC using capillary columns with a flame photometric detector (FPD) or a nitrogen-phosphorus detector (NPD). Triazine herbicides can also be determined with this method when the NPD is used. Although performance data are presented for each of the listed chemicals, it is unlikely that all of them could be determined in a single analysis. This limitation results because the chemical and chromatographic behavior of many of these chemicals can result in co-elution. The analyst must select columns, detectors and calibration procedures for the specific analytes of interest in a study. Any listed chemical is a potential method interference when it is not a target analyte.

Compound Name	CAS Registry No.
OP Pesticides	
Aspon,[b]	3244-90-4
Azinphos-methyl	86-50-0
Azinphos-ethyl[a]	2642-71-9
Bolstar (Sulprofos)	35400-43-2
Carbophenothion[a]	786-19-6
Chlorfenvinphos[a]	470-90-6
Chlorpyrifos	2921-88-2
Chlorpyrifos methyl[a]	5598-13-0
Coumaphos	56-72-4
Crotoxyphos[a]	7700-17-6
Demeton-O[c]	8065-48-3
Demeton-S[c]	8065-48-3
Diazinon	333-41-5
Dichlorofenthion[a]	97-17-6
Dichlorvos (DDVP)	62-73-7
Dicrotophos[a]	141-66-2
Dimethoate	60-51-5
Dioxathion[a,c]	78-34-2
Disulfoton	298-04-4
EPN	2104-64-5
Ethion[a]	563-12-2
Ethoprop	13194-48-4
Famphur[a]	52-85-7
Fenithrothion[a]	122-14-5
Fensulfothion	115-90-2

Compound Name	CAS Registry No.
Fonophos[a]	944-22-9
Fenthion	55-38-9
Leptophos[a,d]	21609-90-5
Malathion	121-75-5
Merphos[c]	150-50-5
Mevinphos[e]	7786-34-7
Monocrotophos	6923-22-4
Naled	300-76-5
Parathion, ethyl	56-38-2
Parathion, methyl	298-00-0
Phorate	298-02-2
Phosmet[a]	732-11-6
Phosphamidon[a]	13171-21-6
Ronnel	299-84-3
Stirophos (Tetrachlorovinphos)	22248-79-9
Sulfotepp	3689-24-5
TEPP[d]	21646-99-1
Terbufos[a]	13071-79-9
Thionazin[a,b] (Zinophos)	297-97-2
Tokuthion[b] (Protothiofos)	34643-46-4
Trichlorfon[a]	52-68-6
Trichloronate[b]	327-98-0
Industrial Chemicals	
Hexamethylphosphoramide[a] (HMPA)	680-31-9
Tri-o-cresylphosphate[a,d] (TOCP)	78-30-8
Triazine Herbicides (NPD only)	
Atrazine[a]	1912-24-9
Simazine[a]	122-34-9

a. This analyte has been evaluated using a 30-m column only.
b. Production discontinued in the U.S., standard not readily available.
c. Standards may have multiple components because of oxidation.
d. Compound is extremely toxic or neurotoxic.
e. Adjacent major/minor peaks can be observed due to cis/trans isomers.

1.2 A dual-column/dual-detector approach can be used for the analysis of relatively clean extracts. Two 15- or 30-m x 0.53-mm ID fused-silica, open-tubular columns of different polarities are connected to an injection tee and each is connected to a detector. Analysts are cautioned on the use of a dual column configuration when their instrument is subject to mechanical stress, when many samples are analyzed over a short time, or when extracts of contaminated samples are analyzed.

1.3 Two detectors can be used for the listed OP chemicals. The FPD works by measuring the emission of phosphorus- or sulfur-containing species. Detector performance is optimized by selecting the proper optical filter and adjusting the hydrogen and air flows to the flame. The NPD is a flame ionization detector with a rubidium ceramic flame tip which enhances the response of phosphorus- and nitrogen-containing analytes. The FPD is more sensitive and more selective but is a less common detector in environmental laboratories.

1.4 Table 1 lists method detection limits (MDLs) for the target analytes, using 15-m columns and FPD, for water and soil matrices. Table 2 lists the estimated quantitation limits (EQLs) for other matrices. MDLs and EQLs using 30-m columns will be very similar to those obtained from 15-m columns.

1.5 The use of a 15-m column system has not been fully validated for the determination of the following compounds. The analyst must demonstrate chromatographic resolution of all analytes, recoveries of greater than 70 percent, with precision of no more than 15 percent RSD, before data generated on the 15-m column system can be reported for these, or any additional, analytes:

Azinphos-ethyl	Ethion	Phosmet
Carbophenothion	Famphur	Phosphamidon
Chlorfenvinphos	HMPA	Terbufos
Dioxathion	Leptophos	TOCP

1.6 When Method 8141 is used to analyze unfamiliar samples, compound identifications should be supported by confirmatory analysis. Section 8.0 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

1.7 This method is restricted to use by, or under the supervision of, analysts experienced in the use of capillary gas chromatography and in the interpretation of chromatograms.

2.0 SUMMARY OF METHOD

2.1 Method 8141 provides gas chromatographic conditions for the detection of ppb concentrations of organophosphorus compounds. Prior to the use of this method, appropriate sample preparation techniques must be used. Water samples are extracted at a neutral pH with methylene chloride by using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Soxhlet extraction (Method 3540) or ultrasonic extraction (Method 3550) using methylene chloride/acetone (1:1) are used for solid samples. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. A gas chromatograph with a flame photometric or nitrogen-phosphorus detector is used for this multiresidue procedure.

2.2 Organophosphorus esters and thioesters can hydrolyze under both acid and base conditions. Samples prepared using acid and base partitioning procedures are not suitable for analysis by Method 8141.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000, as well as to Section 1.1.

3.2 The use of Florisil Cleanup (Method 3620) for some of the compounds in this method has been demonstrated to yield recoveries less than 85 percent and is therefore not recommended for all compounds. Refer to Table 2 of Method 3620 for recoveries of organophosphorus compounds. Use of an FPD often eliminates the need for sample cleanup. If particular circumstances demand the use of an alternative cleanup procedure, the analyst must determine the elution profile and demonstrate that the recovery of each analyte is not less than 85 percent.

3.3 The use of Gel Permeation Cleanup (GPC) (Method 3640) for sample cleanup has been demonstrated to yield recoveries of less than 85 percent for many method analytes because they elute before bis-(2-ethylhexyl) phthalate. Method 3640 is therefore not recommended for use with this method, unless analytes of interest are listed in Method 3640 or are demonstrated to give greater than 85 percent recovery.

3.4 Use of a flame photometric detector in the phosphorus mode will minimize interferences from materials that do not contain phosphorus or sulfur. Elemental sulfur will interfere with the determination of certain organophosphorus compounds by flame photometric gas chromatography. If Method 3660 is used for sulfur cleanup, only the tetrabutylammonium (TBA)-sulfite option should be employed, since copper and mercury may destroy OP pesticides. The stability of each analyte must be tested to ensure that the recovery from the TBA-sulfite sulfur cleanup step is not less than 85 percent.

3.5 A halogen-specific detector (i.e., electrolytic conductivity or microcoulometry) is very selective for the halogen-containing compounds and may be used for the determination of Chlorpyrifos, Ronnel, Coumaphos, Tokuthion, Trichloronate, Dichlorvos, EPN, Naled, and Stirophos only. Many of the OP pesticides may also be detected by the electron capture detector (ECD); however, the ECD is not as specific as the NPD or FPD. The ECD should only be used when previous analyses have demonstrated that interferences will not adversely effect quantitation, and that the detector sensitivity is sufficient to meet regulatory limits.

3.6 Certain analytes will coelute, particularly on 15-m columns (Table 3). If coelution is observed, analysts should (1) select a second column of different polarity for confirmation, (2) use 30-m x 0.53-mm columns, or (3) use 0.25- or 0.32-mm ID columns. See Figures 1 through 4 for combinations of compounds that do not coelute on 15-m columns.

3.7 The following pairs coeluted on the DB-5/DB-210 30-m column pair:

DB-5 Terbufos/tri-o-cresyl phosphate
Naled/Simazine/Atrazine
Dichlorofenthion/Demeton-O
Trichloronate/Aspon
Bolstar/Stirophos/Carbophenothion
Phosphamidon/Crotoxyphos
Fensulfothion/EPN

DB-210 Terbufos/tri-o-cresyl phosphate
Dichlorofenthion/Phosphamidon
Chlorpyrifos, methyl/Parathion, methyl
Chlorpyrifos/Parathion, ethyl
Aspon/Fenthion
Demeton-O/Dimethoate
Leptophos/Azinphos-methyl
EPN/Phosmet
Famphur/Carbophenothion

See Table 4 for retention times of these compounds on 30-m columns.

3.8 Analytical difficulties encountered for target analytes include:

3.8.1 Tetraethyl pyrophosphate (TEPP) is an unstable diphosphate which is readily hydrolyzed in water and is thermally labile (TEPP decomposes at 170°C). Care must be taken to minimize loss during GC analysis and during sample preparation. Identification of bad standard lots is difficult since the electron impact (EI) mass spectrum of TEPP is nearly identical to its major breakdown product, triethyl phosphate.

3.8.2 The water solubility of Dichlorvos (DDVP) is 10 g/L at 20°C, and recovery is poor from aqueous solution.

3.8.3 Naled is converted to Dichlorvos (DDVP) on column by debromination. This reaction may also occur during sample workup. The extent of debromination will depend on the nature of the matrix being analyzed. The analyst must consider the potential for debromination when Naled is to be determined.

3.8.4 Trichlorfon rearranges and is dehydrochlorinated in acidic, neutral, or basic media to form Dichlorvos (DDVP) and hydrochloric acid. If this method is to be used for the determination of organophosphates in the presence of Trichlorfon, the analyst should be aware of the possibility of rearrangement to Dichlorvos to prevent misidentification.

3.8.5 Demeton (Systox) is a mixture of two compounds; O,O-diethyl O-[2-(ethylthio)ethyl]phosphorothioate (Demeton-O) and O,O-diethyl S-[2-(ethylthio)ethyl]phosphorothioate (Demeton-S). Two peaks are observed in all the chromatograms corresponding to these two isomers. It is recommended that the early eluting compound (Demeton-S) be used for quantitation.

3.8.6 Dioxathion is a single-component pesticide. However, several extra peaks are observed in the chromatograms of standards. These peaks appear to be the result of spontaneous oxygen-sulfur isomerization. Because of this, Dioxathion is not included in composite standard mixtures.

3.8.7 Merphos (tributyl phosphorotrithioite) is a single-component pesticide that is readily oxidized to its phosphorotrithioate (Merphos oxone). Chromatographic analysis of Merphos almost always results two peaks (unoxidized Merphos elutes first). As the relative amount of oxidation of the sample and the standard is probably different,

quantitation based on the sum of both peaks may be most appropriate.

3.8.8 Retention times of some analytes, particularly Monocrotophos may increase with increasing concentrations in the injector. Analysts should check for retention time shifts in highly contaminated samples.

3.8.9 Many analytes will degrade on reactive sites in the chromatographic system. Analysts must ensure that injectors and splitters are free from contamination and are silanized. Columns should be installed and maintained properly.

3.8.10 Performance of chromatographic systems will degrade with time. Column resolution, analyte breakdown and baselines may be improved by column washing (Section 7). Oxidation of columns is not reversible.

3.9 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts or elevated baselines in gas chromatograms. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by analyzing reagent blanks (Section 8.0).

3.10 NP Detector interferences: Triazine herbicides, such as atrazine and simazine, and other nitrogen-containing compounds may interfere.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph: An analytical system complete with a gas chromatograph suitable for on-column or split/splitless injection, and all required accessories, including syringes, analytical columns, gases, suitable detector(s), and a recording device. The analyst should select the detector for the specific measurement application, either the flame photometric detector or the nitrogen-phosphorus detector. A data system for measuring peak areas and dual display of chromatograms is highly recommended.

4.1.1 Capillary Columns (0.53-mm, 0.32-mm, or 0.25-mm ID x 15-m or 30-m length, depending on the resolution required). Columns of 0.53-mm ID are recommended for most environmental and waste analysis applications. Dual-column, single-injector analysis requires columns of equal length and bore. See Section 3.0 and Figures 1 through 4 for guidance on selecting the proper length and diameter for the column(s).

4.1.1.1 Column 1 - 15- or 30-m x 0.53-mm wide-bore capillary column, 1.0-μm film thickness, chemically bonded with 50% trifluoropropyl polysiloxane, 50% methyl polysiloxane (DB-210), or equivalent.

4.1.1.2 Column 2 - 15- or 30-m x 0.53-mm wide-bore capillary column, 0.83-μm film thickness, chemically bonded with 35% phenyl methyl polysiloxane (DB-608, SPB-608, RTx-35), or equivalent.

4.1.1.3 Column 3 - 15- or 30-m x 0.53-mm wide-bore capillary column, 1.0 μm film thickness, chemically bonded with 5%

phenyl polysiloxane, 95% methyl polysiloxane (DB-5, SPB-5, RTx-5), or equivalent.

4.1.1.4 Column 4 - 15- or 30-m x 0.53-mm ID fused-silica open-tubular column, chemically bonded with methyl polysiloxane (DB-1, SPB-1, or equivalent), 1.0-µm or 1.5-µm film thickness.

4.1.1.5 (optional) Column rinsing kit: Bonded-phase column rinse kit (J&W Scientific, Catalog no. 430-3000 or equivalent).

4.1.2 Splitter: If a dual-column, single-injector configuration is used, the open tubular columns should be connected to one of the following splitters, or equivalent:

4.1.2.1 Splitter 1 - J&W Scientific press-fit Y-shaped glass 3-way union splitter (J&W Scientific, Catalog no. 705-0733).

4.1.2.2 Splitter 2 - Supelco 8-in glass injection tee, deactivated (Supelco, Catalog no. 2-3665M).

4.1.2.3 Splitter 3 - Restek Y-shaped fused-silica connector (Restek, Catalog no. 20405).

4.1.3 Injectors:

4.1.3.1 Packed column, 1/4-in injector port with hourglass liner are recommended for 0.53-mm column. These injector ports can be fitted with splitters (Section 4.0) for dual-column analysis.

4.1.3.2 Split/splitless capillary injectors operated in the split mode are required for 0.25-mm and 0.32-mm columns.

4.1.4 Detectors:

4.1.4.1 Flame Photometric Detector (FPD) operated in the phosphorus-specific mode is recommended.

4.1.4.2 Nitrogen-Phosphorus Detector (NPD) operated in the phosphorus-specific mode is less selective but can detect triazine herbicides.

4.1.4.3 Halogen-Specific Detectors (electrolytic conductivity or microcoulometry) may be used only for a limited number of halogenated or sulfur-containing analytes (Section 3.0).

4.1.4.4 Electron-capture detectors may be used for a limited number of analytes (Section 3.0).

4.1.5 Data system:

4.1.5.1 Data system capable of presenting chromatograms, retention time, and peak integration data is strongly recommended.

4.1.5.2 Use of a data system that allows storage of raw chromatographic data is strongly recommended.

5.0 REAGENTS

5.1 Solvents

5.1.1 Isooctane, $(CH_3)_3CCH_2CH(CH_3)_2$ - Pesticide quality or equivalent.

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

5.1.3 Acetone, CH_3COCH_3 - Pesticide quality or equivalent.

5.1.4 Tetrahydrofuran (THF), C_4H_8O - Pesticide quality or equivalent (for triazine standards only).

5.1.5 Methyl *tert*-butyl-ether (MTBE), $CH_3Ot\text{-}C_4H_9$ - Pesticide quality or equivalent (for triazine standards only).

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

5.2.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure compounds. Dissolve the compounds in suitable mixtures of acetone and hexane and dilute to volume in a 10-mL volumetric flask. If compound purity is 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard solution. Commercially prepared stock standard solutions can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.2 Both Simazine and Atrazine have low solubilities in hexane. If Simazine and Atrazine standards are required, Atrazine should be dissolved in MTBE, and Simazine should be dissolved in acetone/MTBE/THF (1:3:1).

5.2.3 Composite stock standard: This standard can be prepared from individual stock solutions. The analyst must demonstrate that the individual analytes and common oxidation products are resolved by the chromatographic system. For composite stock standards containing less than 25 components, take exactly 1 mL of each individual stock solution at 1000 mg/L, add solvent, and mix the solutions in a 25-mL volumetric flask. For example, for a composite containing 20 individual standards, the resulting concentration of each component in the mixture, after the volume is adjusted to 25 mL, will be 40 mg/L. This composite solution can be further diluted to obtain the desired concentrations. Composite stock standards containing more than 25 components are not recommended.

5.2.4 Store the standard solutions (stock, composite, calibration, internal, and surrogate) at 4°C in Teflon-sealed containers in the dark. All standard solutions should be replaced after two months, or sooner if routine QC (Section 8.0) indicates a problem. Standards for easily hydrolyzed chemicals including TEPP, Methyl Parathion, and Merphos should

be checked every 30 days.

5.2.5 It is recommended that lots of standards be subdivided and stored in small vials. Individual vials should be used as working standards to minimize the potential for contamination or hydrolysis of the entire lot.

5.3 Calibration standards should be prepared at a minimum of five concentrations by dilution of the composite stock standard with isooctane or hexane. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector. Organophosphorus calibration standards should be replaced after one or two months, or sooner if comparison with check samples or historical data indicates that there is a problem. Laboratories may wish to prepare separate calibration solutions for the easily hydrolyzed standards identified above.

5.4 Internal standard: Internal standards should only be used on well characterized samples by analysts experienced in the technique. Use of internal standards is complicated by co-elution of some OP pesticides and by the differences in detector response to dissimilar chemicals.

5.4.1 FPD response for organophosphorus compounds is enhanced by the presence of sulfur atoms bonded to the phosphorus atom. It has not been established that a thiophosphate can be used as an internal standard for an OP with a different numbers of sulfur atoms (e.g., phosphorothioates [P=S] as an internal standard for phosphates [PO_4]) or phosphorodithioates [$P=S_2$]).

5.4.2 If internal standards are to be used, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences.

5.4.3 When 15-m columns are used, it may be difficult to fully resolve internal standards from target analytes, method interferences and matrix interferences. The analyst must demonstrate that the measurement of the internal standard is not affected by method or matrix interferences.

5.4.4 The following NPD internal standard has been used for a 30-m column pair. Make a solution of 1000 mg/L of 1-bromo-2-nitrobenzene. For spiking, dilute this solution to 5 mg/L. Use a spiking volume of 10 µL/mL of extract. The spiking concentration of the internal standards should be kept constant for all samples and calibration standards. Since its FPD response is small, 1-bromo-2-nitrobenzene is not an appropriate internal standard for that detector. No FPD internal standard is suggested.

5.5 Surrogate standard spiking solutions - The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system, and the effectiveness of the method in dealing with each sample matrix, by spiking each sample, standard, and blank with one or two surrogates (e.g., organophosphorus compounds not expected to be present in the sample). If

multiple analytes are to be measured, two surrogates (an early and a late eluter) are recommended. Deuterated analogs of analytes are not appropriate surrogates for gas chromatographic/FPD/NPD analysis.

5.5.1 If surrogates are to be used, the analyst must select one or more compounds that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of a surrogate is not affected by method or matrix interferences. General guidance on the selection and use of surrogates is provided in Section 5.0 of Method 3500.

5.5.2 Tributyl phosphate and triphenyl phosphate are used as FPD and NPD surrogates. A volume of 1.0 mL of a 1-µg/L spiking solution (1 ng of surrogate) is added to each water sample and each soil/sediment sample. If there is a co-elution problem, 4-chloro-3-nitrobenzo-trifluoride has also been used as an NPD-only surrogate.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to Chapter Four, "Organic Analytes," Section 4.0.

6.2 Extracts are to be refrigerated at 4°C and analyzed within 40 days of extraction. See Section 5.2.4 for storage of standards.

6.3 Organophosphorus esters will hydrolyze under acidic or basic conditions. Adjust samples to a pH of 5 to 8 using sodium hydroxide or sulfuric acid solution as soon as possible after sample collection. Record the volume used.

6.4 Even with storage at 4°C and use of mercuric chloride as a preservative, most OPs in groundwater samples collected for the national pesticide survey degraded within a 14-day period. Begin sample extraction within 7 days of collection.

7.0 PROCEDURE

7.1 Extraction and cleanup:

7.1.1 Refer to Chapter Two and Method 8140 for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550 with methylene chloride/acetone (1:1) as the extraction solvent.

7.1.2 Extraction and cleanup procedures that use solutions below pH 4 or above pH 8 are not appropriate for this method.

7.1.3 If required, the samples may be cleaned up using the Methods presented in Chapter Four, Section 2. Florisil Column Cleanup (Method 3620) and Sulfur Cleanup (Method 3660, TBA-sulfite option) may have particular application for OPs. Gel Permeation Cleanup (Method 3640)

should not generally be used for OP pesticides.

7.1.3.1 If sulfur cleanup by Method 3660 is required, do not use mercury or copper.

7.1.3.2 GPC may only be employed if all target OP pesticides are listed as analytes of Method 3640, or if the laboratory has demonstrated a recovery of greater than 85 percent for target OPs at a concentration not greater than 5 times the regulatory action level. Laboratories must retain data demonstrating acceptable recovery.

7.1.4 Prior to gas chromatographic analysis, the extraction solvent may be exchanged to hexane. The analyst must ensure quantitative transfer of the extract concentrate. Single-laboratory data indicate that samples should not be transferred with 100-percent hexane during sample workup, as the more polar organophosphorus compounds may be lost. Transfer of organophosphorus esters is best accomplished using methylene chloride or a hexane/acetone solvent mixture.

7.1.5 Methylene chloride may be used as an injection solvent with both the FPD and the NPD.

7.2 Gas chromatographic conditions:

7.2.1 Four 0.53-mm ID capillary columns are suggested for the determination of organophosphates by this method. Column 1 (DB-210 or equivalent) and Column 2 (SPB-608 or equivalent) of 30-m length are recommended if a large number of organophosphorus analytes are to be determined. If superior chromatographic resolution is not required, 15-m lengths columns may be appropriate. Operating conditions for 15-m columns are listed in Table 5. Operating conditions for 30-m columns are listed in Table 6.

7.2.2 Retention times for analytes on each set of columns are presented in Tables 3 and 4.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 5 and Table 6 for establishing the proper operating parameters for the set of columns being employed in the analyses.

7.4 Gas chromatographic analysis: Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows and identification criteria.

7.4.1 Automatic injections of 1 μL are recommended. Hand injections of no more than 2 μL may be used if the analyst demonstrates quantitation precision of $\leq$ 10 percent relative standard deviation. The solvent flush technique may be used if the amount of solvent is kept at a minimum. If the internal standard calibration technique is used, add 10 μL of internal standard to each mL of sample prior to injection. Chromatograms of the target organophosphorus compounds are shown in Figures 1 through 4.

7.4.2 Figures 5 and 6 show chromatograms with and without Simazine, Atrazine, and Carbophenothion on 30-m columns.

7.5 Record the sample volume injected to the nearest 0.05 µL and the resulting peak sizes (in area units or peak heights). Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes. See Method 8000 for calculation equations.

7.5.1 If peak detection and identification is prevented by the presence of interferences, the use of an FPD or further sample cleanup is required. Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to establish elution patterns and to determine recovery of target compounds. The absence of interference from reagents must be demonstrated by routine processing of reagent blanks through the chosen cleanup procedure. Refer to Section 3.0 for interferences.

7.5.2 If the responses exceed the linear range of the system, dilute the extract and reanalyze. It is recommended that extracts be diluted so that all peaks are on scale. Overlapping peaks are not always evident when peaks are off-scale. Computer reproduction of chromatograms, manipulated to ensure all peaks are on scale over a 100-fold range, are acceptable if linearity is demonstrated. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

7.5.3 If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The analyst should consult with the source of the sample to determine whether further concentration of the sample extract is warranted.

7.5.4 If partially overlapping or coeluting peaks are found, change columns or try a GC/MS technique. Refer to Section 8.0 and Method 8270.

7.6 Suggested chromatograph maintenance: Corrective measures may require any one or more of the following remedial actions.

7.6.1 Refer to Method 8000 for general information on the maintenance of capillary columns and injectors.

7.6.2 Splitter connections: For dual columns which are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector (J&W Scientific, Restek, or equivalent), clean and deactivate the splitter. Reattach the columns after cleanly cutting off at least one foot from the injection port side of the column using a capillary cutting tool or scribe. The accumulation of high boiling residues can change split ratios between dual columns and thereby change calibration factors.

7.6.3 Columns will be damaged permanently and irreversibly by contact with oxygen at elevated temperature. Oxygen can enter the column during a septum change, when oxygen traps are exhausted, through neoprene diaphragms of regulators, and through leaks in the gas manifold. Polar

columns including the DB-210 and DB-608 are more prone to oxidation. Oxidized columns will exhibit baselines that rise rapidly during temperature programming.

7.7 Detector maintenance:

7.7.1 Older FPDs may be susceptible to stray light in the photomultiplier tube compartment. This stray light will decrease the sensitivity and the linearity of the detector. Analysts can check for leaks by initiating an analysis in a dark room and turning on the lights. A shift in the baseline indicates that light may be leaking into the photomultiplier tube compartment. Additional shielding should be applied to eliminate light leaks and minimize stray light interference.

7.7.2 The bead of the NPD will become exhausted with time which will decrease the sensitivity and the selectivity of the detector. The collector may become contaminated which decreased detector sensitivity.

7.7.3 Both types of detectors use a flame to generate a response. Flow rates of air and hydrogen should be optimized to give the most sensitive, linear detector response for target analytes.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Include a mid-level check standard after each group of 10 samples in the analysis sequence. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000.

8.3 GC/MS confirmation

8.3.1 GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. Follow the GC/MS operating requirements specified in Method 8270.

8.3.2 When available, chemical ionization mass spectra may be employed to aid in the qualitative identification process.

8.3.3 To confirm an identification of a compound, the background-corrected mass spectrum of the compound must be obtained from the sample extract and must be compared with a mass spectrum from a stock or calibration standard analyzed under the same chromatographic conditions. At least 25 ng of material should be injected into the GC/MS. The following criteria must be met for qualitative confirmation:

8.3.3.1 The qualitative identification of compounds determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The

reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met.

8.3.3.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

8.3.3.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

8.3.3.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

8.3.3.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

8.3.3.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

8.3.3.2 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.

8.3.4 Where available, chemical ionization mass spectra may be employed to aid in the qualitative identification process because of the extensive fragmentation of organophosphorus pesticides during electron impact MS processes.

8.3.5 Should the MS procedure fail to provide satisfactory results, additional steps may be taken before reanalysis. These steps may include the use of alternate packed or capillary GC columns or additional sample cleanup.

9.0 METHOD PERFORMANCE

9.1 Estimated MDLs and associated chromatographic conditions for water and clean soil (uncontaminated with synthetic organics) are listed in Table 1. As detection limits will vary with the particular matrix to be analyzed, guidance for determining EQLs is given in Table 2. Recoveries for several method analytes are provided in Table 7.

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TABLE 1
METHOD DETECTION LIMITS IN A WATER AND A SOIL
MATRIX USING 15-m COLUMNS AND A FLAME PHOTOMETRIC DETECTOR

Compound	Reagent Water (3510)[a] (µg/L)	Soil (3540)[b] (µg/kg)
Azinphos-methyl	0.10	5.0
Bolstar (Sulprofos)	0.07	3.5
Chlorpyrifos	0.07	5.0
Coumaphos	0.20	10.0
Demeton, -O, -S	0.12	6.0
Diazinon	0.20	10.0
Dichlorvos (DDVP)	0.80	40.0
Dimethoate	0.26	13.0
Disulfoton	0.07	3.5
EPN	0.04	2.0
Ethoprop	0.20	10.0
Fensulfothion	0.08	4.0
Fenthion	0.08	5.0
Malathion	0.11	5.5
Merphos	0.20	10.0
Mevinphos	0.50	25.0
Naled	0.50	25.0
Parathion, ethyl	0.06	3.0
Parathion, methyl	0.12	6.0
Phorate	0.04	2.0
Ronnel	0.07	3.5
Sulfotepp	0.07	3.5
TEPP[c]	0.80	40.0
Tetrachlorovinphos	0.80	40.0
Tokuthion (Protothiofos)[c]	0.07	5.5
Trichloronate[c]	0.80	40.0

[a] Sample extracted using Method 3510, Separatory Funnel Liquid-Liquid Extraction.

[b] Sample extracted using Method 3540, Soxhlet Extraction.

[c] Purity of these standards not established by the EPA Pesticides and Industrial Chemicals Repository, Research Triangle Park, NC.

TABLE 2
DETERMINATION OF ESTIMATED QUANTITATION LIMITS
(EQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water (Methods 3510 or 3520)	10
Low-concentration soil by Soxhlet and no cleanup	10[c]
Low-concentration soil by ultrasonic extraction with GPC cleanup	6.7[c]
High-concentration soil and sludges by ultrasonic extraction	500[c]
Non-water miscible waste (Method 3580)	1000[c]

[a] Sample EQLs are highly matrix dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

[b] EQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

[c] Multiply this factor times the soil MDL.

TABLE 3.
RETENTION TIMES FOR METHOD 8141A ANALYTES
EMPLOYING 15-m COLUMNS

Compound	Capillary Column DB-5	SPB-608	DB-210
TEPP	6.44	5.12	10.66
Dichlorvos (DDVP)	9.63	7.91	12.79
Mevinphos	14.18	12.88	18.44
Demeton, -O and -S	18.31	15.90	17.24
Ethoprop	18.62	16.48	18.67
Naled		19.01	17.40	19.35
Phorate	19.94	17.52	18.19
Monochrotophos	20.04	20.11	31.42
Sulfotepp	20.11	18.02	19.58
Dimethoate	20.64	20.18	27.96
Disulfoton	23.71	19.96	20.66
Diazinon	24.27	20.02	19.68
Merphos	26.82	21.73	32.44
Ronnel	29.23	22.98	23.19
Chlorpyrifos	31.17	26.88	25.18
Malathion	31.72	28.78	32.58
Parathion, methyl	31.84	23.71	32.17
Parathion, ethyl	31.85	27.62	33.39
Trichloronate	32.19	28.41	29.95
Tetrachlorovinphos	34.65	32.99	33.68
Tokuthion (Protothiofos)	34.67	24.58	39.91
Fensulfothion	35.85	35.20	36.80
Bolstar (Sulprofos)	36.34	35.08	37.55
Famphur*	36.40	36.93	37.86
EPN		37.80	36.71	36.74
Azinphos-methyl	38.34	38.04	37.24
Fenthion	38.83	29.45	28.86
Coumaphos	39.83	38.87	39.47

*Method 8141A has not been fully validated for Famphur.

Initial temperature	130°C	50°C	50°C
Initial time	3 minutes	1 minute	1 minute
Program 1 rate	5°C/min	5°C/min	5°C/min
Program 1 final temp.	180°C	140°C	140°C
Program 1 hold	10 minutes	10 minutes	10 minutes
Program 2 rate	2°C/min	10°C/min	10°C/min
Program 2 final temp.	250°C	240°C	240°C
Program 2 hold	15 minutes	10 minutes	10 minutes

TABLE 4.
RETENTION TIMES FOR METHOD 8141A ANALYTES
EMPLOYING 30-m COLUMNS[a]

No.	Compound	RT (min) DB-5	DB-210	DB-608	DB-1
1	Trimethylphosphate	b	2.36		
2	Dichlorvos (DDVP)	7.45	6.99	6.56	10.43
3	Hexamethylphosphoramide	b	7.97		
4	Trichlorfon	11.22	11.63	12.69	
5	TEPP	b	13.82		
6	Thionazin	12.32	24.71		
7	Mevinphos	12.20	10.82	11.85	14.45
8	Ethoprop	12.57	15.29	18.69	18.52
9	Diazinon	13.23	18.60	24.03	21.87
10	Sulfotepp	13.39	16.32	20.04	19.60
11	Terbufos	13.69	18.23	22.97	
12	Tri-o-cresyl phosphate	13.69	18.23		
13	Naled	14.18	15.85	18.92	18.78
14	Phorate	12.27	16.57	20.12	19.65
15	Fonophos	14.44	18.38		
16	Disulfoton	14.74	18.84	23.89	21.73
17	Merphos	14.89	23.22		26.23
	oxidized Merphos	20.25	24.87	35.16	
18	Dichlorofenthion	15.55	20.09	26.11	
19	Chlorpyrifos, methyl	15.94	20.45	26.29	
20	Ronnel	16.30	21.01	27.33	23.67
21	Chlorpyrifos	17.06	22.22	29.48	24.85
22	Trichloronate	17.29	22.73	30.44	
23	Aspon	17.29	21.98		
24	Fenthion	17.87	22.11	29.14	24.63
25	Demeton-S	11.10	14.86	21.40	20.18
	Demeton-O	15.57	17.21	17.70	
26	Monocrotophos[c]	19.08	15.98	19.62	19.3
27	Dimethoate	18.11	17.21	20.59	19.87
28	Tokuthion	19.29	24.77	33.30	27.63
29	Malathion	19.83	21.75	28.87	24.57
30	Parathion, methyl	20.15	20.45	25.98	22.97
31	Fenithrothion	20.63	21.42		
32	Chlorfenvinphos	21.07	23.66	32.05	
33	Parathion, ethyl	21.38	22.22	29.29	24.82
34	Bolstar	22.09	27.57	38.10	29.53
35	Stirophos	22.06	24.63	33.40	26.90
36	Ethion	22.55	27.12	37.61	

(continued)

TABLE 4. (Continued)

No.	Compound	RT (min) DB-5	DB-210	DB-608	DB-1
37	Phosphamidon	22.77	20.09	25.88	
38	Crotoxyphos	22.77	23.85	32.65	
39	Leptophos	24.62	31.32	44.32	
40	Fensulfothion	27.54	26.76	36.58	28.58
41	EPN	27.58	29.99	41.94	31.60
42	Phosmet	27.89	29.89	41.24	
43	Azinphos-methyl	28.70	31.25	43.33	32.33
44	Azinphos-ethyl	29.27	32.36	45.55	
45	Famphur	29.41	27.79	38.24	
46	Coumaphos	33.22	33.64	48.02	34.82
47	Atrazine	13.98	17.63		
48	Simazine	13.85	17.41		
49	Carbophenothion	22.14	27.92		
50	Dioxathion	d	d	22.24	
51	Trithion methyl	e		36.62	
52	Dicrotophos	e	e	19.33	
IS	1-Bromo-2-nitrobenzene	8.11	9.07		
SU	Tributyl phosphate			11.1	
SU	Triphenyl phosphate			33.4	
SU	4-Cl-3-nitrobenzotrifluoride	5.73		5.40	

[a] The GC operating conditions were as follows:

DB-5 and DB-210 - 30-m x 0.53-mm ID column, DB-5 (1.50- m film thickness) and DB-210 (1.0- m film thickness). Both connected to a press-fit Y-shaped inlet splitter. Temperature program: 120°C (3-min hold) to 270°C (10-min hold) at 5°C/min; injector temperature 250°C; detector temperature 300°C; bead temperature 400°C; bias voltage 4.0; hydrogen gas pressure 20 psi; helium carrier gas 6 mL/min; helium makeup gas 20 mL/min.

DB-608 - 30-m x 0.53-mm ID column, DB-608 (1.50- m film thickness) installed in an 0.25-in packed-column inlet . Temperature program: 110°C (0.5-min hold) to 250°C (4-min hold) at 3°C/min; injector temperature 250°C; helium carrier gas 5 mL/min; flame photometric detector.

DB-1 30-m x 0.32-mm ID column, DB-1 (0.25- m film thickness) split/splitless with head pressure of 10 psi, split valve closure at 45 sec, injector temp. 250°C, 50°C (1-min hold) to 280°C (2-min hold) at 6°C/min, mass spectrometer full scan 35-550 amu.

[b] Not detected at 20 ng per injection.
[c] Retention times may shift to longer times with larger amounts injected (shifts of over 30 seconds have been observed, Hatcher et. al.)
[d] Shows multiple peaks; therefore, not included in the composite.
[e] Not available.

TABLE 5.

SUGGESTED OPERATING CONDITIONS FOR 15-m COLUMNS

Columns 1 and 2 (DB-210 and SPB-608 or their equivalent)	
Carrier gas (He) flow rate =	5 mL/min
Initial temperature =	50°C, hold for 1 minute
Temperature program =	50°C to 140°C at 5°C/min, hold for 10 minutes, followed by 140°C to 240°C at 10°C/min, hold for 10 minutes (or a sufficient amount of time for last compound to elute).
Column 3 (DB-5 or equivalent)	
Carrier gas (He) flow rate =	5 mL/min
Initial temperature =	130°C, hold for 3 minutes
Temperature program =	130°C to 180°C at 5°C/min, hold for 10 minutes, followed by 180°C to 250°C at 2°C/min, hold for 15 minutes (or a sufficient amount of time for last compound to elute).

TABLE 6
SUGGESTED OPERATING CONDITIONS FOR 30-m COLUMNS

Column 1:

Type: DB-210
Dimensions: 30-m x 0.53-mm ID
Film Thickness (µm): 1.0

Column 2:

Type: DB-5
Dimensions: 30-m x 0.53-mm ID
Film Thickness (µm): 1.5

Carrier gas flowrate (mL/min): 6 (Helium)

Makeup gas flowrate (mL/min): 20 (Helium)

Temperature program: 120°C (3-min hold) to 270°C (10-min hold) at 5°C/min

Injector temperature: 250°C

Detector temperature: 300°C

Injection volume: 2 µL

Solvent: Hexane

Type of injector: Flash vaporization

Detector type: Dual NPD

Range: 1

Attenuation: 64

Type of splitter: Y-shaped or Tee

Data system: Integrator

Hydrogen gas pressure: 20 psi

Bead temperature: 400°C

Bias voltage: 4

TABLE 7
RECOVERY OF METHOD 8141A ANALYTES FROM WATER AND SOIL

Compound	Method 3510 Water % Recovery	Spike (µg/L)	Method 3550 Soil % Recovery	Spike (µg/kg)
Azinphos-methyl	143 ± 8	1.50	27 ± 10	50
Bolstar (Sulprofos)	141 ± 8	1.63	103 ± 15	63
Chlorpyrifos	89 ± 6	1.56	79 ± 7	52
Coumaphos	90 ± 6	1.57	60	52
Demeton, -O, -S	67 ± 11	2.05	16	690
Diazinon	121 ± 10	1.74	90 ± 14	58
Dichlorvos (DDVP)	79 ± 11	14.3	13 ± 9	475
Dimethoate	47 ± 3	1.60	67	53
Disulfoton	92 ± 7	2.16	44 ± 22	72
EPN	125 ± 9	1.86	86 ± 38	62
Ethoprop	90 ± 6	1.83	34 ± 26	61
Fensulfothion	82 ± 12	2.07	37	69
Fenthion	48 ± 10	2.23	35	74
Malathion	92 ± 6	1.80	67	60
Merphos	79	1.71	71	57
Mevinphos	55	21	23	700
Monocrotophos	18 ± 4	12.7	ND	425
Naled	ND	2.29	40	76
Parathion, ethyl	94 ± 5	2.02	74 ± 13	67
Parathion, methyl	46 ± 4	1.92	17	640
Phorate	77 ± 6	2.0	51 ± 9	69
Ronnel	97 ± 5	1.57	84 ± 8	52
Sulfotepp	85 ± 4	1.99	68 ± 10	66
TEPP	55 ± 72	19.5	7	651
Tetrachlorovinphos	90 ± 7	1.54	47 ± 24	51
Tokuthion (Protothiofos)	45 ± 3	2.08	82	690
Trichloronate	35	1.87	31	620

ND - Not detected

TABLE 8
QUANTITATION AND CHARACTERISTIC IONS FOR OP PESTICIDES

Compound Name	Quantitation ions	Characteristic ions
Azinphos-methyl	160	77,132
Bolstar (Sulprofos)	156	140,143,113,33
Chlorpyrifos	197	97,199,125.314
Coumaphos	109	97,226,362,21
Demeton-S	88	60,114,170
Diazinon	137	179,152,93,199,304
Dichlorvos (DDVP)	109	79,185,145
Dimethoate	87	93,125,58,143
Disulfoton	88	89,60,61,97,142
EPN	157	169,141,63,185
Ethoprop	158	43,97,41,126
Fensulfothion	293	97,125,141,109,308
Fenthion	278	125,109,93,169
Malathion	173	125,127,93,158
Merphos	209	57,153,41,298
Mevinphos	127	109,67,192
Monocrotophos	127	67,97,192,109
Naled	109	145,147,79
Parathion, ethyl	291	97,109,139,155
Parathion, methyl	109	125,263,79
Phorate	75	121,97,47,260
Ronnel	285	125,287,79,109
Stirophos	109	329,331,79
Sulfotepp	322	97,65,93,121,202
TEPP	99	155,127,81,109
Tokuthion	113	43,162,267,309

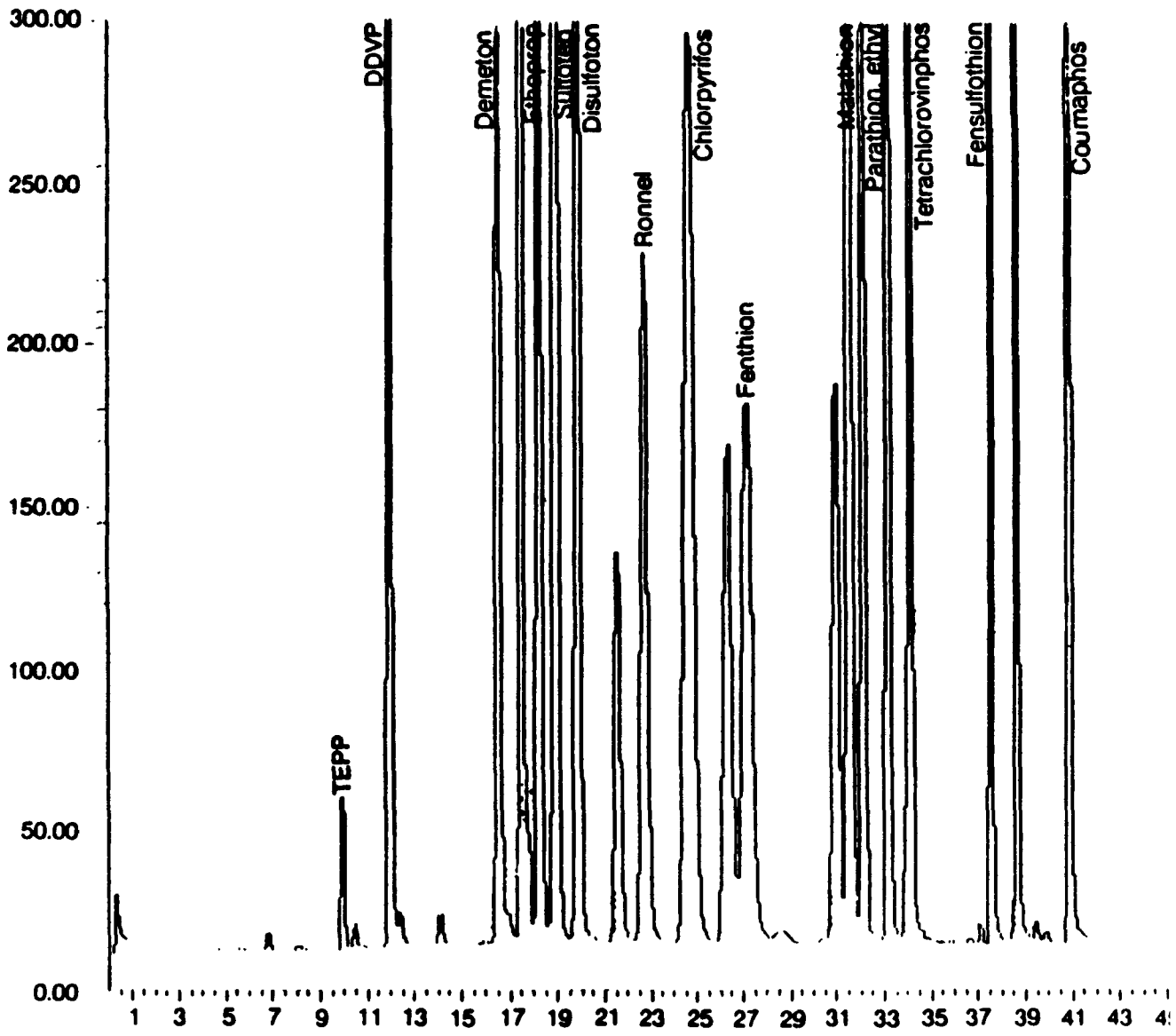


Figure 1.Chromatogram of target organophosphorus compounds from a 15-m DB-210 column with FPD detector. More compounds are shown in Figure 2. See Table 3 for retention times and Table 5 for GC operating conditions.

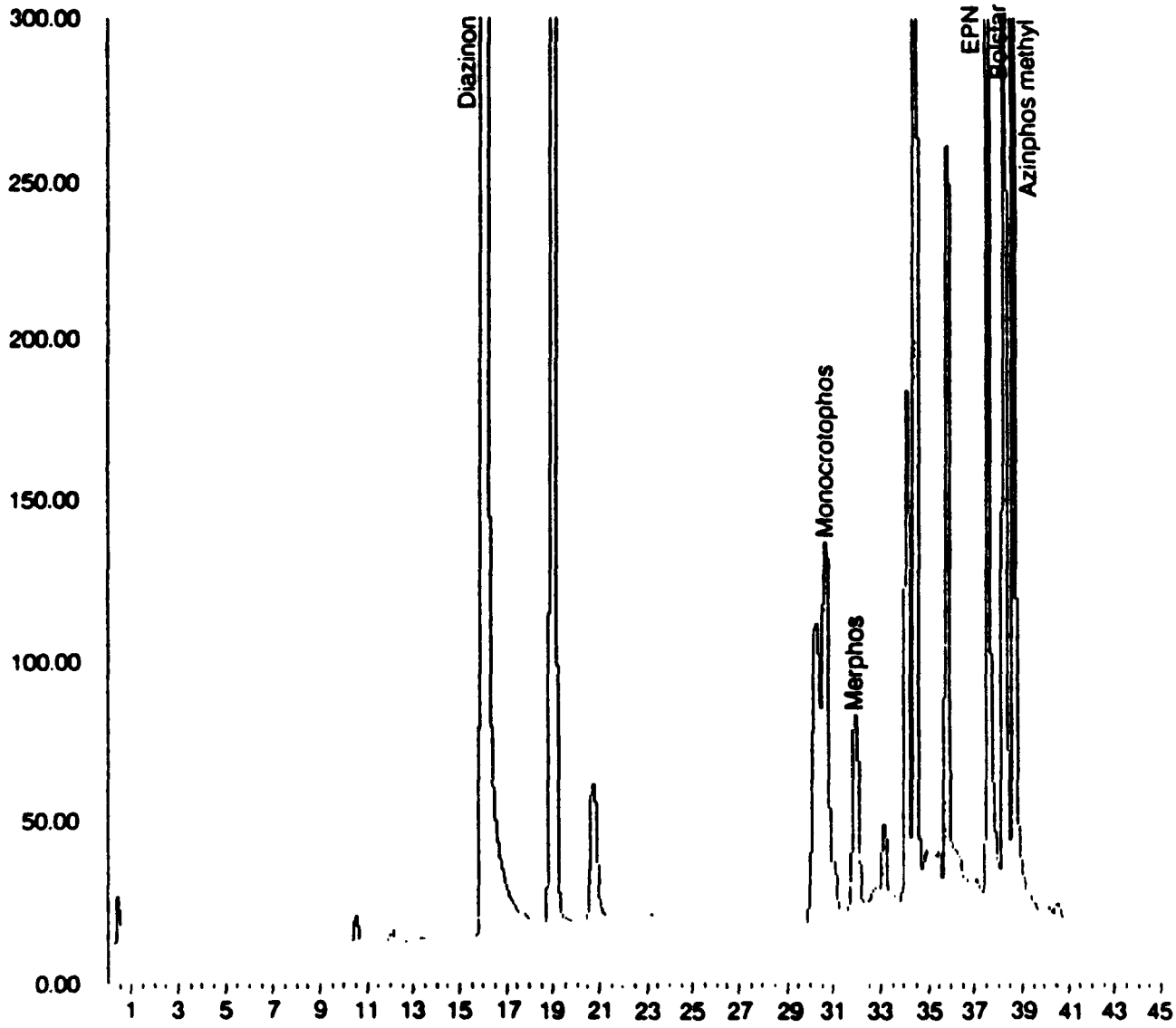


Figure 2.Chromatogram of target organophosphorus compounds from a 15-m DB-210 column with FPD detector. More compounds are shown in Figure 1. See Table 3 for retention times and Table 5 for GC operating conditions.

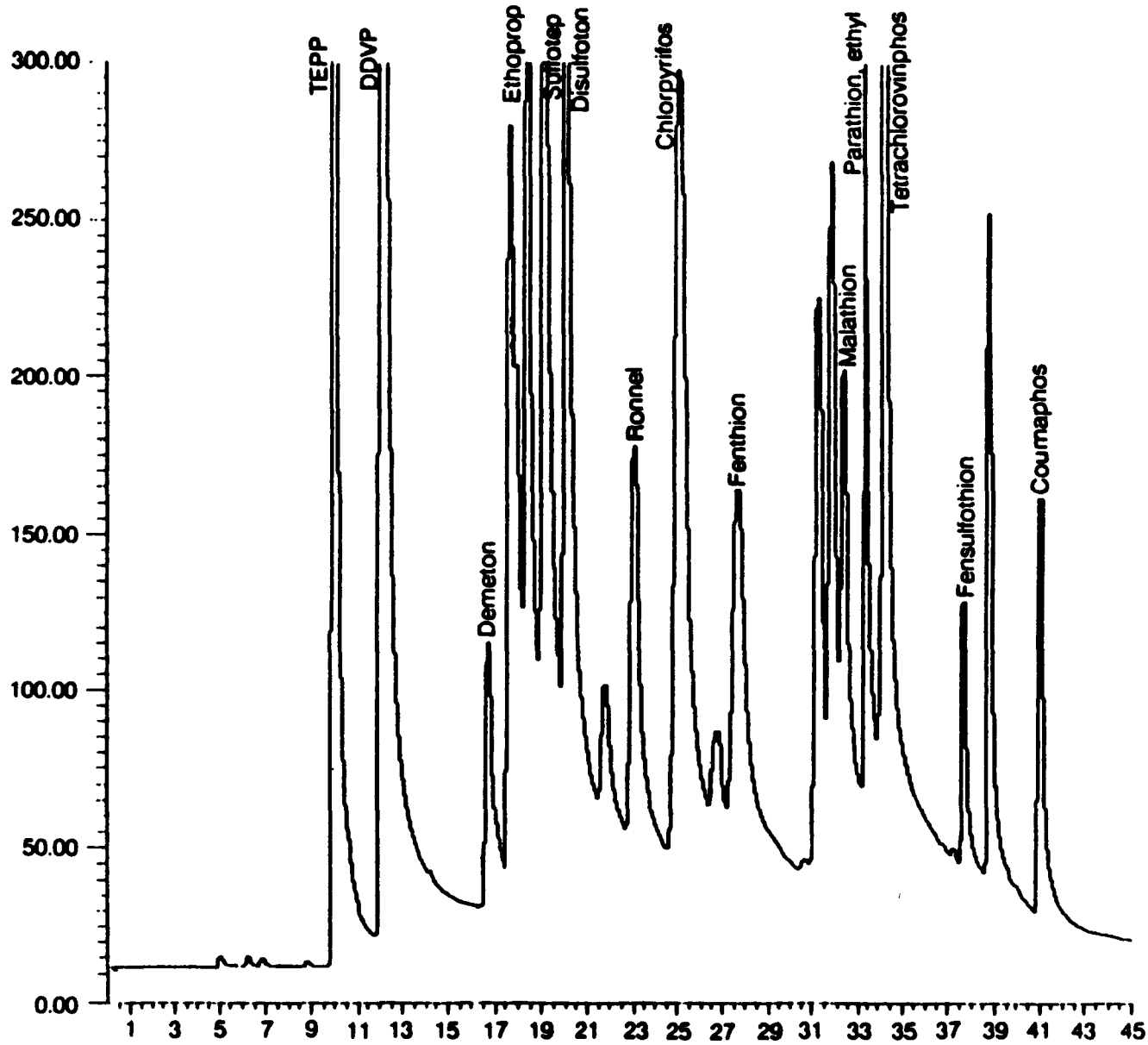


Figure 3.Chromatogram of target organophosphorus compounds from a 15-m DB-210 column with NPD detector. More compounds are shown in Figure 4. See Table 3 for retention times and Table 5 for GC operating conditions.

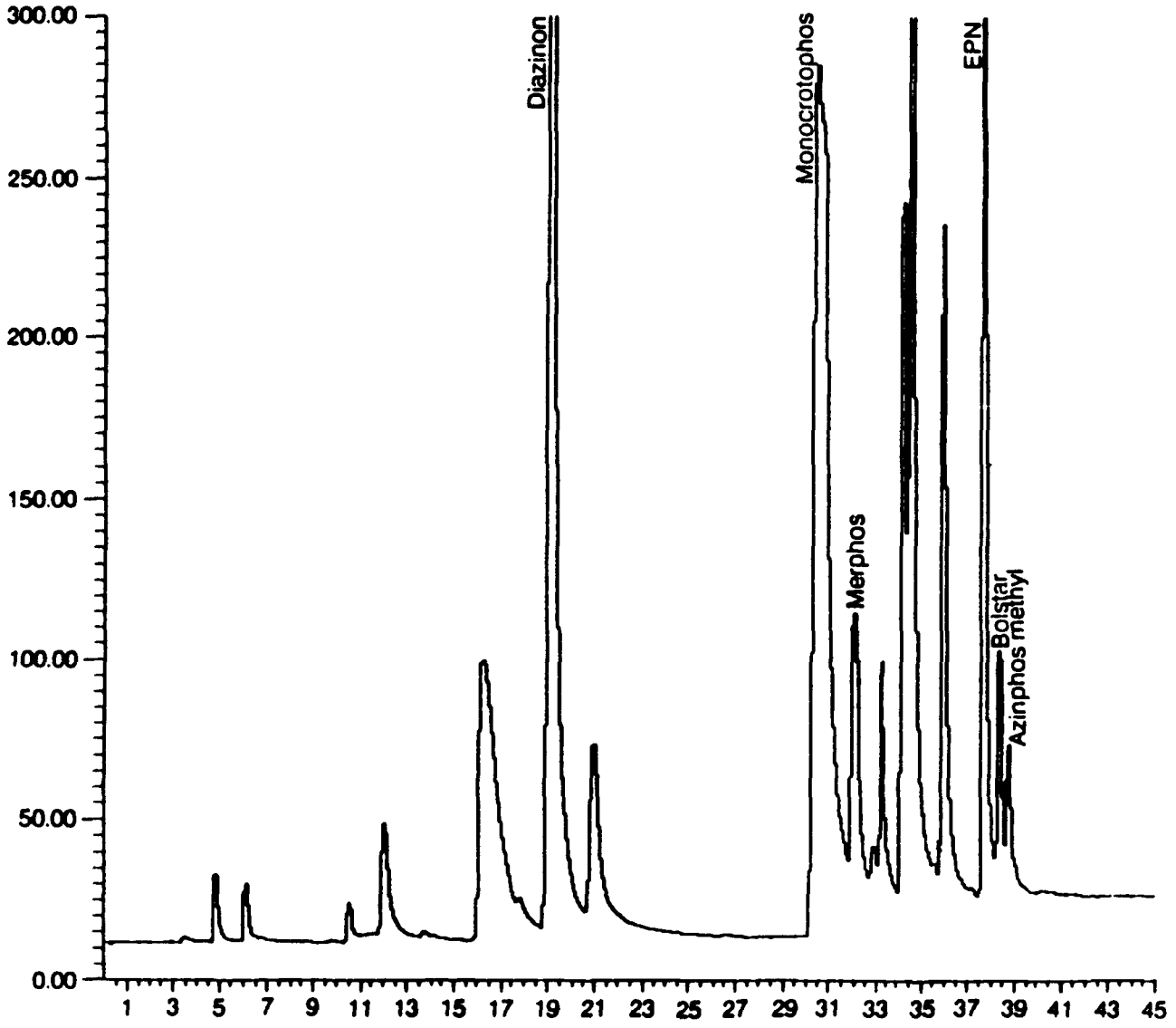


Figure 4.Chromatogram of target organophosphorus compounds from a 15-m DB-210 column with NPD detector. More compounds are shown in Figure 3. See Table 3 for retention times and Table 5 for GC operating conditions.

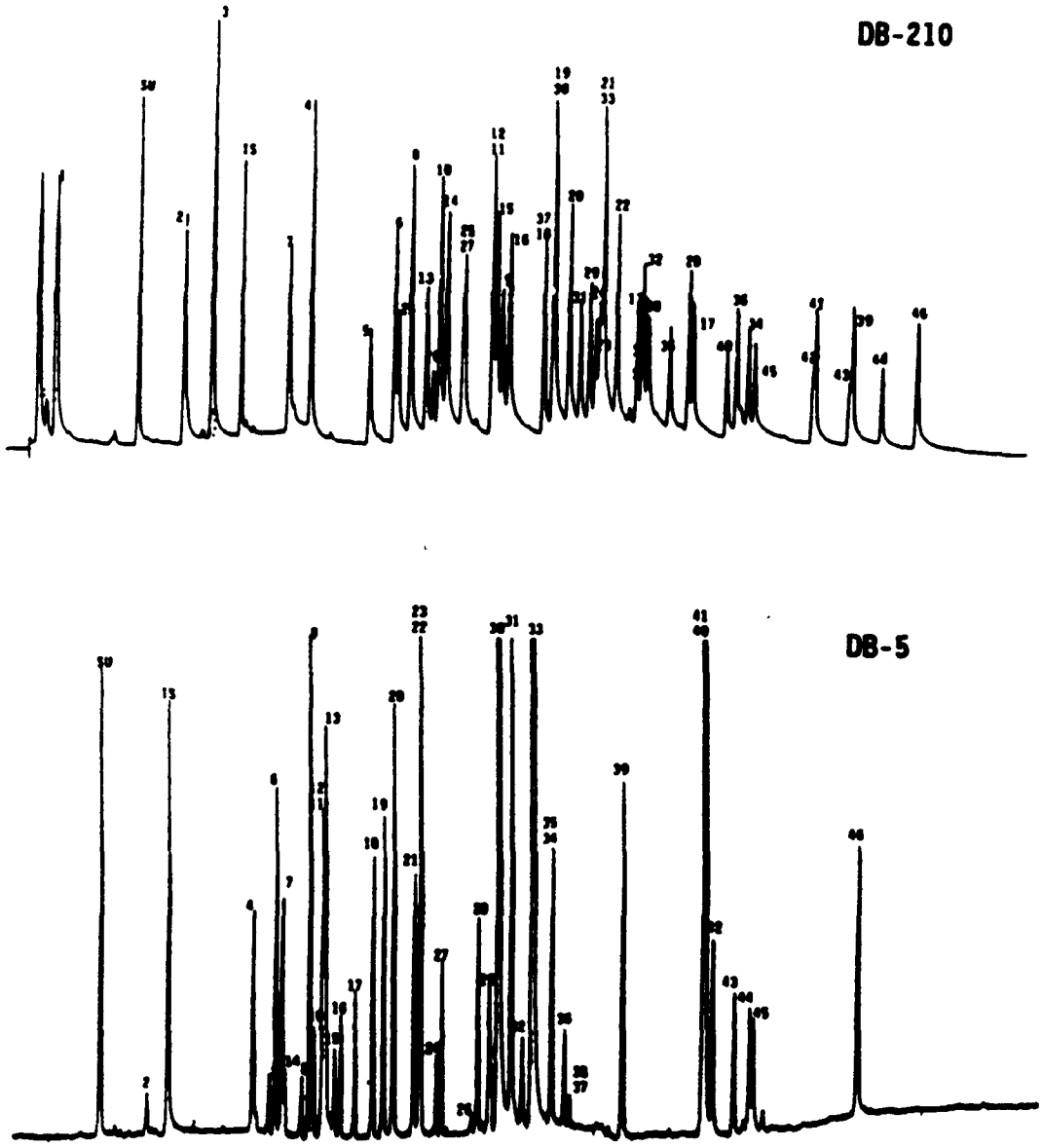


Figure 5.Chromatogram of target organophosphorus compounds on a 30-m DB-5/DB-210 column pair with NPD detector, without Simazine, Atrazine and Carbophenothion. See Table 4 for retention times and Table 6 for GC operating conditions.

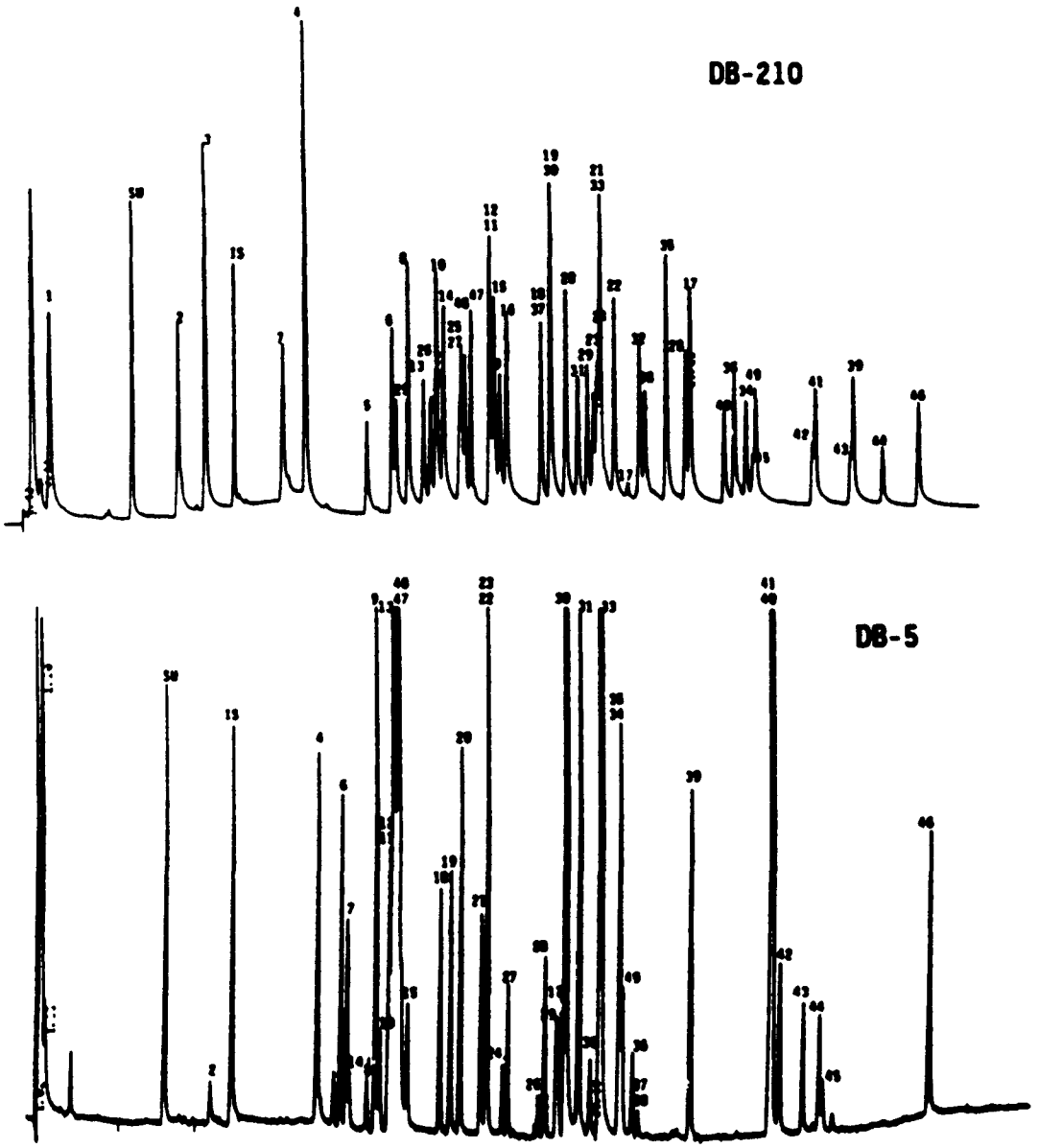
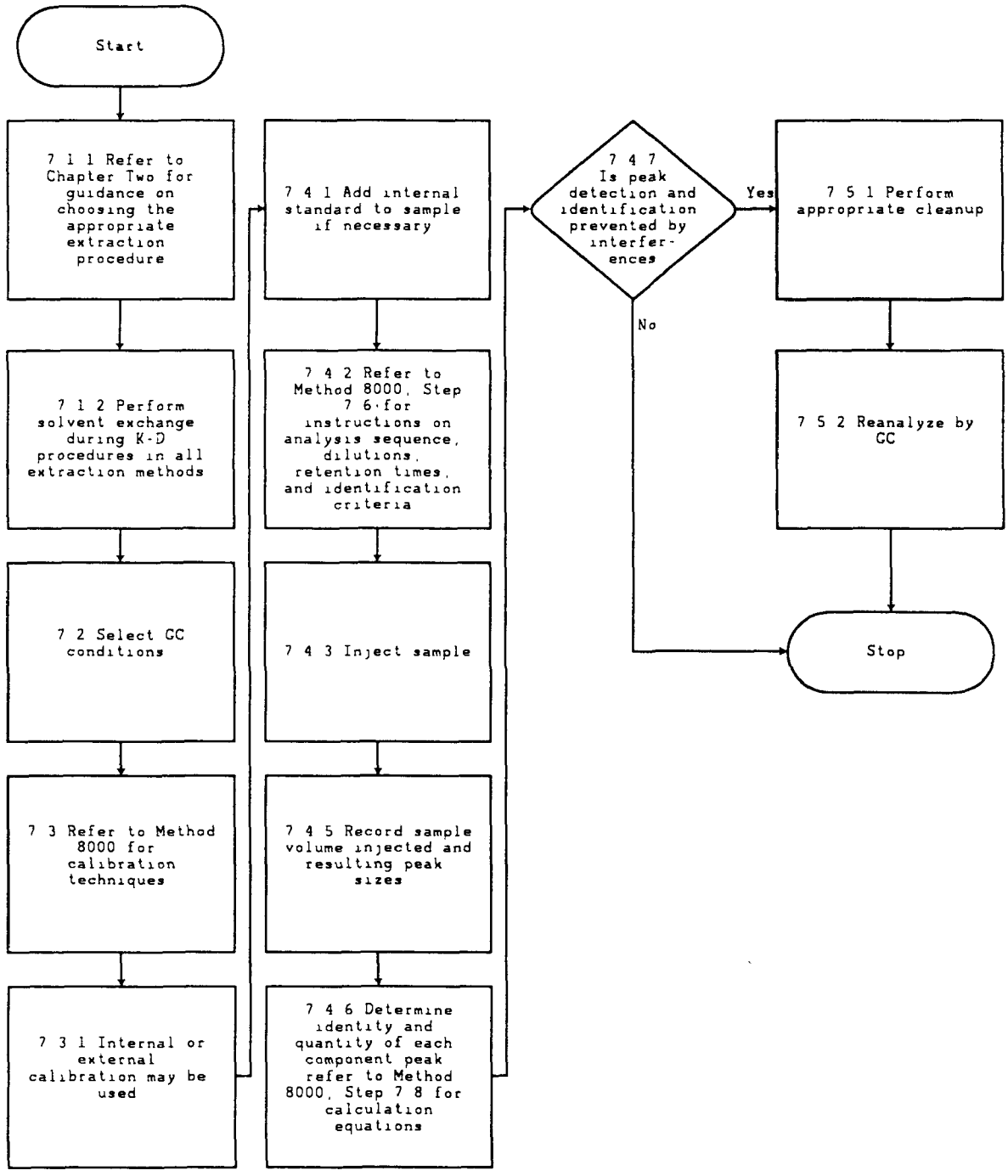


Figure 6.Chromatogram of target organophosphorus compounds on a 30-m DB-5/DB-210 column pair with NPD detector, with Simazine, Atrazine and Carbophenothion. See Table 4 for retention times and Table 6 for GC operating conditions.

ORGANOPHOSPHORUS COMPOUNDS BY GAS CHROMATOGRAPHY: CAPILLARY COLUMN TECHNIQUE



METHOD 8150B

CHLORINATED HERBICIDES BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8150 is a gas chromatographic (GC) method for determining certain chlorinated acid herbicides. The following compounds can be determined by this method:

Compound Name	CAS No.[a]
2,4-D	94-75-7
2,4-DB	94-82-6
2,4,5-TP (Silvex)	93-72-1
2,4,5-T	93-76-5
Dalapon	75-99-0
Dicamba	1918-00-9
Dichlorprop	120-36-5
Dinoseb	88-85-7
MCPA	94-74-6
MCPP	93-65-2

[a] Chemical Abstract Services Registry Number.

1.2 Table 1 lists the method detection limit for each compound in organic-free reagent water. Table 2 lists the estimated quantitation limit (EQL) for other matrices.

1.3 When Method 8150 is used to analyze unfamiliar samples, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Section 8.4 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

1.4 Only experienced analysts should be allowed to work with diazomethane due to the potential hazards associated with its use (the compound is explosive and carcinogenic).

2.0 SUMMARY OF METHOD

2.1 Method 8150 provides extraction, esterification, and gas chromatographic conditions for the analysis of chlorinated acid herbicides. Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. The esters are hydrolyzed with potassium hydroxide, and extraneous organic material is removed by a solvent wash. After

acidification, the acids are extracted with solvent and converted to their methyl esters using diazomethane as the derivatizing agent. After excess reagent is removed, the esters are determined by gas chromatography employing an electron capture detector, microcoulometric detector, or electrolytic conductivity detector (Goerlitz and Lamar, 1967). The results are reported as the acid equivalents.

2.2 The sensitivity of Method 8150 usually depends on the level of interferences rather than on instrumental limitations.

3.0 INTERFERENCES

3.1 Refer to Method 8000.

3.2 Organic acids, especially chlorinated acids, cause the most direct interference with the determination. Phenols, including chlorophenols, may also interfere with this procedure.

3.3 Alkaline hydrolysis and subsequent extraction of the basic solution remove many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis.

3.4 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware and glass wool must be acid rinsed, and sodium sulfate must be acidified with sulfuric acid prior to use to avoid this possibility.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

4.1.1 Gas chromatograph, analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, analytical columns, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.2 Columns

4.1.2.1 Column 1a and 1b - 1.8 m x 4 mm ID glass, packed with 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 mesh) or equivalent.

4.1.2.2 Column 2 - 1.8 m x 4 mm ID glass, packed with 5% OV-210 on Gas Chrom Q (100/120 mesh) or equivalent.

4.1.2.3 Column 3 - 1.98 m x 2 mm ID glass, packed with 0.1% SP-1000 on 80/100 mesh Carbopack C or equivalent.

4.1.3 Detector - Electron capture (ECD).

4.2 Erlenmeyer flasks - 250 and 500 mL Pyrex, with 24/40 ground glass joint.

4.3 Beaker - 500 mL.

4.4 Diazomethane generator - Refer to Section 7.4 to determine which method of diazomethane generation should be used for a particular application.

4.4.1 Diazald kit - recommended for the generation of diazomethane using the procedure given in Section 7.4.2 (Aldrich Chemical Co., Cat. No. 210,025-2 or equivalent).

4.4.2 Assemble from two 20 x 150 mm test tubes, two Neoprene rubber stoppers, and a source of nitrogen. Use Neoprene rubber stoppers with holes drilled in them to accommodate glass delivery tubes. The exit tube must be drawn to a point to bubble diazomethane through the sample extract. The generator assembly is shown in Figure 1. The procedure for use of this type of generator is given in Section 7.4.3.

4.5 Vials - 10 to 15 mL, amber glass, with Teflon lined screw cap or crimp top.

4.6 Separatory funnel - 2000 mL, 125 mL, and 60 mL.

4.7 Drying column - 400 mm x 20 mm ID Pyrex chromatographic column 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.

4.8 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 bath should be used in a hood.

4.11 Microsyringe - 10 μL.

4.12 Wrist shaker - Burrell Model 75 or equivalent.

4.13 Glass wool - Pyrex, acid washed.

4.14 Balance - Analytical, capable of accurately weighing to the nearest 0.0001 g.

4.15 Syringe - 5 mL.

4.16 Glass rod.

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 Sulfuric acid solution

5.3.1 ((1:1) (v/v)) - Slowly add 50 mL H_2SO_4 (sp. gr. 1.84) to 50 mL of organic-free reagent water.

5.3.2 ((1:3) (v/v)) - Slowly add 25 mL H_2SO_4 (sp. gr. 1.84) to 75 mL of organic-free reagent water.

5.4 Hydrochloric acid ((1:9) (v/v)), HCl. Add one volume of concentrated HCl to 9 volumes of organic-free reagent water.

5.5 Potassium hydroxide solution (KOH) - 37% aqueous solution (w/v). Dissolve 37 g potassium hydroxide pellets in organic-free reagent water, and dilute to 100 mL.

5.6 Carbitol (Diethylene glycol monoethyl ether), $C_2H_5OCH_2CH_2OCH_2CH_2OH$. Available from Aldrich Chemical Co.

5.7 Solvents

5.7.1 Acetone, CH_3COCH_3 - Pesticide quality or equivalent.

5.7.2 Methanol, CH_3OH - Pesticide quality or equivalent.

5.7.3 Isooctane, $(CH_3)_3CCH_2CH(CH_3)_2$ - Pesticide quality or equivalent.

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

5.7.5 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.

5.8 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.

5.9 N-Methyl-N-nitroso-p-toluenesulfonamide (Diazald), $CH_3C_6H_4SO_2N(CH_3)NO$. Available from Aldrich Chemical Co.

5.10 Silicic acid. Chromatographic grade, nominal 100 mesh. Store at 130°C.

5.11 Stock standard solutions - Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.11.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure acids. Dissolve the acids in pesticide quality acetone and dissolve the esters in 10% acetone/isooctane (v/v) and dilute to volume in a 10 mL volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.11.2 Transfer the stock standard solutions into vials with Teflon lined screw caps or crimp tops. 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.

5.11.3 Stock standard solutions must be replaced after 1 year, or sooner if comparison with check standards indicates a problem.

5.12 Calibration standards - A minimum of five calibration standards for each parameter of interest should be prepared through dilution of the stock standards with diethyl ether. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.13 Internal standards (if internal standard calibration is used) - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.13.1 Prepare calibration standards at a minimum of five concentrations for each parameter of interest as described in Section 5.12.

5.13.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with hexane.

5.13.3 Analyze each calibration standard according to Section 7.0.

5.14 Surrogate standards - The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and organic-free reagent water blank with one or two herbicide surrogates (e.g. herbicides that are not expected to be present in the sample). The surrogates selected should elute over the range of the temperature program used in this method. 2,4-Dichlorophenylacetic acid (DCAA) is recommended as a surrogate compound. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this Chapter, Organic Analytes, Section 4.1. Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Preparation of waste samples

7.1.1 Extraction

7.1.1.1 Follow Method 3580 except use diethyl ether as the dilution solvent, acidified anhydrous sodium sulfate, and acidified glass wool.

7.1.1.2 Transfer 1.0 mL (a lesser volume or a dilution may be required if herbicide concentrations are high) to a 250 mL ground glass-stoppered Erlenmeyer flask. Proceed to Section 7.2.2 hydrolysis.

7.2 Preparation of soil, sediment, and other solid samples

7.2.1 Extraction

7.2.1.1 To a 500 mL, wide mouth Erlenmeyer flask add 50 g (dry weight) of the well mixed, moist solid sample. Adjust the pH to 2 with concentrated HCl and monitor the pH for 15 minutes with occasional stirring. If necessary, add additional HCl until the pH remains at 2.

7.2.1.2 Add 20 mL acetone to the flask and mix the contents with the wrist shaker for 20 minutes. Add 80 mL diethyl ether to the same flask and shake again for 20 minutes. Decant the extract and measure the volume of solvent recovered.

7.2.1.3 Extract the sample twice more using 20 mL of acetone followed by 80 mL of diethyl ether. After addition of each solvent, the mixture should be shaken with the wrist shaker for 10 minutes and the acetone-ether extract decanted.

7.2.1.4 After the third extraction, the volume of extract recovered should be at least 75% of the volume of added solvent. If this is not the case, additional extractions may be necessary. Combine the extracts in a 2 liter separatory funnel containing 250 mL of 5% acidified sodium sulfate. If an emulsion forms, slowly add 5 g of acidified sodium sulfate (anhydrous) until the solvent-water mixture separates. A quantity of acidified sodium sulfate equal to the weight of the sample may be added, if necessary.

7.2.1.5 Check the pH of the extract. If it is not at or below pH 2, add more concentrated HCl until stabilized at the desired pH. Gently mix the contents of the separatory funnel for 1 minute and allow the layers to separate. Collect the aqueous phase in a clean beaker and the extract phase (top layer) in a 500 mL ground glass-stoppered Erlenmeyer flask. Place the aqueous phase back into the separatory funnel and re-extract using 25 mL of diethyl ether. Allow the layers to separate and discard the aqueous layer. Combine the ether extracts in the 500 mL Erlenmeyer flask.

7.2.2 Hydrolysis

7.2.2.1 Add 30 mL of organic-free reagent water, 5 mL of 37% KOH, and one or two clean boiling chips to the flask. Place a three ball Snyder column on the flask, evaporate the diethyl ether on a water bath, and continue to heat for a total of 90 minutes.

7.2.2.2 Remove the flask from the water bath and allow to cool. Transfer the water solution to a 125 mL separatory funnel and extract the basic solutions once with 40 mL and then twice with 20 mL of diethyl ether. Allow sufficient time for the layers to separate and discard the ether layer each time. The phenoxy-acid herbicides remain soluble in the aqueous phase as potassium salts.

7.2.3 Solvent cleanup

7.2.3.1 Adjust the pH to 2 by adding 5 mL cold (4°C) sulfuric acid (1:3) to the separatory funnel. Be sure to check the pH at this point. Extract the herbicides once with 40 mL and twice with 20 mL of diethyl ether. Discard the aqueous phase.

7.2.3.2 Combine ether extracts in a 125 mL Erlenmeyer flask containing 5-7 g of acidified anhydrous sodium sulfate. Stopper and allow the extract to remain in contact with the acidified sodium sulfate. If concentration and esterification are not to be performed immediately, store the sample overnight in the refrigerator.

NOTE: The drying step is very critical to ensuring complete esterification. Any moisture remaining in the ether will result in low herbicide recoveries. The amount of sodium sulfate is adequate if some free flowing crystals are visible when swirling the flask. If all the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate and again test by swirling. The 2 hour drying time is a minimum, however, the extracts may be held overnight in contact with the sodium sulfate.

7.2.3.3 Transfer the ether extract, through a funnel plugged with acid washed glass wool, into a 500 mL K-D flask equipped with a 10 mL concentrator tube. Use a glass rod to crush caked sodium sulfate during the transfer. Rinse the Erlenmeyer flask and column with 20-30 mL of diethyl ether to complete the quantitative transfer.

7.2.3.4 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 diethyl ether to the top. Place the apparatus on a hot water bath (60°-65°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in vapor. 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 drain and cool for at least 10 minutes.

7.2.3.5 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of diethyl ether. A 5 mL syringe is recommended for this operation. Add a fresh boiling chip, attach a micro Snyder column to the concentrator tube, and prewet the column by adding 0.5 mL of ethyl ether to the top. Place the micro K-D apparatus on the 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 concentration in 5-10 minutes. When the

apparent volume of the liquid reaches 0.5 mL, remove the micro K-D from the bath and allow it to drain and cool. Remove the Snyder column and add 0.1 mL of methanol. Rinse the walls of the concentrator tube while adjusting the extract volume to 1.0 mL with diethyl ether. Proceed to Section 7.4 for esterification.

7.3 Preparation of aqueous samples

7.3.1 Extraction

7.3.1.1 Using a 1 liter graduated cylinder, measure 1 liter (nominal) of sample, record the sample volume to the nearest 5 mL, and transfer it to the separatory funnel. If high concentrations are anticipated, a smaller volume may be used and then diluted with organic-free reagent water to 1 liter. Adjust the pH to less than 2 with sulfuric acid (1:1).

7.3.1.2 Add 150 mL of diethyl ether to the sample bottle, seal, and shake for 30 seconds to rinse the walls. Transfer the solvent wash to the separatory funnel and extract the sample by shaking the funnel for 2 minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water layer 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. Drain the aqueous phase into a 1 liter Erlenmeyer flask. Collect the solvent extract in a 250 mL ground glass Erlenmeyer flask containing 2 mL of 37% KOH. Approximately 80 mL of the diethyl ether will remain dissolved in the aqueous phase.

7.3.1.3 Repeat the extraction two more times using 50 mL of diethyl ether each time. Combine the extracts in the Erlenmeyer flask. (Rinse the 1 liter flask with each additional aliquot of extracting solvent.)

7.3.2 Hydrolysis

7.3.2.1 Add one or two clean boiling chips and 15 mL of organic-free reagent water to the 250 mL flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of diethyl ether to the top of the column. Place the apparatus on a hot water bath (60°-65°C) so that the bottom of the flask is bathed with hot water vapor. Although the diethyl ether will evaporate in about 15 minutes, continue heating for a total of 60 minutes, beginning from the time the flask is placed in the water bath. Remove the apparatus and let stand at room temperature for at least 10 minutes.

7.3.2.2 Transfer the solution to a 60 mL separatory funnel using 5-10 mL of organic-free reagent water. Wash the basic

solution twice by shaking for 1 minute with 20 mL portions of diethyl ether. Discard the organic phase. The herbicides remain in the aqueous phase.

7.3.3 Solvent cleanup

7.3.3.1 Acidify the contents of the separatory funnel to pH 2 by adding 2 mL of cold (4°C) sulfuric acid (1:3). Test with pH indicator paper. Add 20 mL diethyl ether and shake vigorously for 2 minutes. Drain the aqueous layer into a 250 mL Erlenmeyer flask, and pour the organic layer into a 125 mL Erlenmeyer flask containing about 5-7 g of acidified sodium sulfate. Repeat the extraction twice more with 10 mL aliquots of diethyl ether, combining all solvent in the 125 mL flask. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hours.

NOTE: The drying step is very critical to ensuring complete esterification. Any moisture remaining in the ether will result in low herbicide recoveries. The amount of sodium sulfate is adequate if some free flowing crystals are visible when swirling the flask. If all the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate and again test by swirling. The 2 hour drying time is a minimum, however, the extracts may be held overnight in contact with the sodium sulfate.

7.3.3.2 Transfer the ether extract, through a funnel plugged with acid washed glass wool, into a 500 mL K-D flask equipped with a 10 mL concentrator tube. Use a glass rod to crush caked sodium sulfate during the transfer. Rinse the Erlenmeyer flask and column with 20-30 mL of diethyl ether to complete the quantitative transfer.

7.3.3.3 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 diethyl ether to the top. Place the apparatus on a hot water bath (60°-65°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in vapor. 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 drain and cool for at least 10 minutes.

7.3.3.4 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of diethyl ether. A 5 mL syringe is recommended for this operation. Add a fresh boiling chip, attach a micro Snyder column to the concentrator tube, and prewet the column by adding 0.5 mL of ethyl ether to the top. Place the micro K-D apparatus on the 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 concentration in 5-10 minutes. When the apparent volume of the liquid reaches 0.5 mL, remove the micro K-D from the bath and allow it to drain and cool. Remove the Snyder column and add 0.1 mL of methanol. Rinse the walls of the concentrator tube while adjusting the extract volume to 1.0 mL with diethyl ether.

7.4 Esterification

7.4.1 Two methods may be used for the generation of diazomethane: the bubbler method (set up shown in Figure 1) and the Diazald kit method. The bubbler method is suggested when small batches (10-15) of samples require esterification. The bubbler method works well with samples that have low concentrations of herbicides (e.g. aqueous samples) and is safer to use than the Diazald kit procedure. The Diazald kit method is good for large quantities of samples needing esterification. The Diazald kit method is more effective than the bubbler method for soils or samples that may contain high concentrations of herbicides (e.g. samples such as soils that may result in yellow extracts following hydrolysis may be difficult to handle by the bubbler method). The diazomethane derivatization (U.S. EPA, 1971) procedures, described below, will react efficiently with all of the chlorinated herbicides described in this method and should be used only by experienced analysts, due to the potential hazards associated with its use. The following precautions should be taken:

CAUTION: Diazomethane is a carcinogen and can explode under certain conditions.

- Use a safety screen.
- Use mechanical pipetting aides.
- Do not heat above 90°C -- EXPLOSION may result.
- Avoid grinding surfaces, ground glass joints, sleeve bearings, glass stirrers -- EXPLOSION may result.
- Store away from alkali metals -- EXPLOSION may result.
- Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips.

7.4.2 Diazald kit method - Instructions for preparing diazomethane are provided with the generator kit.

7.4.2.1 Add 2 mL of diazomethane solution and let sample stand for 10 minutes with occasional swirling.

7.4.2.2 Rinse inside wall of ampule with several hundred µL of diethyl ether. Allow solvent to evaporate spontaneously at room temperature to about 2 mL.

7.4.2.3 Dissolve the residue in 5 mL of hexane. Analyze by gas chromatography.

7.4.3 Bubbler method - Assemble the diazomethane bubbler (see Figure 1).

7.4.3.1 Add 5 mL of diethyl ether to the first test tube. Add 1 mL of diethyl ether, 1 mL of carbitol, 1.5 mL of 37% KOH, and 0.1-0.2 g Diazald to the second test tube. Immediately place the exit tube into the concentrator tube containing the sample extract.

Apply nitrogen flow (10 mL/min) to bubble diazomethane through the extract for 10 minutes or until the yellow color of diazomethane persists. The amount of Diazald used is sufficient for esterification of approximately three sample extracts. An additional 0.1-0.2 g of Diazald may be added (after the initial Diazald is consumed) to extend the generation of the diazomethane. There is sufficient KOH present in the original solution to perform a maximum of approximately 20 minutes of total esterification.

7.4.3.2 Remove the concentrator tube and seal it with a Neoprene or Teflon stopper. Store at room temperature in a hood for 20 minutes.

7.4.3.3 Destroy any unreacted diazomethane by adding 0.1-0.2 g silicic acid to the concentrator tube. Allow to stand until the evolution of nitrogen gas has stopped. Adjust the sample volume to 10.0 mL with hexane. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. It is recommended that the methylated extracts be analyzed immediately to minimize the trans-esterification and other potential reactions that may occur. Analyze by gas chromatography.

7.5 Gas chromatographic conditions (Recommended)

7.5.1 Column 1a

Carrier gas (5% methane/95% argon) flow rate:	70 mL/min
Temperature program:	185°C, isothermal.

7.5.2 Column 1b

Carrier gas (5% methane/95% argon) flow rate:	70 mL/min
Initial temperature:	140°C, hold for 6 minutes
Temperature program:	140°C to 200°C at 10°C/min, hold until last compound has eluted.

7.5.3 Column 2

Carrier gas (5% methane/95% argon) flow rate:	70 mL/min
Temperature program:	185°C, isothermal.

7.5.4 Column 3

Carrier gas (ultra-high purity N_2) flow rate:	25 mL/min
Initial temperature:	100°C, no hold
Temperature program:	100°C to 150°C at 10°C/min, hold until last compound has eluted.

7.6 Calibration - Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.6.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.6.2 The following gas chromatographic columns are recommended for the compounds indicated:

Analyte	Column	Analyte	Column
Dicamba	1a,2	Dalapon	3
2,4-D	1a,2	MCPP	1b
2,4,5-TP	1a,2	MCPA	1b
2,4,5-T	1a,2	Dichloroprop	1b
2,4-DB	1a	Dinoseb	1b

7.7 Gas chromatographic analysis

7.7.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 μL of internal standard to the sample prior to injection.

7.7.2 Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration check standard after each group of 10 samples in the analysis sequence.

7.7.3 Examples of chromatograms for various chloro-phenoxy herbicides are shown in Figures 2 through 4.

7.7.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.7.5 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes.

7.7.6 If calibration standards have been analyzed in the same manner as the samples (e.g. have undergone hydrolysis and esterification), then the calculation of concentration given in Method 8000 should be used. However, if calibration is done using standards made from methyl ester compounds (compounds not esterified by application of this method), then the calculation of concentration must include a correction for the molecular weight of the methyl ester versus the acid herbicide.

7.7.7 If peak detection and identification are prevented due to interferences, further cleanup is required. Before using any cleanup procedure, the analyst must process a series of standards through the procedure to validate elution patterns and the absence of interferences from reagents.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000.

8.2.1 Select a representative spike concentration for each compound (acid or ester) to be measured. Using stock standards, prepare a quality control check sample concentrate in acetone 1,000 times more concentrated than the selected concentrations.

8.2.2 Table 3 indicates Single Operator Accuracy and Precision for this method. Compare the results obtained with the results given in Table 3 to determine if the data quality is acceptable.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000).

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

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if none of the above checks reveal a problem.
- Re-extract and re-analyze the sample if none of the above are a problem or flag the data as "estimated concentration".

8.4 GC/MS confirmation

8.4.1 GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. Refer to Method 8270 for the appropriate GC/MS operating conditions and analysis procedures.

8.4.2 When available, chemical ionization mass spectra may be employed to aid the qualitative identification process.

8.4.3 Should these MS procedures fail to provide satisfactory results, additional steps may be taken before reanalysis. These steps may include the use of alternate packed or capillary GC columns or additional cleanup.

9.0 METHOD PERFORMANCE

9.1 In a single laboratory, using organic-free reagent water and effluents from publicly owned treatment works (POTW), the average recoveries presented in Table 3 were obtained. The standard deviations of the percent recoveries of these measurements are also included in Table 3.

10.0 REFERENCES

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TABLE 1.
CHROMATOGRAPHIC CONDITIONS AND DETECTION LIMITS
FOR CHLORINATED HERBICIDES

Compound	Retention time (min)[a]				Method detection limit (µg/L)
	Col.1a	Col.1b	Col.2	Col.3	
2,4-D	2.0	-	1.6	-	1.2
2,4-DB	4.1	-	-	-	0.91
2,4,5-T	3.4	-	2.4	-	0.20
2,4,5-TP (Silvex)	2.7	-	2.0	-	0.17
Dalapon	-	-	-	5.0	5.8
Dicamba	1.2	-	1.0	-	0.27
Dichloroprop	-	4.8	-	-	0.65
Dinoseb	-	11.2	-	-	0.07
MCPA	-	4.1	-	-	249
MCPP	-	3.4	-	-	192

[a]Column conditions are given in Sections 4.1 and 7.5.

TABLE 2.
DETERMINATION OF ESTIMATED QUANTITATION
LIMITS (EQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water (based on one liter sample size)	10
Soil/sediment and other solids	200
Waste samples	100,000

[a]Sample EQLs are highly matrix dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

[b]EQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet weight basis.

TABLE 3.
SINGLE OPERATOR ACCURACY AND PRECISION[a]

Compound	Sample Type	Spike (µg/L)	Mean Recovery (%)	Standard deviation (%)
2,4-D	DW	10.9	75	4
	MW	10.1	77	4
	MW	200	65	5
Dalapon	DW	23.4	66	8
	MW	23.4	96	13
	MW	468	81	9
2,4-DB	DW	10.3	93	3
	MW	10.4	93	3
	MW	208	77	6
Dicamba	DW	1.2	79	7
	MW	1.1	86	9
	MW	22.2	82	6
Dichlorprop	DW	10.7	97	2
	MW	10.7	72	3
	MW	213	100	2
Dinoseb	MW	0.5	86	4
	MW	102	81	3
MCPA	DW	2020	98	4
	MW	2020	73	3
	MW	21400	97	2
MCPP	DW	2080	94	4
	MW	2100	97	3
	MW	20440	95	2
2,4,5-T	DW	1.1	85	6
	MW	1.3	83	4
	MW	25.5	78	5
2,4,5-TP	DW	1.0	88	5
	MW	1.3	88	4
	MW	25.0	72	5

[a]All results based upon seven replicate analyses. Esterification performed using the bubbler method. Data obtained from reference 9.

DW = ASTM Type II
MW = Municipal water

FIGURE 1.
DIAZOMETHANE GENERATOR

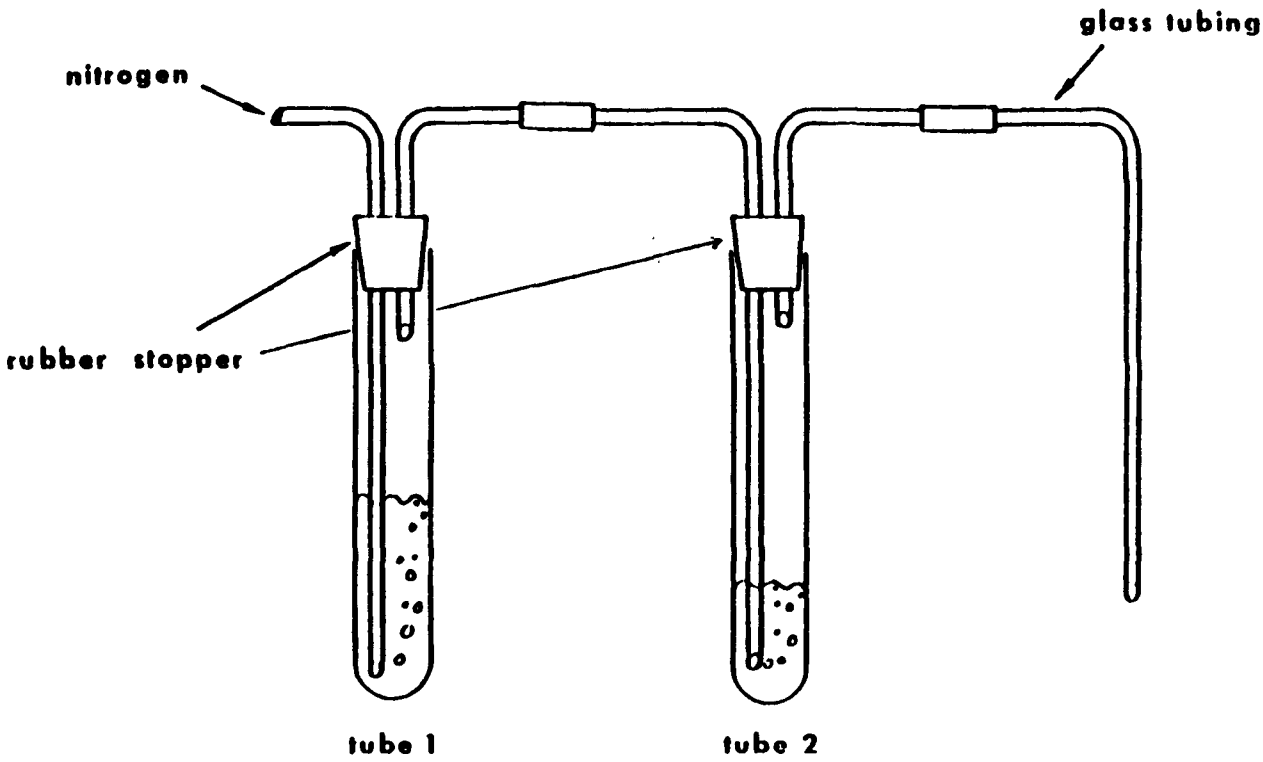


FIGURE 2.
GAS CHROMATOGRAM OF CHLORINATED HERBICIDES

Column: 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 Mesh)
Temperature: Isothermal at 185°C
Detector: Electron Capture

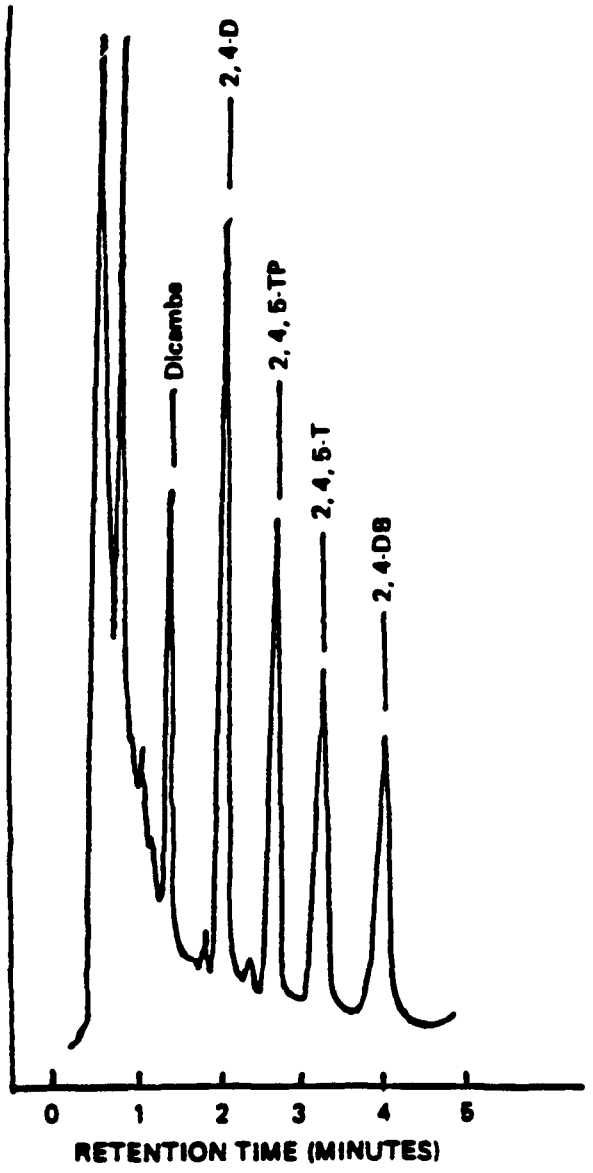


FIGURE 3.
GAS CHROMATOGRAM OF CHLORINATED HERBICIDES

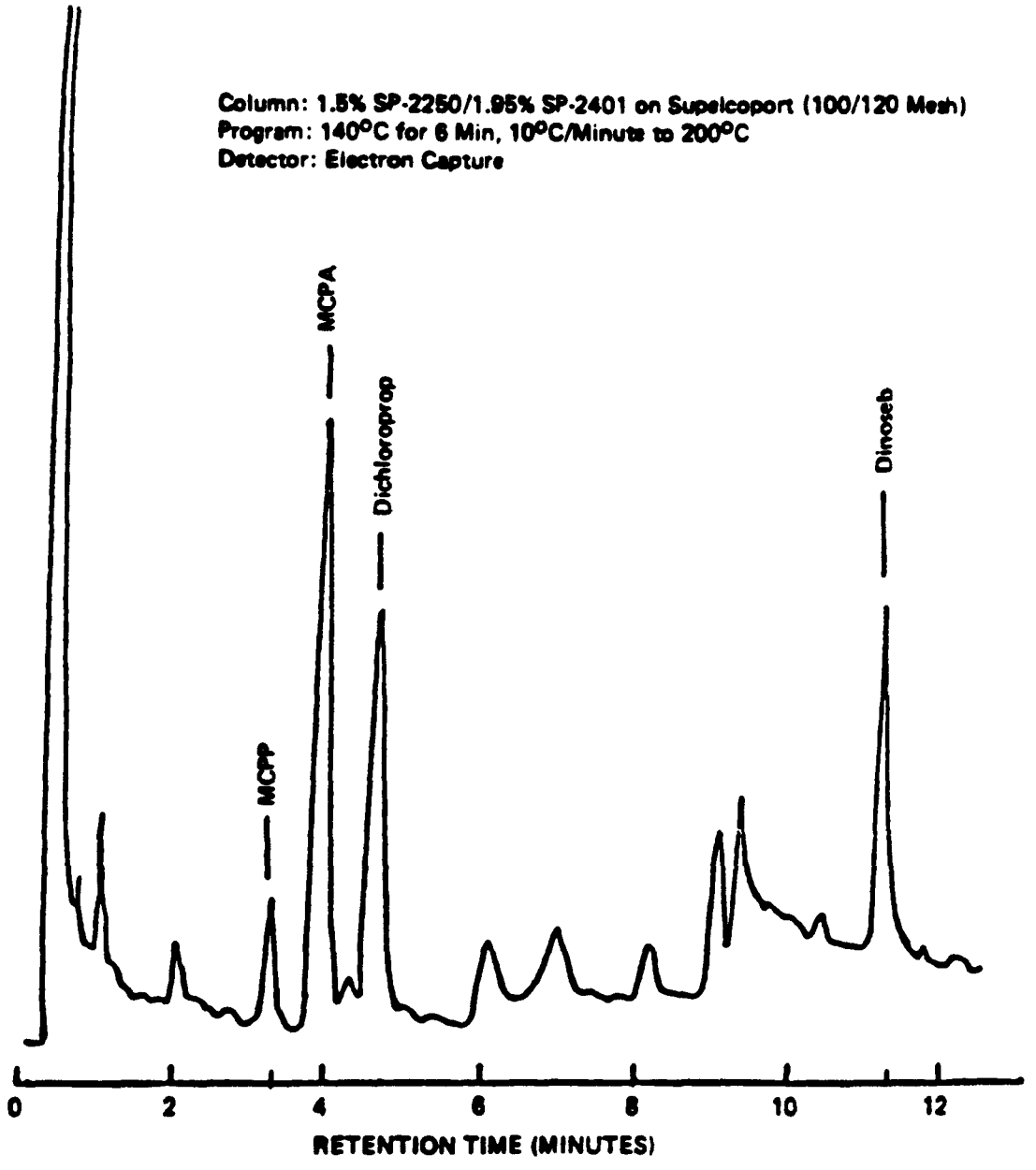
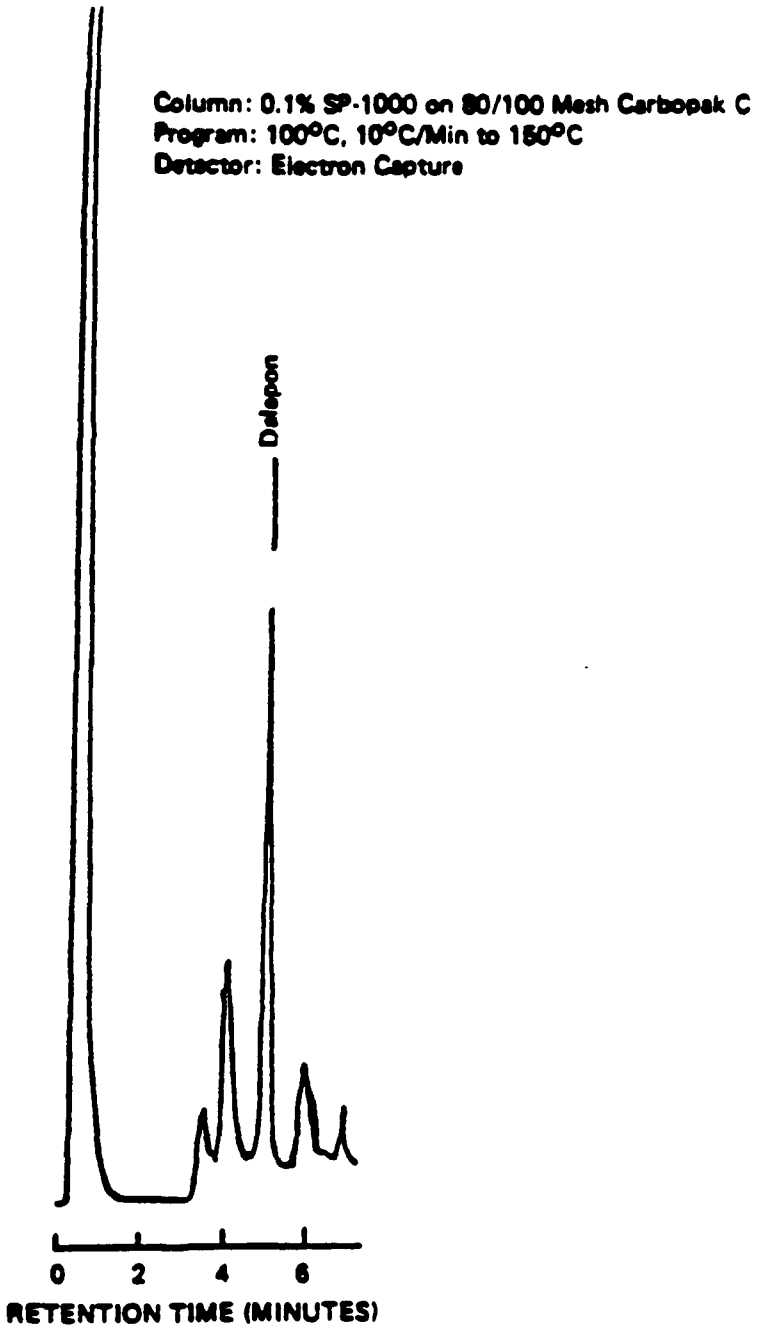
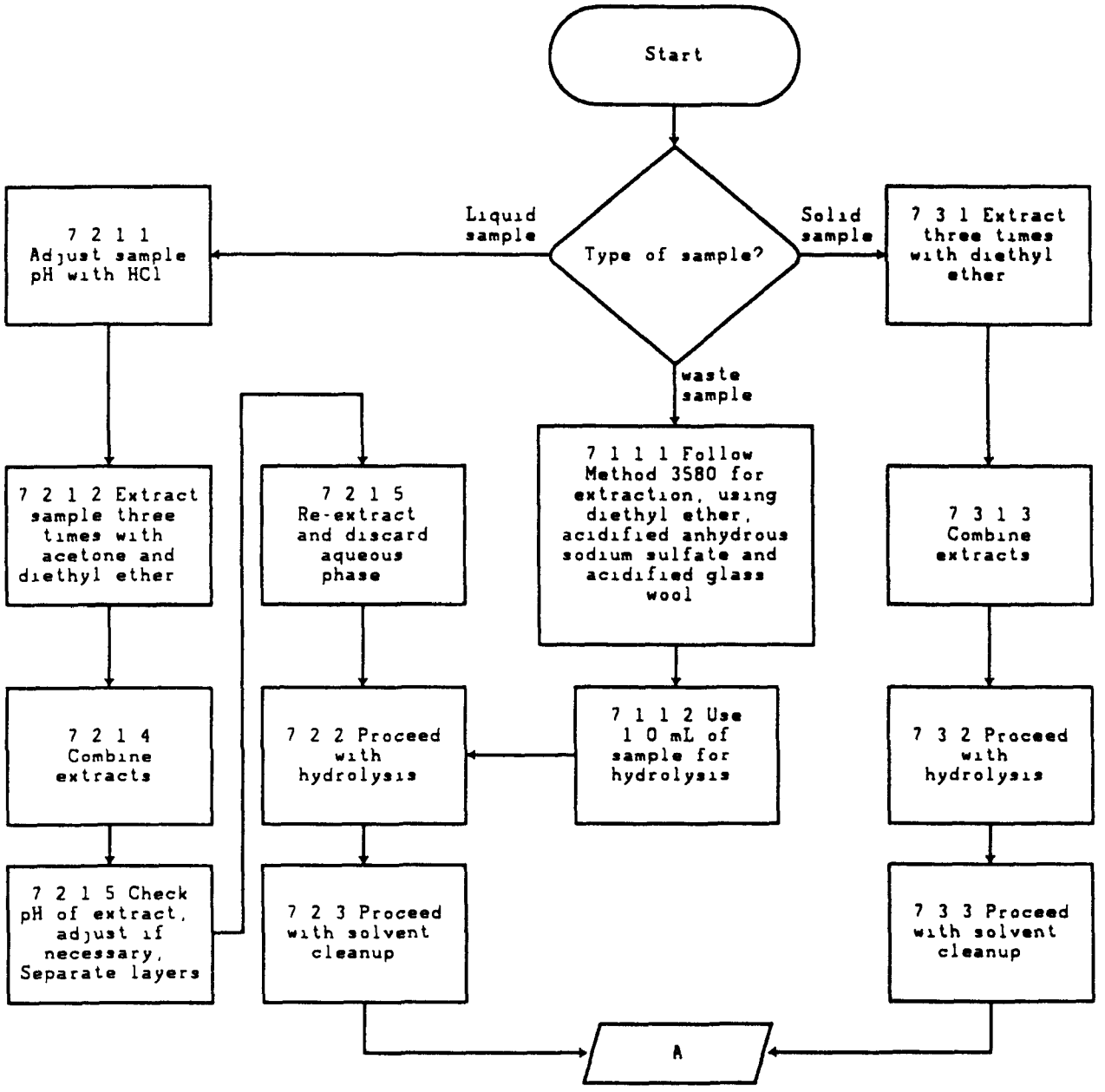
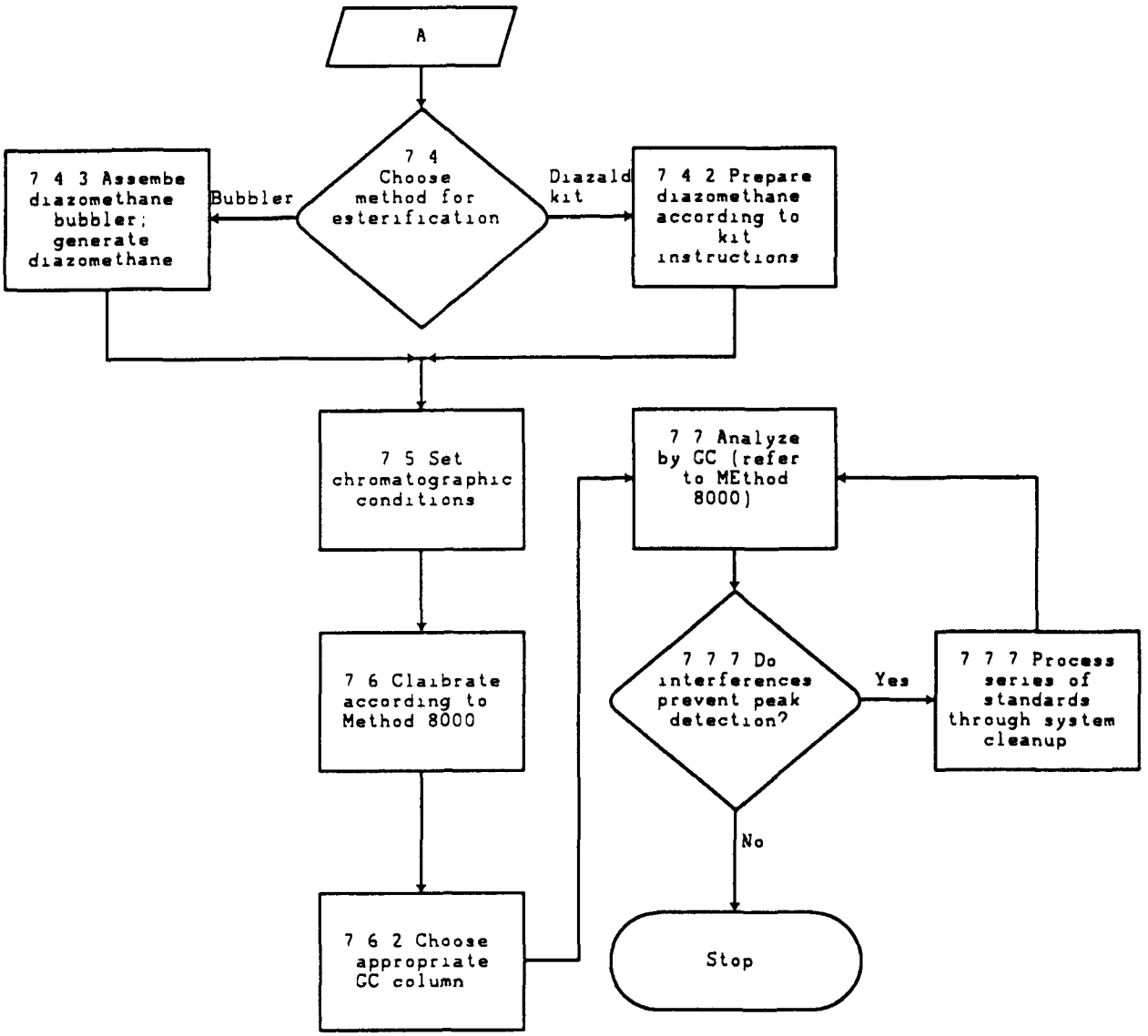


FIGURE 4.
GAS CHROMATOGRAM OF DALAPON, COLUMN 3




Start
Type of sample?
Liquid sample
Solid sample
waste sample
7 2 1 1 Adjust sample pH with HCl
7 3 1 Extract three times with diethyl ether
7 1 1 1 Follow Method 3580 for extraction, using diethyl ether, acidified anhydrous sodium sulfate and acidified glass wool
7 2 1 2 Extract sample three times with acetone and diethyl ether
7 2 1 5 Re-extract and discard aqueous phase
7 3 1 3 Combine extracts
7 2 1 4 Combine extracts
7 2 2 Proceed with hydrolysis
7 1 1 2 Use 1 0 mL of sample for hydrolysis
7 3 2 Proceed with hydrolysis
7 2 1 5 Check pH of extract, adjust if necessary, Separate layers
7 2 3 Proceed with solvent cleanup
7 3 3 Proceed with solvent cleanup
A


A
7 4
Choose
method for
esterification
Bubbler
Diazald
kit
7 4 3 Assembe
diazomethane
bubbler;
generate
diazomethane
7 4 2 Prepare
diazomethane
according to
kit
instructions
7 5 Set
chromatographic
conditions
7 6 Claibrate
according to
Method 8000
7 6 2 Choose
appropriate
GC column
7 7 Analyze
by GC (refer
to MEthod
8000)
7 7 7 Do
interferences
prevent peak
detection?
Yes
7 7 7 Process
series of
standards
through system
cleanup
No
Stop

METHOD 8151

CHLORINATED HERBICIDES BY GC USING METHYLATION OR PENTAFLUOROBENZYLATION DERIVATIZATION: CAPILLARY COLUMN TECHNIQUE

.0 SCOPE AND APPLICATION

1.1 Method 8151 is a capillary gas chromatographic (GC) method for etermining certain chlorinated acid herbicides in aqueous, soil and waste atrices. Specifically, Method 8151 may be used to determine the following :ompounds:

Compound Name	CAS No.[a]
Acifluorfen	50594-66-6
Bentazon	25057-89-0
Chloramben	133-90-4
2,4-D	94-75-7
Dalapon	75-99-0
2,4-DB	94-82-6
DCPA diacid[b]	2136-79-0
Dicamba	1918-00-9
3,5-Dichlorobenzoic acid	51-36-5
Dichlorprop	120-36-5
Dinoseb	88-85-7
5-Hydroxydicamba	7600-50-2
MCPA	94-74-6
MCPP	93-65-2
4-Nitrophenol	100-02-1
Pentachlorophenol	87-86-5
Picloram	1918-02-1
2,4,5-TP (Silvex)	93-72-1
2,4,5-T	93-76-5

[a] Chemical Abstract Services Registry Number.

[b] DCPA monoacid and diacid metabolites included in method scope; DCPA diacid metabolite used for validation studies. DCPA is a dimethyl ester.

Because these compounds are produced and used in various forms (i.e., acid, salt, ester, etc.), Method 8151 describes a hydrolysis step that can be used to convert herbicide esters into the acid form prior to analysis. Herbicide esters generally have a half-life of less than one week in soil.

1.2 When Method 8151 is used to analyze unfamiliar samples, compound identifications should be supported by at least one additional qualitative

technique. Section 8.4 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

1.3 The estimated detection limits for each of the compounds in aqueous and soil matrices are listed in Table 1. The detection limits for a specific waste sample may differ from those listed, depending upon the nature of the interferences and the sample matrix.

1.4 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatographs and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.5 Only experienced analysts should be allowed to work with diazomethane due to the potential hazards associated with its use (explosive, carcinogenic).

2.0 SUMMARY OF METHOD

2.1 Method 8151 provides extraction, derivatization and gas chromatographic conditions for the analysis of chlorinated acid herbicides in water, soil and waste samples. An option for the hydrolysis of esters is also described.

2.1.1 Water samples are extracted with diethyl ether and then esterified with either diazomethane or pentafluorobenzyl bromide. The derivatives are determined by gas chromatography with an electron capture detector (GC/ECD). The results are reported as acid equivalents.

2.1.2 Soil and waste samples are extracted and esterified with either diazomethane or pentafluorobenzyl bromide. The derivatives are determined by gas chromatography with an electron capture detector (GC/ECD). The results are reported as acid equivalents.

2.1.3 If herbicide esters are to be determined using this method, hydrolysis conditions for the esters in water and soil extracts are described.

2.2 The sensitivity of Method 8151 depends on the level of interferences in addition to instrumental limitations. Table 1 lists the GC/ECD and GC/MS limits of detection that can be obtained in aqueous and soil matrices in the absence of interferences. Detection limits for a typical waste sample should be higher.

3.0 INTERFERENCES

3.1 Refer to Method 8000.

3.2 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts or elevated baselines in gas chromatograms. All these materials must

be routinely demonstrated to be free from interferences under the conditions of the analysis, by analyzing reagent blanks.

3.2.1 Glassware must be scrupulously cleaned. Clean each piece of glassware as soon as possible after use by rinsing it with the last solvent used in it. This should be followed by detergent washing with hot water and rinses with tap water, then with organic-free reagent water. Glassware should be solvent-rinsed with acetone and pesticide-quality hexane. After rinsing and drying, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store glassware inverted or capped with aluminum foil. Immediately prior to use, glassware should be rinsed with the next solvent to be used.

3.2.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from waste to waste, depending upon the nature and diversity of the waste being sampled.

3.4 Organic acids, especially chlorinated acids, cause the most direct interference with the determination by methylation. Phenols, including chlorophenols, may also interfere with this procedure. The determination using pentafluorobenzylation is more sensitive, and more prone to interferences from the presence of organic acids or phenols than by methylation.

3.5 Alkaline hydrolysis and subsequent extraction of the basic solution removes many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis. However, hydrolysis may result in the loss of dinoseb and the formation of aldol condensation products if any residual acetone remains from the extraction of solids.

3.6 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware must be acid-rinsed and then rinsed to constant pH with organic-free reagent water. Sodium sulfate must be acidified.

3.7 Sample extracts should be dry prior to methylation or else poor recoveries will be obtained.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

4.1.1 Gas chromatograph - Analytical system complete with gas chromatograph suitable for Grob-type injection using capillary columns, and all required accessories including detector, capillary analytical columns, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.2 Columns

4.1.2.1 Narrow Bore Columns

4.1.2.1.1 Primary Column 1 - 30 m x 0.25 mm, 5% phenyl/95% methyl silicone (DB-5, J&W Scientific, or equivalent), 0.25 μm film thickness.

4.1.2.1.2 Primary Column 1a (GC/MS) - 30 m x 0.32 mm, 5% phenyl/95% methyl silicone, (DB-5, J&W Scientific, or equivalent), 1 μm film thickness.

4.1.2.1.3 Column 2 - 30 m x 0.25 mm DB-608 (J&W Scientific or equivalent) with a 25 μm film thickness.

4.1.2.1.4 Confirmation Column - 30 m x 0.25 mm, 14% cyanopropyl phenyl silicone, (DB-1701, J&W Scientific, or equivalent), 0.25 μm film thickness.

4.1.2.2 Megabore Columns

4.1.2.2.1 Primary Column - 30 m x 0.53 mm DB-608 (J&W Scientific or equivalent) with 0.83 μm film thickness.

4.1.2.2.2 Confirmation Column - 30 m x 0.53 mm, 14% cyanopropyl phenyl silicone, (DB-1701, J&W Scientific, or equivalent), 1.0 μm film thickness.

4.1.3 Detector - Electron Capture Detector (ECD)

4.2 Kuderna-Danish (K-D) apparatus

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

4.2.2 Evaporation flask - 500 mL (Kontes K-570001-500 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 K-569001-0219 or equivalent).

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

4.3 Diazomethane Generator: Refer to Section 7.5 to determine which method of diazomethane generation should be used for a particular generation.

4.3.1 Diazald Kit - Recommended for the generation of diazomethane (Aldrich Chemical Co., Cat No. 210,025-0, or equivalent).

4.3.2 As an alternative, assemble from two 20 mm x 150 mm test tubes, two Neoprene rubber stoppers, and a source of nitrogen. Use Neoprene rubber stoppers with holes drilled in them to accommodate glass delivery tubes. The exit tube must be drawn to a point to bubble diazomethane through the sample extract. The generator assembly is shown in Figure 1. The procedure for use of this type of generator is given in Section 7.5.

4.4 Other Glassware

4.4.1 Beaker - 400 mL, thick walled.

4.4.2 Funnel - 75 mm diameter.

4.4.3 Separatory funnel - 500 mL, with Teflon stopcock.

4.4.4 Centrifuge bottle - 500 mL (Pyrex 1260 or equivalent).

4.4.5 Centrifuge bottle - 24/40 500 mL

4.4.6 Continuous Extractor (Hershberg-Wolfe type, Lab Glass No. LG-6915, or equivalent)

4.4.7 Pipet - Pasteur, glass, disposable (140 mm x 5 mm ID).

4.4.8 Vials - 10 mL, glass, with Teflon lined screw-caps.

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

4.5 Filter paper - 15 cm diameter (Whatman No. 1 or equivalent).

4.6 Glass Wool - Pyrex, acid washed.

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

4.8 Water bath - Heated, with concentric ring cover, capable of temperature control ($\pm$ 2°C). The bath should be used in a hood.

4.9 Balance - Analytical, capable of accurately weighing to the nearest 0.0001 g.

4.10 Centrifuge.

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

4.11.1 Ultrasonic Disrupter - The disrupter must have a minimum power wattage of 300 watts, with pulsing capability. A device designed to reduce the cavitation sound is recommended. Follow the manufacturers instructions for preparing the disrupter for extraction of samples. Use a 3/4" horn for most samples.

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

4.13 Filter paper - Whatman #1, or equivalent.

4.14 pH paper.

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 water, as defined in Chapter One.

5.3 Sodium hydroxide solution (0.1 N), NaOH. Dissolve 4 g NaOH in organic-free reagent water and dilute to 1.0 L.

5.4 Potassium hydroxide solution (37% aqueous solution (w/v)), KOH. Dissolve 37 g potassium hydroxide pellets in organic-free reagent water and dilute to 100 mL.

5.5 Phosphate buffer pH = 2.5 (0.1 M). Dissolve 12 g sodium phosphate (NaH_2PO_4) in organic-free reagent water and dilute to 1.0 L. Add phosphoric acid to adjust the pH to 2.5.

5.6 N-methyl-N-nitroso-p-toluenesulfonamide (Diazald). High purity, available from Aldrich Chemical Co. or equivalent.

5.7 Silicic acid, H_2SiO_5. 100 mesh powder, store at 130°C.

5.8 Potassium carbonate, K_2CO_3.

5.9 2,3,4,5,6-Pentafluorobenzyl bromide (PFBBr), $C_6F_5CH_2Br$. Pesticide quality or equivalent.

5.10 Sodium sulfate (granular, acidified, 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. Acidify by slurrying 100 g sodium sulfate with enough diethyl ether to just cover the solid; then add 0.1 mL of concentrated sulfuric acid and mix thoroughly. Remove the ether under vacuum. Mix 1 g of the resulting solid with 5 mL of organic-free reagent water and measure the pH of the mixture. It must be below a pH of 4. Store the remaining solid at 130°C.

5.11 Solvents

5.11.1 Methylene chloride, CH_2Cl_2. Pesticide quality or equivalent.

5.11.2 Acetone, CH_3COCH_3. Pesticide quality or equivalent.

5.11.3 Methanol, CH_3OH. Pesticide quality or equivalent.

5.11.4 Toluene, $C_6H_5CH_3$. Pesticide quality or equivalent.

5.11.5 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.

5.11.6 Isooctane, $(CH_3)_3CH_2CH(CH_3)_2$. Pesticide quality or equivalent.

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

5.11.8 Ethanol, absolute. C_2H_5OH

5.11.9 Carbitol (diethylene glycol monoethyl ether), $C_2H_5OCH_2CH_2OCH_2CH_2O$ - optional for producing alcohol free diazomethane.

5.12 Stock standard solutions (1000 mg/L) - Can be prepared from pure standard materials or can be purchased as certified solutions. Commercially prepared stock standards can be used if they are verified against EPA standards. If EPA standards are not available for verification, then standards certified by the manufacturer and verified against a standard made from pure material is acceptable.

5.12.1 Prepare stock standard solutions by accurately weighing about 0.010 g of pure acid. Dissolve the material in pesticide quality acetone and dilute to volume in a 10 mL volumetric flask. Stocks prepared from pure methyl esters are dissolved in 10% acetone/isooctane (v/v). Larger volumes may be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard.

5.12.2 Transfer the stock standard solutions to vials with Teflon lined screw-caps. Store at 4°C, protected from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially immediately prior to preparing calibration standards from them.

5.12.3 Stock standard solutions of the derivatized acids must be replaced after 1 year, or sooner, if comparison with check standards indicates a problem. Stock standard solutions of the free acids degrade more quickly and should be replaced after two months, or sooner if comparison with check standards indicates a problem.

5.13 Internal Standard Spiking Solution (if internal standard calibration is used) - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. The compound 4,4'-dibromooctafluorobiphenyl (DBOB) has been shown to be an effective internal standard, but other compounds, such as 1,4-dichlorobenzene, may be used if there is a DBOB interference.

5.13.1 Prepare an internal standard spiking solution by accurately weighing approximately 0.0025 g of pure DBOB. Dissolve the DBOB in acetone and dilute to volume in a 10 mL volumetric flask. Transfer the internal standard spiking solution to a vial with a Teflon lined screw-cap, and store at room temperature. Addition of 10 µL of the internal standard spiking solution to 10 mL of sample extract results in a final internal standard concentration of 0.25 µg/L. The solution should be replaced if there is a change in internal standard response greater than 20 percent of the original response recorded.

5.14 Calibration standards - Calibration standards, at a minimum of five concentrations for each parameter of interest, should be prepared through dilution of the stock standards with diethyl ether. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.14.1 Derivatize each calibration standard prepared from free acids in a 10 mL K-D concentrator tube, according to the procedures beginning at Section 7.5.

5.14.2 Add a known constant amount of one or more internal standards to each derivatized calibration standard, and dilute to volume with the solvent indicated in the derivative option used.

5.15 Surrogate standards - The analyst should monitor the performance of the extraction, cleanup (when used), and determinative step, and the effectiveness of the method in dealing with each sample matrix, by spiking each sample, standard, and blank with one or two herbicide surrogates (e.g., herbicides that are not expected to be present in the sample) recommended to encompass the range of the temperature program used in this method. Deuterated analogs of analytes should not be used as surrogates in gas chromatographic analysis due to coelution problems. The surrogate standard recommended for use is 2,4-Dichlorophenylacetic acid (DCAA).

5.15.1 Prepare a surrogate standard spiking solution by accurately weighing approximately 0.001 g of pure DCAA. Dissolve the DCAA in acetone, and dilute to volume in a 10 mL volumetric flask. Transfer the surrogate standard spiking solution to a vial with a Teflon lined screw-cap, and store at room temperature. Addition of 50 µL of the surrogate standard spiking solution to 1 L of sample, prior to extraction, results in a final concentration in the extract of 0.5 mg/L.

5.16 pH Adjustment Solutions

5.16.1 Sodium hydroxide, NaOH, 6 N.

5.16.2 Sulfuric acid, H_2SO_4, 12 N.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

6.2 Extracts must be stored under refrigeration (4°C).

7.0 PROCEDURE

7.1 Preparation of High Concentration Waste Samples

7.1.1 Extraction

7.1.1.1 Follow Method 3580, Waste Dilution, with the following exceptions:

- use diethyl ether as the dilution solvent,
- use acidified anhydrous sulfate, and acidified glass wool,
- spike the sample with surrogate compound(s) according to Section 5.16.1.

7.1.1.2 If the sample is to be analyzed for both herbicide esters and acids, then the sample extract must be hydrolyzed. In this case, transfer 1.0 mL (a smaller volume or a dilution may be required if herbicide concentrations are large) to a 250 mL ground glass Erlenmeyer flask. Proceed to Section 7.2.1.8. If the analysis is for acid herbicides only, proceed to Section 7.4.5 for derivatization by diazomethane (if PFB derivatization is selected, reduce the volume of diethyl ether to 0.1 - 0.5 mL as per Section 7.4.2 and then dilute to 4 mL with acetone).

7.2 Preparation of Soil, Sediment, and Other Solid Samples

7.2.1 Extraction

7.2.1.1 To a 400 mL, thick-wall beaker add 30 g (dry weight) of the well-mixed solid sample. Adjust the pH to 2 with concentrated hydrochloric acid or acidify solids in each beaker with 85 mL of 0.1 M phosphate buffer (pH = 2.5) and thoroughly mix the contents with a glass stirring rod. Spike the sample with surrogate compound(s) according to Section 5.16.1.

7.2.1.2 The ultrasonic extraction of solids must be optimized for each type of sample. In order for the ultrasonic extractor to efficiently extract solid samples, the sample must be

free flowing when the solvent is added. Acidified anhydrous sodium sulfate should be added to clay type soils (normally 1:1), or any other solid that is not a free flowing sandy texture, until a free flowing mixture is obtained.

7.2.1.3 Add 100 mL of methylene chloride/acetone (1:1 v/v) to the beaker. Perform ultrasonic extraction 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). Allow the solids to settle. Transfer the organic layer into a 500 mL centrifuge bottle.

7.2.1.4 Ultrasonically extract the sample twice more using 100 mL of methylene chloride and the same ultrasonic conditions.

7.2.1.5 Combine the three organic extracts from the sample in the centrifuge bottle and centrifuge 10 minutes to settle the fine particles. Filter the combined extract through filter paper (Whatman #1, or equivalent) containing 7-10 g of acidified sodium sulfate into 500 mL 24/40 Erlenmeyer flask. Add 10 g of acidified anhydrous sodium sulfate. Periodically, vigorously shake the extract and drying agent and allow the drying agent to remain in contact with the extract for a minimum of 2 hours. See NOTE in Section 7.3.1.6 that emphasizes the need for a dry extract prior to esterification.

7.2.1.6 Quantitatively transfer the contents of the flask to a 500-mL Kuderna-Danish flask with a 10-mL concentrator tube attached. Add boiling chips and attach the macro Snyder column. Evaporate the extract on the water bath to a volume of approximately 5 mL. Remove the flasks from the water bath and allow them to cool.

7.2.1.7 If hydrolysis or additional cleanup is not required and the sample is dry, proceed to Section 7.4.4 - Nitrogen Blow Down.

7.2.1.8 <u>Use this step only if herbicide esters in addition to herbicide acids are to be determined:</u>

7.2.1.8.1 Add 5 mL of 37% aqueous potassium hydroxide and 30 mL of water to the extract. Add additional boiling chips to the flask. Reflux the mixture on a water bath at 60-65°C for 2 hours. Remove the flasks from the water bath and cool to room temperature. CAUTION - the presence of residual acetone will result in the formation of aldol condensation products which will cause GC interference.

7.2.1.8.2 Transfer the hydrolyzed aqueous solution to a 500 mL separatory funnel and extract the solution three times with 100 mL portions of methylene chloride. Discard the methylene chloride phase. At this point the basic (aqueous) solution contains the herbicide salts.

7.2.1.8.3 Adjust the pH of the solution to <2 with cold (4°C) sulfuric acid (1+3) and extract once with 40 mL of diethyl ether and twice with 20 mL portions of ether. Combine the extracts and pour them through a pre-rinsed drying column containing 7 to 10 cm of acidified anhydrous sodium sulfate. Collect the dried extracts in a 500 mL Erlenmeyer flask (with a 24/40 joint) containing 10 g of acidified anhydrous sodium sulfate. Periodically, vigorously shake the extract and drying agent and allow the drying agent to remain in contact with the extract for a minimum of 2 hours. See NOTE in Section 7.3.1.6 that emphasizes the need for a dry extract prior to esterification. Quantitatively transfer the contents of the flask to a 500-mL Kuderna-Danish flask with a 10-mL concentrator tube attached when the extract is known to be dry.

7.2.1.8.4 Proceed to Section 7.4, Extract concentration. If additional cleanup is required, proceed to Section 7.2.1.9.

7.2.1.9 Use this step if additional clean up of the non-hydrolyzed herbicides is required:

7.2.1.9.1 Partition the herbicides by extracting the methylene chloride with 3 x 15 mL portions of aqueous base prepared by carefully mixing 30 mL of reagent water into 15 mL of 37% aqueous potassium hydroxide. Discard the methylene chloride phase. At this point the basic (aqueous) solution contains the herbicide salts.

7.2.1.9.2 Adjust the pH of the solution to <2 with cold (4°C) sulfuric acid (1+3) and extract once with 40 mL of diethyl ether and twice with 20 mL portions of ether. Combine the extracts and pour them through a pre-rinsed drying column containing 7 to 10 cm of acidified anhydrous sodium sulfate. Collect the dried extracts in a 500 mL Erlenmeyer flask (with a 24/40 joint) containing 10 g of acidified anhydrous sodium sulfate. Periodically, vigorously shake the extract and drying agent and allow the drying agent to remain in contact with the extract for a minimum of 2 hours. See NOTE in Section 7.3.1.6 that emphasizes the need for a dry extract prior to esterification. Quantitatively transfer the contents of the flask to a 500-mL Kuderna-Danish flask with a 10-mL concentrator tube attached when the extract is known to be dry.

7.2.1.9.3 Proceed to section 7.4 for extract concentration.

7.3 Preparation of Aqueous Samples

7.3.1 Separatory Funnel

7.3.1.1 Using a graduated cylinder, measure out a 1 liter of sample and transfer it into a 2 L separatory funnel. Spike the sample with surrogate compound(s) according to Section 5.16.1.

7.3.1.2 Add 250 g of NaCl to the sample, seal, and shake to dissolve the salt.

7.3.1.3 Use this step only if herbicide esters in addition to herbicide acids are to be determined:

7.3.1.3.1 Add 17 mL of 6 N NaOH to the sample, seal, and shake. Check the pH of the sample with pH paper; if the sample does not have a pH greater than or equal to 12, adjust the pH by adding more 6 N NaOH. Let the sample sit at room temperature for 1 hour, shaking the separatory funnel and contents periodically.

7.3.1.3.2 Add 60 mL of methylene chloride to the sample bottle to rinse the bottle. Transfer the methylene chloride to the separatory funnel and extract the sample by vigorously shaking the funnel for 2 minutes, with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between the layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Discard the methylene chloride phase.

7.3.1.3.3 Add a second 60 mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, discarding the methylene chloride layer. Perform a third extraction in the same manner.

7.3.1.4 Add 17 mL of cold (4°C) 12 N sulfuric acid to the sample (or hydrolyzed sample), seal, and shake to mix. Check the pH of the sample with pH paper: if the sample does not have a pH less than or equal to 2, adjust the pH by adding more acid.

7.3.1.5 Add 120 mL diethyl ether to the sample, seal, and extract the sample by vigorously shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum techniques to complete the phase separation depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Remove the aqueous phase to a 2 L

Erlenmeyer flask and collect the ether phase in a 500 mL Erlenmeyer flask containing approximately 10 g of acidified anhydrous sodium sulfate. Periodically, vigorously shake the extract and drying agent.

7.3.1.6 Return the aqueous phase to the separatory funnel, add 60 mL of diethyl ether to the sample, and repeat the extraction procedure a second time, combining the extracts in the 500 mL Erlenmeyer flask. Perform a third extraction with 60 mL diethyl ether in the same manner. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hours.

NOTE: The drying step is very critical to ensuring complete esterification. Any moisture remaining in the ether will result in low herbicide recoveries. The amount of sodium sulfate is adequate if some free flowing crystals are visible when swirling the flask. If all of the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate and again test by swirling. The 2 hour drying time is a minimum, however, the extracts may be held in contact with the sodium sulfate overnight.

7.3.1.7 Pour the dried extract through a funnel plugged with acid washed glass wool, and collect the extract in the K-D concentrator. Use a glass rod to crush any caked sodium sulfate during the transfer. Rinse the round bottom flask and funnel with 20 to 30 mL of diethyl ether to complete the quantitative transfer. Proceed to section 7.4 for extract concentration.

7.4 Extract Concentration

7.4.1 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 diethyl ether 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 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.4.2 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of diethyl ether. The extract may be further concentrated by using either the micro Snyder column technique (Section 7.4.3) or nitrogen blowdown technique (Section 7.4.4).

7.4.3 Micro Snyder Column Technique

7.4.3.1 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 diethyl ether 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 diethyl ether and add to the concentrator tube. Proceed to Section 7.4.5.

7.4.4 Nitrogen Blowdown Technique

7.4.4.1 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.

7.4.4.2 The internal wall of the tube must be rinsed down several times with diethyl ether 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. Proceed to Section 7.4.5.

7.4.5 Dilute the extract with 1 mL of isooctane and 0.5 mL of methanol. Dilute to a final volume of 4 mL with diethyl ether. The sample is now ready for methylation with diazomethane. If PFB derivation is being performed, dilute to 4 mL with acetone.

7.5 Esterification - For diazomethane derivatization proceed with Section 7.5.1. For PFB derivatization proceed with Section 7.5.2.

7.5.1 Diazomethane Derivatization - Two methods may be used for the generation of diazomethane: the bubbler method (see Figure 1), Section 7.5.1.1, and the Diazald kit method, Section 7.5.1.2.

CAUTION: Diazomethane is a carcinogen and can explode under certain conditions.

The bubbler method is suggested when small batches of samples (10-15) require esterification. The bubbler method works well with samples that have low concentrations of herbicides (e.g., aqueous samples) and is safer to use than the Diazald kit procedure. The Diazald kit

method is good for large quantities of samples needing esterification. The Diazald kit method is more effective than the bubbler method for soils or samples that may contain high concentrations of herbicides (e.g., samples such as soils that may result in yellow extracts following hydrolysis may be difficult to handle by the bubbler method). The diazomethane derivatization (U.S.EPA, 1971) procedures, described below, will react efficiently with all of the chlorinated herbicides described in this method and should be used only by experienced analysts, due to the potential hazards associated with its use. The following precautions should be taken:

- Use a safety screen.
- Use mechanical pipetting aides.
- Do not heat above 90°C - EXPLOSION may result.
- Avoid grinding surfaces, ground-glass joints, sleeve bearings, and glass stirrers - EXPLOSION may result.
- Store away from alkali metals - EXPLOSION may result.
- Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips.

7.5.1.1 Bubbler method - Assemble the diazomethane bubbler (see Figure 1).

7.5.1.1.1 Add 5 mL of diethyl ether to the first test tube. Add 1 mL of diethyl ether, 1 mL of carbitol, 1.5 mL of 37% KOH, and 0.1-0.2 g of Diazald to the second test tube. Immediately place the exit tube into the concentrator tube containing the sample extract. Apply nitrogen flow (10 mL/min) to bubble diazomethane through the extract for 10 minutes or until the yellow color of diazomethane persists. The amount of Diazald used is sufficient for esterification of approximately three sample extracts. An additional 0.1-0.2 g of Diazald may be added (after the initial Diazald is consumed) to extend the generation of the diazomethane. There is sufficient KOH present in the original solution to perform a maximum of approximately 20 minutes of total esterification.

7.5.1.1.2 Remove the concentrator tube and seal it with a Neoprene or Teflon stopper. Store at room temperature in a hood for 20 minutes.

7.5.1.1.3 Destroy any unreacted diazomethane by adding 0.1-0.2 g of silicic acid to the concentrator tube. Allow to stand until the evolution of nitrogen gas has stopped. Adjust the sample volume to 10.0 mL with hexane. Stopper the concentrator tube or transfer 1 mL of sample to a GC vial, and store refrigerated if further processing will not be performed immediately. It is recommended that the methylated extracts be analyzed immediately to minimize the trans-esterification and other potential reactions that may occur. Analyze by gas chromatography.

7.5.1.1.4 Extracts should be stored at 4°C away from light. Preservation study results indicate that most analytes are stable for 28 days; however, it is recommended that the methylated extracts be analyzed immediately to minimize the trans-esterification and other potential reactions that may occur. Analyze by gas chromatography.

7.5.1.2 Diazald kit method - Instructions for preparing diazomethane are provided with the generator kit.

7.5.1.2.1 Add 2 mL of diazomethane solution and let the sample stand for 10 minutes with occasional swirling. The yellow color of diazomethane should be evident and should persist for this period.

7.5.1.2.2 Rinse the inside wall of the ampule with 700 µL of diethyl ether. Reduce the sample volume to approximately 2 mL to remove excess diazomethane by allowing the solvent to evaporate spontaneously at room temperature. Alternatively, 10 mg of silicic acid can be added to destroy the excess diazomethane.

7.5.1.2.3 Dilute the sample to 10.0 mL with hexane. Analyze by gas chromatography.

7.5.2 PFB Method

7.5.2.1 Add 30 µL of 10% K_2CO_3 and 200 µL of 3% PFBBr in acetone. Close the tube with a glass stopper and mix on a vortex mixer. Heat the tube at 60°C for 3 hours.

7.5.2.2 Evaporate the solution to 0.5 mL with a gentle stream of nitrogen. Add 2 mL of hexane and repeat evaporation just to dryness at ambient temperature.

7.5.2.3 Redissolve the residue in 2 mL of toluene:hexane (1:6) for column cleanup.

7.5.2.4 Top the silica column with 0.5 cm of anhydrous sodium sulfate. Prewet the column with 5 mL hexane and let the solvent drain to the top of the adsorbent. Quantitatively transfer the reaction residue to the column with several rinsings of the toluene:hexane solution (total 2 - 3 mL).

7.5.2.5 Elute the column with sufficient toluene:hexane to collect 8 mL of eluent. Discard this fraction which contains excess reagent.

7.5.2.6 Elute the column with toluene:hexane (9:1) to collect 8 mL of eluent containing PFB derivatives in a 10 mL volumetric flask. Dilute to 10 mL with hexane. Analyze by GC/ECD.

7.6 Gas chromatographic conditions (recommended):

7.6.1 Narrow Bore

7.6.1.1 Primary Column 1:

Temperature program:	60°C to 300°C, at 4°C/min
Helium carrier flow:	30 cm/sec
Injection volume:	2 µL, splitless, 45 sec delay
Injector temperature:	250°C
Detector temperature:	320°C

7.6.1.2 Primary Column 1a:

Temperature program:	60°C to 300°C, at 4°C/min
Helium carrier flow:	30 cm/sec
Injection volume:	2 µL, splitless, 45 sec delay
Injector temperature:	250°C
Detector temperature:	320°C

7.6.1.3 Column 2:

Temperature program:	60°C to 300°C, at 4°C/min
Helium carrier flow:	30 cm/sec
Injection volume:	2 µL, splitless, 45 sec delay
Injector temperature:	250°C
Detector temperature:	320°C

7.6.1.4 Confirmation Column:

Temperature program:	60°C to 300°C, at 4°C/min
Helium carrier flow:	30 cm/sec
Injection volume:	2 µL, splitless, 45 sec delay
Injector temperature:	250°C
Detector temperature:	320°C

7.6.2 Megabore

7.6.2.1 Primary Column:

Temperature program:	0.5 minute at 150°C, 150°C to 270°C at 5°C/min
Helium carrier flow:	7 mL/min
Injection volume:	1 µL

7.6.2.2 Confirmatory Column:

Temperature program:	0.5 minute at 150°C, 150°C to 270°C at 5°C/min
Helium carrier flow:	7 mL/min
Injection volume:	1 µL

7.7 Calibration

7.7.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures. Use Table 1 for guidance on selecting the lowest point on the calibration curve.

7.8 Gas chromatographic analysis

7.8.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 µL of internal standard to the sample prior to injection.

7.8.2 Follow Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

7.8.3 An example of a chromatogram for a methylated chlorophenoxy herbicide is shown in Figure 2. Tables 2 and 3 present retention times for the target analytes after esterification, using the diazomethane derivatization procedure and the PFB derivatization procedure, respectively.

7.8.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.8.5 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes.

7.8.6 If calibration standards have been analyzed in the same manner as the samples (e.g. have undergone hydrolysis and esterification), then the calculation of concentration given in Method 8000 should be used. However, if calibration is performed using standards made from methyl ester compounds (compounds not esterified by application of this method), then the calculation of concentration must include a correction for the molecular weight of the methyl ester versus the acid herbicide.

7.8.7 If peak detection and identification are prevented due to interferences, further cleanup is required. Before using any cleanup procedure, the analyst must process a series of standards through the procedure to validate elution patterns and the absence of interferences from reagents.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000.

8.2.1 Select a representative spike concentration for each compound (acid or ester) to be measured. Using stock standards, prepare a quality control check sample concentrate, in acetone, that is 1000 times more concentrated than the selected concentrations. Use this quality control check sample concentrate to prepare quality control check samples.

8.2.2 Tables 4 and 5 present bias and precision data for water and clay matrices, using the diazomethane derivatization procedure. Table 6 presents relative recovery data generated using the PFB derivatization procedure and water samples. Compare the results obtained with the results given in these Tables to determine if the data quality is acceptable.

8.3 Calculate surrogate standard recovery on all standards, samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000).

8.3.1 If recovery is not within limits, the following procedures are required:

8.3.1.1 Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.

8.3.1.2 Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

8.3.1.3 Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.4 GC/MS confirmation

8.4.1 GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. Refer to Method 8270 for the appropriate GC/MS operating conditions and analysis procedures.

8.4.2 When available, chemical ionization mass spectra may be employed to aid the qualitative identification process.

8.4.3 Should these MS procedures fail to provide satisfactory results, additional steps may be taken before reanalysis. These steps may include the use of alternate packed or capillary GC columns or additional cleanup.

9.0 METHOD PERFORMANCE

9.1 In single laboratory studies using organic-free reagent water and clay/still bottom samples, the mean recoveries presented in Tables 4 and 5 were obtained for diazomethane derivatization. The standard deviations of the percent recoveries of these measurements are also in Tables 4 and 5.

9.2 Table 6 presents relative recoveries of the target analytes obtained using the PFB derivatization procedure with spiked water samples.

10.0 REFERENCES

1. Fed. Reg. 1971, 38, No. 75, Pt. II.

2. Goerlitz, D. G.; Lamar, W.L., "Determination of Phenoxy Acid Herbicides in Water by Electron Capture and Microcoulometric Gas Chromatography,". U.S. Geol. Survey Water Supply Paper 1967, 1817-C.

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4. "Extraction and Cleanup Procedures for the Determination of Phenoxy Acid Herbicides in Sediment"; U.S. Environmental Protection Agency. EPA Toxicant and Analysis Center: Bay St. Louis, MS, 1972.

5. Shore, F.L.; Amick, E.N.; Pan, S. T. "Single Laboratory Validation of EPA Method 8151 for the Analysis of Chlorinated Herbicides in Hazardous Waste"; U.S. Environmental Protection Agency. Environmental Monitoring Systems Laboratory. Office of Research and Development, Las Vegas, NV, 1985; EPA-60014-85-060.

6. Method 515.1, "Determination of Chlorinated Acids in Water by Gas Chromatography with an Electron Capture Detector", Revision 4.0, USEPA, Office of Research and Development, Environmental Monitoring Systems Laboratory, Cincinnati, Ohio.

7. Method 1618, "Organo-halide and Organo-phosphorus Pesticides and Phenoxy-acid Herbicides by Wide Bore Capillary Column Gas Chromatography with Selective Detectors", Revision A, July 1989, USEPA, Office of Water Regulations and Standards, Washington, DC.

Figure 1
DIAZOMETHANE GENERATOR

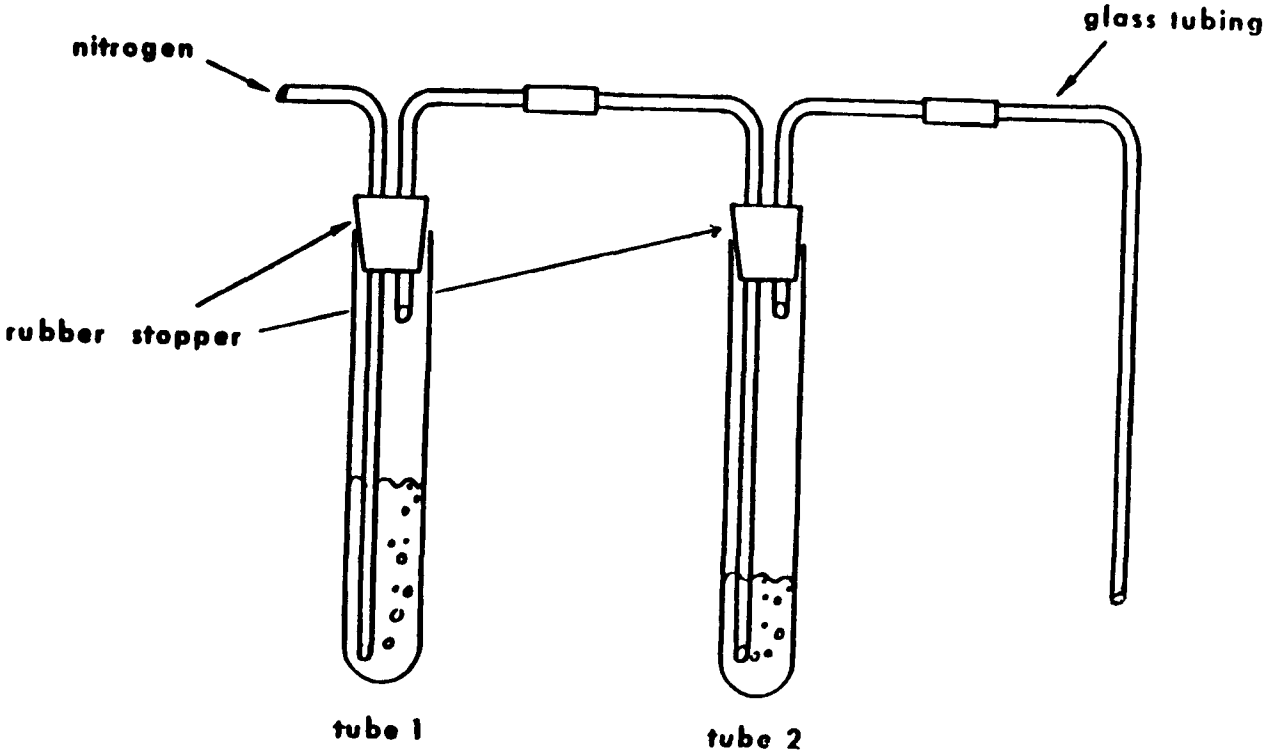


TABLE 1
ESTIMATED METHOD DETECTION LIMITS FOR METHOD 8151,
DIAZOMETHANE DERIVATIZATION

Analyte	Aqueous Samples GC/ECD Estimated Detection Limit[a] (µg/L)	Soil Samples GC/ECD Estimated Detection Limit[b] (µg/kg)	Soil Samples GC/MS Estimated Identification Limit[c] (ng)
Acifluorfen	0.096		
Bentazon	0.2		
Chloramben	0.093	4.0	1.7
2,4-D	0.2	0.11	1.25
Dalapon	1.3	0.12	0.5
2,4-DB	0.8		
DCPA diacid[e]	0.02		
Dicamba	0.081		
3,5-Dichlorobenzoic acid	0.061	0.38	0.65
Dichlorprop	0.26		
Dinoseb	0.19		
5-Hydroxydicamba	0.04		
MCPP	0.09[d]	66	0.43
MCPA	0.056[d]	43	0.3
4-Nitrophenol	0.13	0.34	0.44
Pentachlorophenol	0.076	0.16	1.3
Picloram	0.14		
2,4,5-T	0.08		
2,4,5-TP	0.075	0.28	4.5

a EDL = estimated detection limit; defined as either the MDL (40 CFR Part 136, Appendix B, Revision 1.11), or a concentration of analyte in a sample yielding a peak in the final extract with signal-to-noise ratio of approximately 5, whichever value is higher.

b Detection limits determined from standard solutions corrected back to 50 g samples, extracted and concentrated to 10 mL, with 5 µL injected. Chromatography using narrow bore capillary column, 0.25 µm film, 5% phenyl/95% methyl silicone.

c The minimum amount of analyte to give a Finnigan INCOS FIT value of 800 as the methyl derivative vs. the spectrum obtained from 50 ng of the respective free acid herbicide.

d 40 CFR Part 136, Appendix B (49 FR 43234). Chromatography using megabore capillary column.

e DCPA monoacid and diacid metabolites included in method scope; DCPA diacid metabolite used for validation studies. DCPA is a dimethyl ester.

TABLE 2
RETENTION TIMES (MINUTES) OF METHYL DERIVATIVES OF CHLORINATED HERBICIDES

	Narrow Bore Columns		Megabore Columns	
Analyte	Primary[a] Column	Confirmation[a] Column	Primary[b] Column	Confirmation[b] Column
Dalapon	3.4	4.7		
3,5-Dichlorobenzoic acid	18.6	17.7		
4-Nitrophenol	18.6	20.5		
DCAA (surrogate)	22.0	14.9		
Dicamba	22.1	22.6	4.39	4.39
Dichlorprop	25.0	25.6	5.15	5.46
2,4-D	25.5	27.0	5.85	6.05
DBOB (internal std.)	27.5	27.6		
Pentachlorophenol	28.3	27.0		
Chloramben	29.7	32.8		
2,4,5-TP	29.7	29.5	6.97	7.37
5-Hydroxydicamba	30.0	30.7		
2,4,5-T	30.5	30.9	7.92	8.20
2,4-DB	32.2	32.2	8.74	9.02
Dinoseb	32.4	34.1		
Bentazon	33.3	34.6		
Picloram	34.4	37.5		
DCPA diacid[c]	35.8	37.8		
Acifluorfen	41.5	42.8		
MCPP			4.24	4.55
MCPA			4.74	4.94

TABLE 2 (continued)

a	Primary Column:	5% phenyl/95% methyl silicone
	Confirmation Column:	14% cyanopropyl phenyl silicone
	Temperature program:	60°C to 300°C, at 4°C/min
	Helium carrier flow:	30 cm/sec
	Injection volume:	2 µL, splitless, 45 sec delay
	Injector temperature:	250°C
	Detector temperature:	320°C
b	Primary Column:	DB-608
	Confirmatory Column:	14% cyanopropyl phenyl silicone
	Temperature program:	0.5 minute at 150°C, 150°C to 270°C, at 5°C/min
	Helium carrier flow:	7 mL/min
	Injection volume:	1 µL

c DCPA monoacid and diacid metabolites included in method scope; DCPA diacid metabolite used for validation studies. DCPA is a dimethyl ester.

TABLE 3
RETENTION TIMES (MINUTES) OF PFB DERIVATIVES OF CHLORINATED HERBICIDES

Herbicide	Gas chromatographic column		
	Thin-film DB-5[a]	SP-2250[b]	Thick-film DB-5[c]
Dalapon	10.41	12.94	13.54
MCPP	18.22	22.30	22.98
Dicamba	18.73	23.57	23.94
MCPA	18.88	23.95	24.18
Dichlorprop	19.10	24.10	24.70
2,4-D	19.84	26.33	26.20
Silvex	21.00	27.90	29.02
2,4,5-T	22.03	31.45	31.36
Dinoseb	22.11	28.93	31.57
2,4-DB	23.85	35.61	35.97

a DB-5 capillary column, 0.25 μm film thickness, 0.25 mm ID x 30 m long. Column temperature, programmed: 70°C for 1 minute, program 10°C/min. to 240°C, hold for 17 minutes.

b SP-2550 capillary column, 0.25 μm film thickness, 0.25 mm ID x 30 m long. Column temperature, programmed: 70°C for 1 minute, program 10°C/min. to 240°C, hold for 10 minutes.

c DB-5 capillary column, 1.0 μm film thickness, 0.32 mm ID x 30 m long. Column temperature, programmed: 70°C for 1 minute, program 10°C/min. to 240°C, hold for 10 minutes.

TABLE 4
ACCURACY AND PRECISION FOR METHOD 8151
DIAZOMETHANE DERIVATIZATION, ORGANIC-FREE REAGENT WATER MATRIX

Analyte	Spike Concentration (µg/L)	Mean[a] Percent Recovery	Standard Deviation of Percent Recovery
Acifluorfen	0.2	121	15.7
Bentazon	1	120	16.8
Chloramben	0.4	111	14.4
2,4-D	1	131	27.5
Dalapon	10	100	20.0
2,4-DB	4	87	13.1
DCPA diacid[b]	0.2	74	9.7
Dicamba	0.4	135	32.4
3,5-Dichlorobenzoic Acid	0.6	102	16.3
Dichlorprop	2	107	20.3
Dinoseb	0.4	42	14.3
5-Hydroxydicamba	0.2	103	16.5
4-Nitrophenol	1	131	23.6
Pentachlorophenol	0.04	130	31.2
Picloram	0.6	91	15.5
2,4,5-TP	0.4	117	16.4
2,4,5-T	0.2	134	30.8

a Mean percent recovery calculated from 7-8 determinations of spiked organic-free reagent water.

b DCPA monoacid and diacid metabolites included in method scope; DCPA diacid metabolite used for validation studies. DCPA is a dimethyl ester.

TABLE 5
ACCURACY AND PRECISION FOR METHOD 8151
DIAZOMETHANE DERIVATIZATION, CLAY MATRIX

Analyte	Mean[a] Percent Recovery	Linear[b] Concentration Range (ng/g)	Percent Relative[c] Standard Deviation (n=20)
Dicamba	95.7	0.52 - 104	7.5
MCPP	98.3	620 - 61,800	3.4
MCPA	96.9	620 - 61,200	5.3
Dichlorprop	97.3	1.5 - 3,000	5.0
2,4-D	84.3	1.2 - 2,440	5.3
2,4,5-TP	94.5	0.42 - 828	5.7
2,4,5-T	83.1	0.42 - 828	7.3
2,4-DB	90.7	4.0 - 8,060	7.6
Dinoseb	93.7	0.82 - 1,620	8.7

a Mean percent recovery calculated from 10 determinations of spiked clay and clay/still bottom samples over the linear concentration range.

b Linear concentration range was determined on standard solutions and corrected to 50 g solid samples.

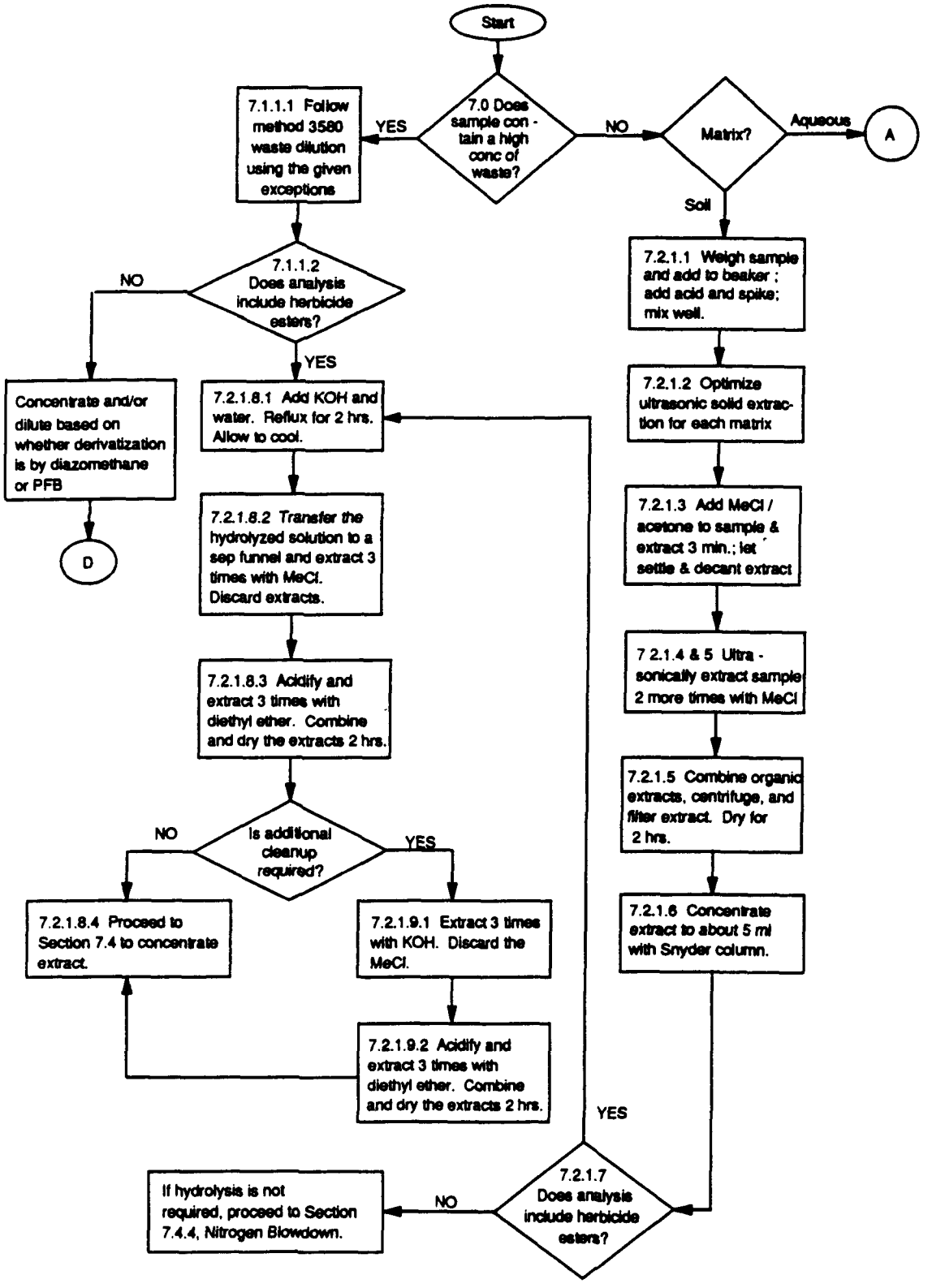
c Percent relative standard deviation was calculated on standard solutions, 10 samples high in the linear concentration range, and 10 samples low in the range.

TABLE 6
RELATIVE RECOVERIES OF PFB DERIVATIVES OF HERBICIDES[a]

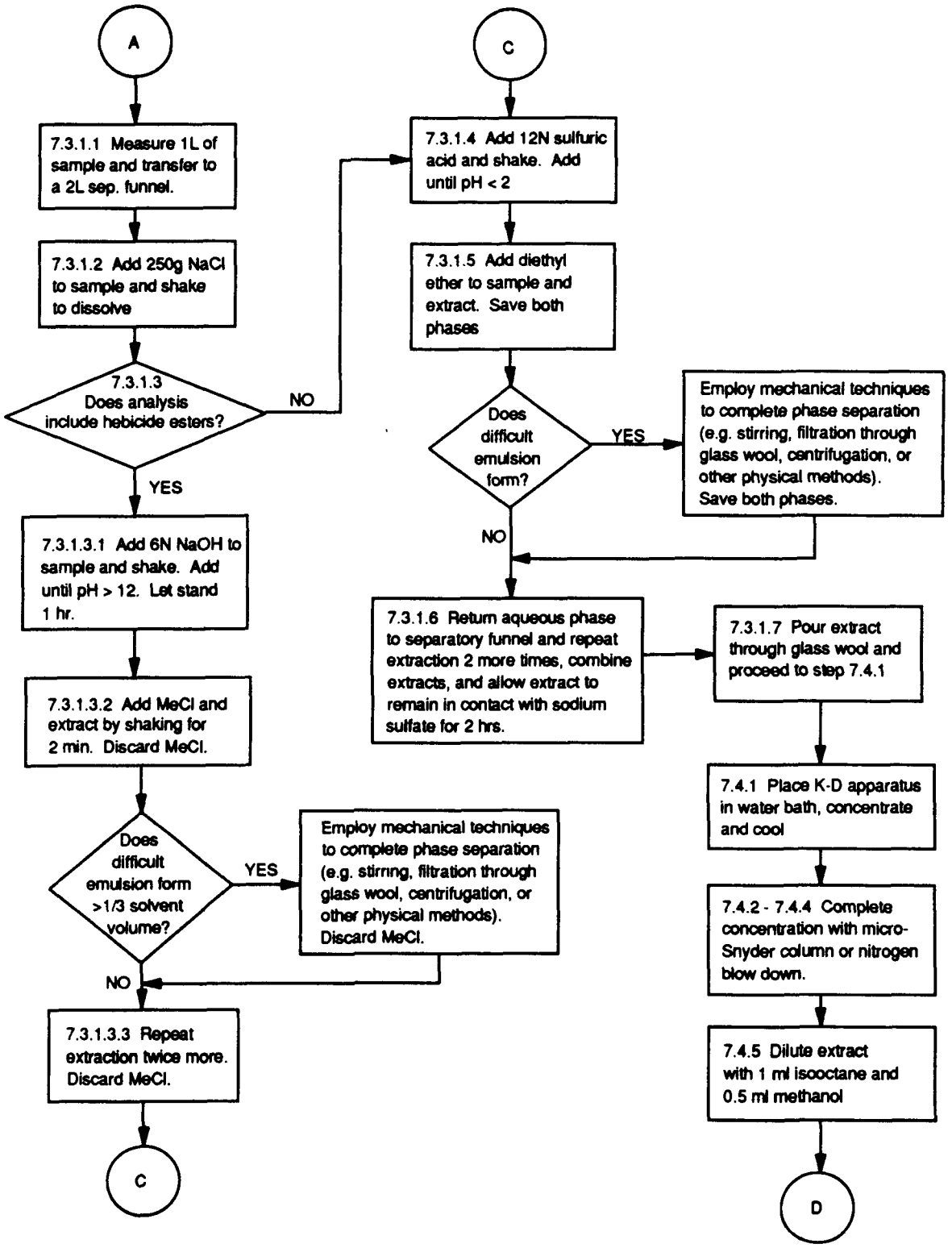
Analyte	Std.concn, mg/L	Relative recoveries, %								
		1	2	3	4	5	6	7	8	Mean
MCPP	5.1	95.6	88.8	97.1	100	95.5	97.2	98.1	98.2	96.3
Dicamba	3.9	91.4	99.2	100	92.7	84.0	93.0	91.1	90.1	92.7
MCPA	10.1	89.6	79.7	87.0	100	89.5	84.9	92.3	98.6	90.2
Dichlorprop	6.0	88.4	80.3	89.5	100	85.2	87.9	84.5	90.5	88.3
2,4-D	9.8	55.6	90.3	100	65.9	58.3	61.6	60.8	67.6	70.0
Silvex	10.4	95.3	85.8	91.5	100	91.3	95.0	91.1	96.0	93.3
2,4,5-T	12.8	78.6	65.6	69.2	100	81.6	90.1	84.3	98.5	83.5
2,4-DB	20.1	99.8	96.3	100	88.4	97.1	92.4	91.6	91.6	95.0
Mean		86.8	85.7	91.8	93.4	85.3	89.0	87.1	91.4	

a Percent recovery determinations made using spiked water samples.

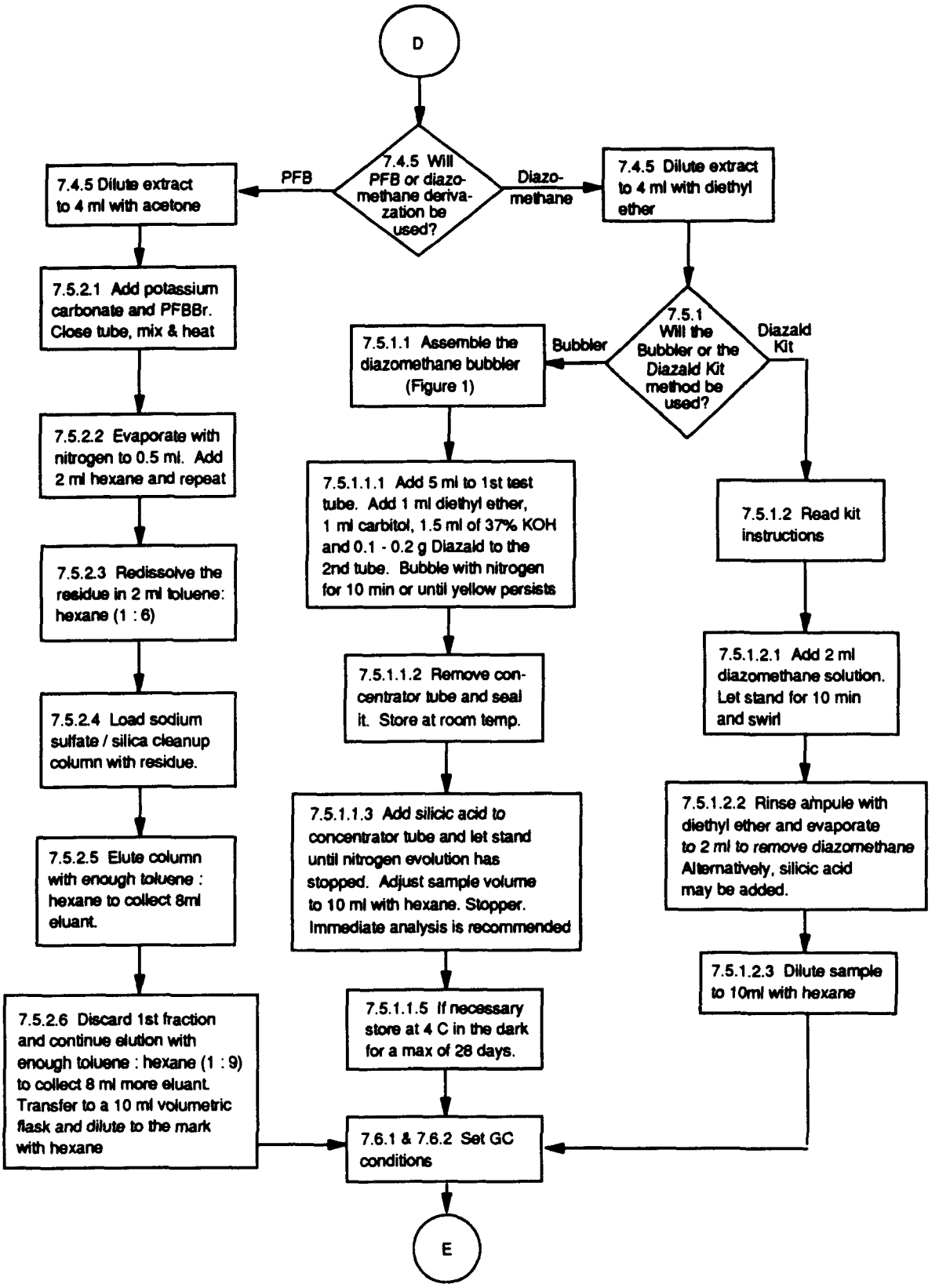
Extraction/Hydrolysis of Waste and Soil Samples



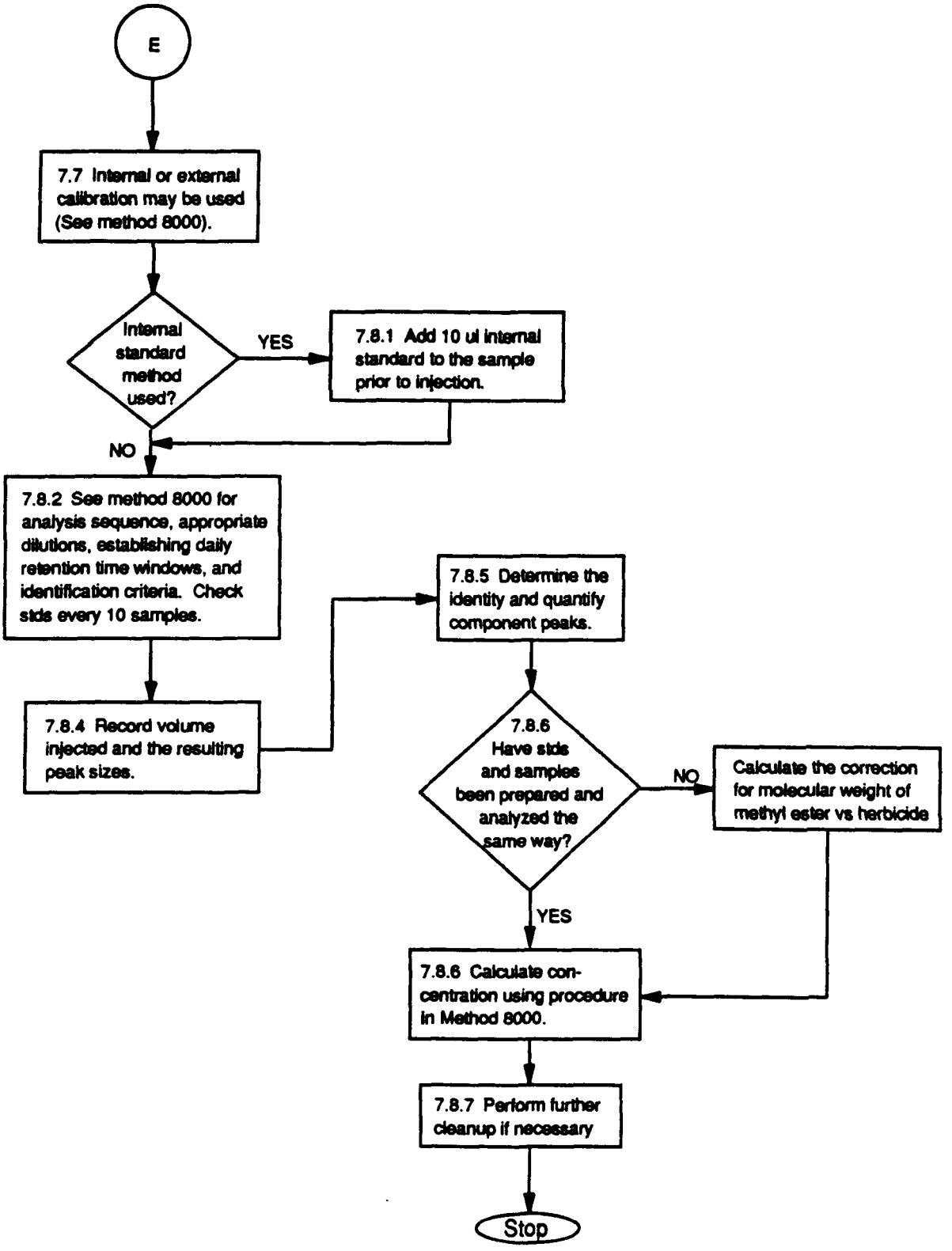
Extraction/Hydrolysis of Aqueous Samples and Extract Concentration



Extract Derivatization



Analysis by Gas Chromatography



METHOD 8240B

VOLATILE ORGANICS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

1.0 SCOPE AND APPLICATION

1.1 Method 8240 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including ground water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. The following compounds can be determined by this method:

Analyte	CAS No.[b]	Appropriate Technique: Purge-and-Trap	Appropriate Technique: Direct Injection
Acetone	67-64-1	pp	a
Acetonitrile	75-05-8	pp	a
Acrolein	107-02-8	pp	a
Acrylonitrile	107-13-1	pp	a
Allyl alcohol	107-18-6	pp	a
Allyl chloride	107-05-1	a	a
Benzene	71-43-2	a	a
Benzyl chloride	100-44-7	pp	a
Bromoacetone	598-31-2	pp	a
Bromochloromethane (I.S.)	74-97-5	a	a
Bromodichloromethane	75-27-4	a	a
4-Bromofluorobenzene (surr.)	460-00-4	a	a
Bromoform	75-25-2	a	a
Bromomethane	74-83-9	a	a
2-Butanone	78-93-3	pp	a
Carbon disulfide	75-15-0	pp	a
Carbon tetrachloride	56-23-5	a	a
Chloral hydrate	302-17-0	pp	a
Chlorobenzene	108-90-7	a	a
Chlorobenzene-d_5 (I.S.)	3114-55-4	a	a
Chlorodibromomethane	124-48-1	a	a
Chloroethane	75-00-3	a	a
2-Chloroethanol	107-07-3	pp	a
bis-(2-Chloroethyl) sulfide	505-60-2	pp	a
2-Chloroethyl vinyl ether	110-75-8	a	a
Chloroform	67-66-3	a	a
Chloromethane	74-87-3	a	a
Chloroprene	126-99-8	a	pc
3-Chloropropionitrile	542-76-7	ND	pc
1,2-Dibromo-3-chloropropane	96-12-8	pp	a
1,2-Dibromoethane	106-93-4	a	a
Dibromomethane	74-95-3	a	a

Analyte	CAS No.[b]	Appropriate Technique: Purge-and-Trap	Appropriate Technique: Direct Injection
1,4-Dichloro-2-butene	764-41-0	pp	a
Dichlorodifluoromethane	75-71-8	a	a
1,1-Dichloroethane	75-34-3	a	a
1,2-Dichloroethane	107-06-2	a	a
1,2-Dichloroethane-d_4(surr.)	107-06-2	a	a
1,1-Dichloroethene	75-35-4	a	a
trans-1,2-Dichloroethene	156-60-5	a	a
1,2-Dichloropropane	78-87-5	a	a
1,3-Dichloro-2-propanol	96-23-1	pp	a
cis-1,3-Dichloropropene	10061-01-5	a	a
trans-1,3-Dichloropropene	10061-02-6	a	a
1,2,3,4-Diepoxybutane	1464-53-5	a	a
1,4-Difluorobenzene (I.S.)	540-36-3	a	a
1,4-Dioxane	123-91-1	pp	a
Epichlorohydrin	106-89-8	i	a
Ethanol	64-17-5	i	a
Ethylbenzene	100-41-4	a	a
Ethylene oxide	75-21-8	pp	a
Ethyl methacrylate	97-63-2	a	a
2-Hexanone	591-78-6	pp	a
2-Hydroxypropionitrile	78-97-7	ND	pc
Iodomethane	74-88-4	a	a
Isobutyl alcohol	78-83-1	pp	a
Malononitrile	109-77-3	pp	a
Methacrylonitrile	126-98-7	pp	a
Methylene chloride	75-09-2	a	a
Methyl iodide	74-88-4	a	a
Methyl methacrylate	80-62-6	a	a
4-Methyl-2-pentanone	108-10-1	pp	a
Pentachloroethane	76-01-7	i	pc
2-Picoline	109-06-8	pp	a
Propargyl alcohol	107-19-7	pp	a
ß-Propiolactone	57-57-8	pp	a
Propionitrile	107-12-0	pp	a
n-Propylamine	107-10-8	a	a
Pyridine	110-86-1	i	a
Styrene	100-42-5	a	a
1,1,1,2-Tetrachloroethane	630-20-6	a	a
1,1,2,2-Tetrachloroethane	79-34-5	a	a
Tetrachloroethene	127-18-4	a	a
Toluene	108-88-3	a	a
Toluene-d_8 (surr.)	2037-26-5	a	a
1,1,1-Trichloroethane	71-55-6	a	a
1,1,2-Trichloroethane	79-00-5	a	a
Trichloroethene	79-01-6	a	a
Trichlorofluoromethane	75-69-4	a	a
1,2,3-Trichloropropane	96-18-4	a	a

Analyte	CAS No.[b]	Appropriate Technique: Purge-and-Trap	Appropriate Technique: Direct Injection
Vinyl acetate	108-05-4	a	a
Vinyl chloride	75-01-4	a	a
Xylene (Total)	1330-20-7	a	a

a Adequate response by this technique.
b Chemical Abstract Services Registry Number.
pp Poor purging efficiency resulting in high EQLs.
i Inappropriate technique for this analyte.
pc Poor chromatographic behavior.

1.2 Method 8240 can be used to quantitate most volatile organic compounds that have boiling points below 200°C and that are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique. However, for the more soluble compounds, quantitation limits are approximately ten times higher because of poor purging efficiency. The method is also limited to compounds that elute as sharp peaks from a GC column packed with graphitized carbon lightly coated with a carbowax. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. See Table 1 for a list of compounds, retention times, and their characteristic ions that have been evaluated on a purge-and-trap GC/MS system.

1.3 The estimated quantitation limit (EQL) of Method 8240 for an individual compound is approximately 5 µg/kg (wet weight) for soil/sediment samples, 0.5 mg/kg (wet weight) for wastes, and 5 µg/L for ground water (see Table 2). EQLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

1.4 Method 8240 is based upon a purge-and-trap, gas chromatographic/mass spectrometric (GC/MS) procedure. This method is restricted to use by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

1.5 To increase purging efficiencies of acrylonitrile and acrolein, refer to Methods 5030 and 8030 for proper purge-and-trap conditions.

2.0 SUMMARY OF METHOD

2.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by direct injection (in limited applications). The components are separated via the gas chromatograph and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information. The chromatographic conditions, as well as typical mass spectrometer operating parameters, are given.

2.2 If the above sample introduction techniques are not applicable, a portion of the sample is dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanolic solution is combined with organic-free reagent water in a specially designed purging chamber. It is then analyzed by purge-and-trap GC/MS following the normal water method.

2.3 The purge-and-trap process - An inert gas is bubbled through the solution at ambient temperature, and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are trapped. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is heated to elute the components, which are detected with a mass spectrometer.

3.0 INTERFERENCES

3.1 Interferences purged or coextracted from the samples will vary considerably from source to source, depending upon the particular sample or extract being tested. The analytical system, however, should be checked to ensure freedom from interferences, under the analysis conditions, by analyzing method blanks.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal into the sample during shipment and storage. A trip blank, prepared from organic-free reagent water and carried through the sampling and handling protocol, can serve as a check on such contamination.

3.3 Cross contamination can occur whenever high-concentration and low-concentration samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by the analysis of organic-free reagent water to check for cross contamination. The purge-and-trap system may require extensive bake-out and cleaning after a high-concentration sample.

3.4 The laboratory where volatile analysis is performed should be completely free of solvents.

3.5 Impurities in the purge gas and from organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running calibration and reagent blanks. The use of non-TFE plastic coating, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

4.0 APPARATUS AND MATERIALS

4.1 Microsyringes - 10 μL, 25 μL, 100 μL, 250 μL, 500 μL, and 1,000 μL. These syringes should be equipped with a 20 gauge (0.006 in. ID) needle having a length sufficient to extend from the sample inlet to within 1 cm of the glass

frit in the purging device. The needle length will depend upon the dimensions of the purging device employed.

4.2 Syringe valve - Two-way, with Luer ends (three each), if applicable to the purging device.

4.3 Syringe - 5 mL, gas-tight with shutoff valve.

4.4 Balances - Analytical, 0.0001 g, and top-loading, 0.1 g.

4.5 Glass scintillation vials - 20 mL, with screw caps and Teflon liners or glass culture tubes with a screw cap and Teflon liner.

4.6 Volumetric flasks, Class A - 10 mL and 100 mL, with ground-glass stoppers.

4.7 Vials - 2 mL, for GC autosampler.

4.8 Spatula - Stainless steel.

4.9 Disposable pipets - Pasteur.

4.10 Heater or heated oil bath - Should be capable of maintaining the purging chamber to within 1°C over the temperature range of ambient to 100°C.

4.11 Purge-and-trap device - The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber. Several complete devices are commercially available.

4.11.1 The recommended purging chamber is designed to accept 5 mL samples with a water column at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The sample purger, illustrated in Figure 1, meets these design criteria. Alternate sample purge devices may be utilized, provided equivalent performance is demonstrated.

4.11.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 in. Starting from the inlet, the trap must contain the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. It is recommended that 1.0 cm of methyl silicone coated packing be inserted at the inlet to extend the life of the trap (see Figure 2). If it is not necessary to analyze for dichlorodifluoromethane or other fluorocarbons of similar volatility, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the room, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 minutes at 180°C with backflushing. The trap may be

vented to the analytical column during daily conditioning. However, the column must be run through the temperature program prior to analysis of samples.

4.11.3 The desorber should be capable of rapidly heating the trap to 180°C for desorption. The polymer section of the trap should not be heated higher than 180°C, and the remaining sections should not exceed 220°C during bake out mode. The desorber design illustrated in Figure 2 meets these criteria.

4.11.4 The purge-and-trap device may be assembled as a separate unit or may be coupled to a gas chromatograph, as shown in Figures 3 and 4.

4.11.5 Trap Packing Materials

4.11.5.1 2,6-Diphenylene oxide polymer - 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

4.11.5.2 Methyl silicone packing - OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

4.11.5.3 Silica gel - 35/60 mesh, Davison, grade 15 or equivalent.

4.11.5.4 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26, lot #M-2649, by crushing through 26 mesh screen (or equivalent).

4.12 Gas chromatograph/mass spectrometer system

4.12.1 Gas chromatograph - An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

4.12.2 Column - 6 ft x 0.1 in. ID glass, packed with 1% SP-1000 on Carbopack-B (60/80 mesh) or equivalent.

4.12.3 Mass spectrometer - Capable of scanning from 35-260 amu every 3 seconds or less, using 70 volts (nominal) electron energy in the electron impact mode and producing a mass spectrum that meets all the criteria in Table 3 when 50 ng of 4-bromofluorobenzene (BFB) are injected through the gas chromatograph inlet.

4.12.4 GC/MS interface - Any GC-to-MS interface that gives acceptable calibration points at 50 ng or less per injection for each of the analytes and achieves all acceptable performance criteria (see Table 3) may be used. GC-to-MS interfaces constructed entirely of glass or of glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

4.12.5 Data system - A computer system that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program

must be interfaced to the mass spectrometer. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting 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.

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 solutions - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol, using assayed liquids or gases, as appropriate.

5.3.1 Place about 9.8 mL of methanol in a 10 mL tared ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.3.2 Add the assayed reference material, as described below.

5.3.2.1 Liquids - Using a 100 μL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.3.2.2 Gases - To prepare standards for any compounds that boil below 30°C (e.g. bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5 mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared by using a lecture bottle equipped with a Hamilton Lecture Bottle Septum (#86600). Attach Teflon tubing to the side-arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.3.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. 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.

5.3.4 Transfer the stock standard solution into a Teflon sealed screw cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light.

5.3.5 Prepare fresh standards every two months for gases. Reactive compounds such as 2-chloroethylvinyl ether and styrene may need to be prepared more frequently. All other standards must be replaced after six months. Both gas and liquid standards must be monitored closely by comparison to the initial calibration curve and by comparison to QC check standards. It may be necessary to replace the standards more frequently if either check exceeds a 25% difference.

5.4 Secondary dilution standards - Using stock standard solutions, prepare in methanol, secondary dilution standards containing the compounds of interest, either singly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.5 Surrogate standards - The surrogates recommended are toluene-d_8, 4-bromofluorobenzene, and 1,2-dichloroethane-d_4. Other compounds may be used as surrogates, depending upon the analysis requirements. A stock surrogate solution in methanol should be prepared as described in Section 5.3, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 250 μg/10 mL in methanol. Each water sample undergoing GC/MS analysis must be spiked with 10 μL of the surrogate spiking solution prior to analysis.

5.6 Internal standards - The recommended internal standards are bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d_5. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected by GC/MS. Prepare internal standard stock and secondary dilution standards in methanol using the procedures described in Sections 5.3 and 5.4. It is recommended that the secondary dilution standard should be prepared at a concentration of 25 mg/L of each internal standard compound. Addition of 10 μL of this standard to 5.0 mL of sample or calibration standard would be the equivalent of 50 μg/L.

5.7 4-Bromofluorobenzene (BFB) standard - A standard solution containing 25 ng/μL of BFB in methanol should be prepared.

5.8 Calibration standards - Calibration standards at a minimum of five concentrations should be prepared from the secondary dilution of stock standards (see Sections 5.3 and 5.4). Prepare these solutions in organic-free reagent water. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected 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 target analytes may be included). Calibration standards must be prepared daily.

5.9 Matrix spiking standards - Matrix spiking standards should be prepared from volatile organic compounds which will be representative of the compounds being investigated. The suggested compounds are 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. The standard should be prepared in methanol, with each compound present at a concentration of 250 µg/10.0 mL.

5.10 Great care must be taken to maintain the integrity of all standard solutions. It is recommended that all standards in methanol be stored at -10°C to -20°C in screw cap amber bottles with Teflon liners.

5.11 Methanol, CH_3OH. Pesticide quality or equivalent. Store apart from other solvents.

5.12 Reagent Tetraglyme - Reagent tetraglyme is defined as tetraglyme in which interference is not observed at the method detection limit of compounds of interest.

5.12.1 Tetraglyme (tetraethylene glycol dimethyl ether, Aldrich #17, 240-5 or equivalent), $C_8H_{18}O_5$. Purify by treatment at reduced pressure in a rotary evaporator. The tetraglyme should have a peroxide content of less than 5 ppm as indicated by EM Quant Test Strips (available from Scientific Products Co., Catalog No. P1126-8 or equivalent).

CAUTION: Glycol ethers are suspected carcinogens. All solvent handling should be done in a hood while using proper protective equipment to minimize exposure to liquid and vapor.

Peroxides may be removed by passing the tetraglyme through a column of activated alumina. The tetraglyme is placed in a round bottom flask equipped with a standard taper joint, and the flask is affixed to a rotary evaporator. The flask is immersed in a water bath at 90-100°C and a vacuum is maintained at < 10 mm Hg for at least two hours using a two stage mechanical pump. The vacuum system is equipped with an all glass trap, which is maintained in a dry ice/methanol bath. Cool the tetraglyme to ambient temperature and add 100 mg/L of 2,6-di-tert-butyl-4-methyl-phenol to prevent peroxide formation. Store the tetraglyme in a tightly sealed screw cap bottle in an area that is not contaminated by solvent vapors.

5.12.2 In order to demonstrate that all interfering volatiles have been removed from the tetraglyme, an organic-free reagent water/tetraglyme blank must be analyzed.

5.13 Polyethylene glycol, $H(OCH_2CH_2)_nOH$. Free of interferences at the detection limit of the analytes.

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 Direct injection - In very limited applications (e.g. aqueous process wastes), direct injection of the sample into the GC/MS system with a 10 µL syringe may be appropriate. One such application is for verification of the alcohol content of an aqueous sample prior to determining if the sample is ignitable (Methods 1010 or 1020). In this case, it is suggested that direct injection be used. The detection limit is very high (approximately 10,000 µg/L); therefore, it is only permitted when concentrations in excess of 10,000 µg/L are expected or for water soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

7.2 Initial calibration for purge-and-trap procedure

7.2.1 Recommended GC/MS operating conditions

Electron energy:	70 volts (nominal).
Mass range:	35-260 amu.
Scan time:	To give 5 scans/peak, but not to exceed 7 sec/scan.
Initial column temperature:	45°C.
Initial column holding time:	3 minutes.
Column temperature program:	8°C/minute.
Final column temperature:	220°C.
Final column holding time:	15 minutes.
Injector temperature:	200-225°C.
Source temperature:	According to manufacturer's specifications.
Transfer line temperature:	250-300°C.
Carrier gas:	Hydrogen at 50 cm/sec or helium at 30 cm/sec.

7.2.2 Each GC/MS system must be hardware tuned to meet the criteria in Table 3 for a 50 ng injection or purging of 4-bromofluorobenzene (2 µL injection of the BFB standard). Analyses must not begin until these criteria are met.

7.2.3 Assemble a purge-and-trap device that meets the specification in Section 4.11. Condition the trap overnight at 180°C in the purge mode with an inert gas flow of at least 20 mL/min. Prior to use, condition the trap daily for 10 min while backflushing at 180°C with the column at 220°C.

7.2.4 Connect the purge-and-trap device to a gas chromatograph.

7.2.5 Prepare the final solutions containing the required concentrations of calibration standards, including surrogate standards, directly in the purging device (use freshly prepared stock solutions when preparing the calibration standards for the initial calibration.) Add 5.0 mL of organic-free reagent water to the purging device. The organic-free reagent water is added to the purging device using a 5 mL glass syringe fitted with a 15 cm, 20 gauge needle. The needle is inserted through the sample inlet shown in Figure 1. The internal diameter of the 14 gauge needle that forms the sample inlet will permit insertion of the 20 gauge needle. Next, using a 10 µL or 25 µL microsyringe equipped with

a long needle (Section 4.1), take a volume of the secondary dilution solution containing appropriate concentrations of the calibration standards (Section 5.6). Add the aliquot of calibration solution directly to the organic-free reagent water in the purging device by inserting the needle through the sample inlet. When discharging the contents of the microsyringe, be sure that the end of the syringe needle is well beneath the surface of the organic-free reagent water. Similarly, add 10 µL of the internal standard solution (Section 5.4). Close the 2 way syringe valve at the sample inlet.

7.2.6 Carry out the purge-and-trap analysis procedure as described in Section 7.4.1.

7.2.7 Tabulate the area response of the characteristic ions (see Table 1) against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard that has a retention time closest to the compound being measured (Section 7.5.2). The RF is calculated 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.
C_x = Concentration of the compound being measured.

7.2.8 The average RRF must be calculated for each compound. A system performance check should be made before this calibration curve is used. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum average relative response factor. These compounds are chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene. The minimum acceptable average RRF for these compounds should be 0.300 (0.250 for bromoform). These compounds typically have RRFs of 0.4-0.6 and are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system. Examples of these occurrences are:

7.2.8.1 Chloromethane - This compound is the most likely compound to be lost if the purge flow is too fast.

7.2.8.2 Bromoform - This compound is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 relative to m/z 95 ratio may improve bromoform response.

7.2.8.3 Tetrachloroethane and 1,1-dichloroethane - These compounds are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.2.9 Using the RRFs from the initial calibration, calculate and record the percent relative standard deviation (%RSD) for all compounds. The percent RSD is calculated as follows:

$$\%RSD = \frac{SD}{\overline{RF}} \times 100$$

where:

RSD = relative standard deviation.
$\overline{RF}$ = mean of 5 initial RRFs for a compound.
SD = standard deviation of average RRFs for a compound.

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(x_i - \bar{x})^2}{N - 1}}$$

The percent relative standard deviation should be less than 15% for each compound. However, the %RSD for each individual Calibration Check Compound (CCC) must be less than 30%. Late-eluting compounds usually have much better agreement. The CCCs are:

1,1-Dichloroethene,
Chloroform,
1,2-Dichloropropane,
Toluene,
Ethylbenzene, and
Vinyl chloride.

7.2.9.1 If a %RSD greater than 30 percent is measured for any CCC, then corrective action to eliminate a system leak and/or column reactive sites is required before reattempting calibration.

7.2.10 Linearity - If the %RSD of any compound is 15% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation (Section 7.5.2.2).

7.2.10.1 If the %RSD of any compound is greater than 15%, construct calibration curves of area ratio (A/Ais) versus concentration using first or second order regression fit of the five calibration points. The analyst should select the regression order which introduces the least calibration error into the quantitation (Section 7.5.3). If the %RSD is <15%, use of calibration curves is a recommended alternative to average response factor calibration, and a useful diagnostic of standard preparation accuracy and absorption activity in the chromatographic system.

7.2.11 These curves are verified each shift by purging a performance standard. Recalibration is required only if calibration and on-going performance criteria cannot be met.

7.3 Daily GC/MS calibration

7.3.1 Prior to the analysis of samples, inject or purge 50 ng of the 4-bromofluorobenzene standard. The resultant mass spectra for the BFB must meet all of the criteria given in Table 3 before sample analysis begins. These criteria must be demonstrated each 12 hour shift.

7.3.2 The initial calibration curve (Section 7.2) for each compound of interest must be checked and verified once every 12 hours of analysis time. This is accomplished by analyzing a calibration standard that is at a concentration near the midpoint concentration for the working range of the GC/MS by checking the SPCC (Section 7.3.3) and CCC (Section 7.3.4).

7.3.3 System Performance Check Compounds (SPCCs) - A system performance check must be made each 12 hours. If the SPCC criteria are met, a comparison of relative response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum relative response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. The minimum relative response factor for volatile SPCCs is 0.300 (0.250 for Bromoform). 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.

7.3.4 Calibration Check Compounds (CCCs): After the system performance check is met, CCCs listed in Section 7.2.9 are used to check the validity of the initial calibration.

Calculate the percent drift using the following equation:

$$\% \text{ Drift} = \frac{C_I - C_c}{C_I} \times 100$$

where:

C_I = Calibration Check Compound standard concentration.
C_c = Measured concentration using selected quantitation method.

If the percent difference for each CCC is less than 20%, the initial calibration is assumed to be valid. If the criterion is not met (> 20% drift), 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 quantitative sample analysis begins. If the CCCs are not required analytes by the permit, then all required analytes must meet the 20% drift criterion.

7.3.5 The internal standard responses and retention times in the check calibration 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. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning are necessary.

7.4 GC/MS analysis

7.4.1 Water samples

7.4.1.1 Screening of the sample prior to purge-and-trap analysis will provide guidance on whether sample dilution is necessary and will prevent contamination of the purge-and-trap system. Two screening techniques that can be used are: the headspace sampler (Method 3810) using a gas chromatograph (GC) equipped with a photo ionization detector (PID) in series with an electrolytic conductivity detector (HECD); and extraction of the sample with hexadecane and analysis of the extract on a GC with a FID and/or an ECD (Method 3820).

7.4.1.2 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

7.4.1.3 Set up the GC/MS system as outlined in Section 7.2.1.

7.4.1.4 BFB tuning criteria and daily GC/MS calibration criteria must be met (Section 7.3) before analyzing samples.

7.4.1.5 Adjust the purge gas (helium) flow rate to 25-40 mL/min on the purge-and-trap device. Optimize the flow rate to provide the best response for chloromethane and bromoform, if these compounds are analytes. Excessive flow rate reduces chloromethane response, whereas insufficient flow reduces bromoform response (see Section 7.2.8).

7.4.1.6 Remove the plunger from a 5 mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one VOA vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed

properly. Filling one 20 mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

7.4.1.7 The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delays until the diluted sample is in a gas tight syringe.

7.4.1.7.1 Dilutions may be made in volumetric flasks (10 to 100 mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

7.4.1.7.2 Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask selected and add slightly less than this quantity of organic-free reagent water to the flask.

7.4.1.7.3 Inject the proper aliquot of samples from the syringe prepared in Section 7.4.1.6 into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with organic-free reagent water. Cap the flask, invert, and shake three times. Repeat above procedure for additional dilutions.

7.4.1.7.4 Fill a 5 mL syringe with the diluted sample as in Section 7.4.1.6.

7.4.1.8 Add 10.0 μL of surrogate spiking solution (Section 5.3) and 10 μL of internal standard spiking solution (Section 5.4) through the valve bore of the syringe; then close the valve. The surrogate and internal standards may be mixed and added as a single spiking solution. The addition of 10 μL of the surrogate spiking solution to 5 mL of sample is equivalent to a concentration of 50 μg/L of each surrogate standard.

7.4.1.9 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

7.4.1.10 Close both valves and purge the sample for 11.0 $\pm$ 0.1 minutes at ambient temperature.

7.4.1.11 At the conclusion of the purge time, attach the trap to the chromatograph, adjust the device to the desorb mode, and begin the gas chromatographic temperature program and GC/MS data acquisition. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 180°C while backflushing the trap with inert gas between 20 and 60 mL/min for 4 minutes. If this rapid heating requirement cannot be met, the gas chromatographic column must be used as a secondary trap by cooling it to 30°C (or subambient, if problems persist) instead of the recommended initial program temperature of 45°C.

7.4.1.12 While the trap is being desorbed into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5 mL flushes of organic-free reagent water (or methanol followed by organic-free reagent water) to avoid carryover of pollutant compounds into subsequent analyses.

7.4.1.13 After desorbing the sample for 4 minutes, recondition the trap by returning the purge-and-trap device to the purge mode. Wait 15 seconds; then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180°C. Trap temperatures up to 220°C may be employed; however, the higher temperature will shorten the useful life of the trap. After approximately 7 minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

7.4.1.14 If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion. When a sample is analyzed that has saturated ions from a compound, this analysis must be followed by a blank organic-free reagent water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences.

7.4.1.15 For matrix spike analysis, add 10 µL of the matrix spike solution (Section 5.7) to the 5 mL of sample to be purged. Disregarding any dilutions, this is equivalent to a concentration of 50 µg/L of each matrix spike standard.

7.4.1.16 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve. Proceed to Sections 7.5.1 and 7.5.2 for qualitative and quantitative analysis.

7.4.2 Water miscible liquids

7.4.2.1 Water miscible liquids are analyzed as water samples after first diluting them at least 50 fold with organic-free reagent water.

7.4.2.2 Initial and serial dilutions can be prepared by pipetting 2 mL of the sample to a 100 mL volumetric flask and diluting to volume with organic-free reagent water. Transfer immediately to a 5 mL gas tight syringe.

7.4.2.3 Alternatively, prepare dilutions directly in a 5 mL syringe filled with organic-free reagent water by adding at least 20 µL, but not more than 100 µL of liquid sample. The sample is ready for addition of internal and surrogate standards.

7.4.3 Sediment/soil and waste samples - It is highly recommended that all samples of this type be screened prior to the purge-and-trap GC/MS analysis. The headspace method (Method 3810) or the hexadecane extraction and screening method (Method 3820) may be used for this purpose. These samples may contain percent quantities of purgeable organics that will contaminate the purge-and-trap system, and require extensive cleanup and instrument downtime. Use the screening data to determine whether to use the low-concentration method (0.005-1 mg/kg) or the high-concentration method (> 1 mg/kg).

7.4.3.1 Low-concentration method - This is designed for samples containing individual purgeable compounds of < 1 mg/kg. It is limited to sediment/soil samples and waste that is of a similar consistency (granular and porous). The low-concentration method is based on purging a heated sediment/soil sample mixed with organic-free reagent water containing the surrogate and internal standards. Analyze all reagent blanks and standards under the same conditions as the samples. See Figure 5 for an illustration of a low soils impinger.

7.4.3.1.1 Use a 5 g sample if the expected concentration is < 0.1 mg/kg or a 1 g sample for expected concentrations between 0.1 and 1 mg/kg.

7.4.3.1.2 The GC/MS system should be set up as in Sections 7.4.1.2-7.4.1.4. This should be done prior to the preparation of the sample to avoid loss of volatiles from standards and samples. A heated purge calibration curve must be prepared and used for the quantitation of all samples analyzed with the low-concentration method. Follow the initial and daily calibration instructions, except for the addition of a 40°C purge temperature.

7.4.3.1.3 Remove the plunger from a 5 mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 5.0 mL. Add 10 µL each of surrogate spiking solution (Section 5.3) and internal standard solution (Section 5.4) to the syringe through the valve. (Surrogate spiking solution and internal standard solution may be mixed together.) The addition of 10 µL of the surrogate spiking solution to 5 g of sediment/soil is equivalent to 50 µg/kg of each surrogate standard.

7.4.3.1.4 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh the amount determined in Section 7.4.3.1.1 into a tared purge device. Note and record the actual weight to the nearest 0.1 g.

7.4.3.1.5 Determine the percent dry weight of the soil/sediment sample. This includes waste samples that are

amenable to percent dry weight determination. Other wastes should be reported on a wet-weight basis.

7.4.3.1.5.1 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 re-weighing. Concentrations of individual analytes are reported relative to the dry weight of sample.

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

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

7.4.3.1.6 Add the spiked water to the purge device, which contains the weighed amount of sample, and connect the device to the purge-and-trap system.

NOTE: Prior to the attachment of the purge device, the procedures in Sections 7.4.3.1.4 and 7.4.3.1.6 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes.

7.4.3.1.7 Heat the sample to 40°C ± 1°C and purge the sample for 11.0 ± 0.1 minute.

7.4.3.1.8 Proceed with the analysis as outlined in Sections 7.4.1.11-7.4.1.16. Use 5 mL of the same organic-free reagent water as in the reagent blank. If saturated peaks occurred or would occur if a 1 g sample were analyzed, the high-concentration method must be followed.

7.4.3.1.9 For low-concentration sediment/soils add 10 µL of the matrix spike solution (Section 5.7) to the 5 mL of organic-free reagent water (Section 7.4.3.1.3). The concentration for a 5 g sample would be equivalent to 50 µg/kg of each matrix spike standard.

7.4.3.2 High-concentration method - The method is based on extracting the sediment/soil with methanol. A waste sample is either extracted or diluted, depending on its solubility in methanol. Wastes (i.e. petroleum and coke wastes) that are insoluble in methanol are diluted with reagent tetraglyme or possibly polyethylene glycol (PEG). An aliquot of the extract is added to organic-free reagent water containing internal standards.

This is purged at ambient temperature. All samples with an expected concentration of > 1.0 mg/kg should be analyzed by this method.

7.4.3.2.1 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. For sediment/soil and solid wastes that are insoluble in methanol, weigh 4 g (wet weight) of sample into a tared 20 mL vial. Use a top loading balance. Note and record the actual weight to 0.1 gram and determine the percent dry weight of the sample using the procedure in Section 7.4.3.1.5. For waste that is soluble in methanol, tetraglyme, or PEG, weigh 1 g (wet weight) into a tared scintillation vial or culture tube or a 10 mL volumetric flask. (If a vial or tube is used, it must be calibrated prior to use. Pipet 10.0 mL of solvent into the vial and mark the bottom of the meniscus. Discard this solvent.)

7.4.3.2.2 Quickly add 9.0 mL of appropriate solvent; then add 1.0 mL of the surrogate spiking solution to the vial. Cap and shake for 2 minutes.

NOTE: Sections 7.4.3.2.1 and 7.4.3.2.2 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free from solvent fumes.

7.4.3.2.3 Pipet approximately 1 mL of the extract to a GC vial for storage, using a disposable pipet. The remainder may be disposed of. Transfer approximately 1 mL of appropriate solvent to a separate GC vial for use as the method blank for each set of samples. These extracts may be stored at 4°C in the dark, prior to analysis. The addition of a 100 µL aliquot of each of these extracts in Section 7.4.3.2.6 will give a concentration equivalent to 6,200 µg/kg of each surrogate standard.

7.4.3.2.4 The GC/MS system should be set up as in Sections 7.4.1.2-7.4.1.4. This should be done prior to the addition of the solvent extract to organic-free reagent water.

7.4.3.2.5 Table 4 can be used to determine the volume of solvent extract to add to the 5 mL of organic-free reagent water for analysis. If a screening procedure was followed (Method 3810 or 3820), use the estimated concentration to determine the appropriate volume. Otherwise, estimate the concentration range of the sample from the low-concentration analysis to determine the appropriate volume. If the sample was submitted as a high-concentration sample, start with 100

µL. All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.4.3.2.6 Remove the plunger from a 5.0 mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 4.9 mL. Pull the plunger back to 5.0 mL to allow volume for the addition of the sample extract and of standards. Add 10 µL of internal standard solution. Also add the volume of solvent extract determined in Section 7.4.3.2.5 and a volume of extraction or dissolution solvent to total 100 µL (excluding methanol in standards).

7.4.3.2.7 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the organic-free reagent water/methanol sample into the purging chamber.

7.4.3.2.8 Proceed with the analysis as outlined in Section 7.4.1.11-7.4.1.16. Analyze all reagent blanks on the same instrument as that use for the samples. The standards and blanks should also contain 100 µL of solvent to simulate the sample conditions.

7.4.3.2.9 For a matrix spike in the high-concentration sediment/soil samples, add 8.0 mL of methanol, 1.0 mL of surrogate spike solution (Section 5.3), and 1.0 mL of matrix spike solution (Section 5.7) as in Section 7.4.3.2.2. This results in a 6,200 µg/kg concentration of each matrix spike standard when added to a 4 g sample. Add a 100 µL aliquot of this extract to 5 mL of organic-free reagent water for purging (as per Section 7.4.3.2.6).

7.5 Data interpretation

7.5.1 Qualitative analysis

7.5.1.1 The qualitative identification of compounds determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met.

7.5.1.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the

presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.5.1.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

7.5.1.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.5.1.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.5.1.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.5.1.2 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 type of analyses being conducted. 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.

Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

7.5.2 Quantitative analysis

7.5.2.1 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).

7.5.2.2 When linearity exists, as per Section 7.2.10, calculate the concentration of each identified analyte in the sample as follows:

Water

$$\text{concentration } (\mu g/L) = \frac{(A_x)(I_s)}{(A_{is})(\overline{RRF})(V_o)}$$

where:

A_x = Area of characteristic ion for compound being measured.

I_s = Amount of internal standard injected (ng).

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

$\overline{RRF}$ = Relative Response factor for compound being measured (Section 7.3.3).

V_o = Volume of water purged (mL), taking into consideration any dilutions made.

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, A_{is}, $\overline{RRF}$, = Same as for water.
V_t = Volume of total extract (μL) (use 10,000 μL or a factor of this when dilutions are made).

V_i = Volume of extract added (μL) for purging.
W_s = Weight of sample extracted or purged (g).
D = % dry weight of sample/100, or 1 for a wet-weight basis.

7.5.2.3 Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formulae 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.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document quality data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control reference sample must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.2 Before processing any samples, the analyst should demonstrate, through the analysis of a calibration blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of sample preparation and measurement.

8.3 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response obtained comparable to the

response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still useable, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g. column changed), recalibration of the system must take place.

8.4 Required instrument QC is found in the following section:

8.4.1 The GC/MS system must be tuned to meet the BFB specifications in Step 7.2.2.

8.4.2 There must be an initial calibration of the GC/MS system as specified in Step 7.2.

8.4.3 The GC/MS system must meet the SPCC criteria specified in Step 7.3.3 and the CCC criteria in Step 7.3.4, each 12 hours.

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

8.5.1 A quality control (QC) reference sample concentrate is required containing each analyte at a concentration of 10 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.

8.5.2 Prepare a QC reference sample to contain 20 µg/L of each analyte by adding 200 µL of QC reference sample concentrate to 100 mL of water.

8.5.3 Four 5-mL aliquots of the well mixed QC reference sample are analyzed according to the method beginning in Step 7.4.1.

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

8.5.5 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.

8.5.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Step 8.5.6.1 or 8.5.6.2.

8.5.6.1 Locate and correct the source of the problem and repeat the test for all analytes beginning with Section 8.5.2.

8.5.6.2 Beginning with Section 8.5.2, 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 8.5.2.

8.6 The laboratory must, on an ongoing basis, analyze a reagent blank and a spiked replicate for each analytical batch (up to a maximum of 20 samples/batch) to assess accuracy. For soil and waste samples where detectable amounts of organics are present, replicate samples may be appropriate in place of spiked replicates. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.6.1 The concentration of the spike in the sample should be determined as follows:

8.6.1.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Step 8.6.2, whichever concentration would be larger.

8.6.1.2 If the concentration of a specific analyte in a water sample is not being checked against a specific limit, the spike should be at 20 µg/L or 1 to 5 times higher than the background concentration determined in Step 8.6.2, whichever concentration would be larger. For other matrices, recommended spiking concentration is 10 times the EQL.

8.6.2 Analyze one 5-mL sample aliquot to determine the background concentration (B) of each analyte. If necessary, prepare a new QC reference sample concentrate (Step 8.5.1) appropriate for the background concentration in the sample. Spike a second 5-mL sample aliquot with 10 µL of the QC reference sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as 100(A-B)%/T, where T is the known true value of the spike.

8.6.3 Compare the percent recovery (p) for each analyte in a water sample with the corresponding QC acceptance criteria found in Table 6. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than 20 µg/L, the analyst must use either the QC acceptance criteria presented in Table 6, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of an analyte: (1) Calculate accuracy (x′) using the equation found in Table 7, substituting the spike concentration (T) for C; (2) calculate overall precision (S′) using the equation in Table 7, substituting x′ for

$\bar{x}$; (3) calculate the range for recovery at the spike concentration as $(100x'/T) \pm 2.44(100S'/T)\%$.

8.6.4 If any individual p falls outside the designated range for recovery, that analyte has failed the acceptance criteria. A check standard containing each analyte that failed the criteria must be analyzed as described in Step 8.7.

8.7 If any analyte in a water sample fails the acceptance criteria for recovery in Step 8.6, a QC reference sample containing each analyte that failed must be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC reference sample will depend upon the number of analytes being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of analytes in Table 6 must be measured in the sample in Step 8.6, the probability that the analysis of a QC reference sample will be required is high. In this case the QC reference sample should be routinely analyzed with the spiked sample.

8.7.1 Prepare the QC reference sample by adding 10 µL of the QC reference sample concentrate (Step 8.5.1 or 8.6.2) to 5 mL of reagent water. The QC reference sample needs only to contain the analytes that failed criteria in the test in Step 8.6.

8.7.2 Analyze the QC reference sample to determine the concentration measured (A) of each analyte. Calculate each percent recovery (p_s) as 100(A/T)%, where T is the true value of the standard concentration.

8.7.3 Compare the percent recovery (p_s) for each analyte with the corresponding QC acceptance criteria found in Table 6. Only analytes that failed the test in Step 8.6 need to be compared with these criteria. If the recovery of any such analyte falls outside the designated range, the laboratory performance for that analyte is judged to be out of control, and the problem must be immediately identified and corrected. The result for that analyte in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.8 As part of the QC program for the laboratory, method accuracy for each matrix studied must be assessed and records must be maintained. After the analysis of five spiked samples (of the same matrix) as in Section 8.6, calculate the average percent recovery ($\bar{p}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{p} - 2s_p$ to $\bar{p} + 2s_p$. If $\bar{p}$ = 90% and s_p = 10%, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each analyte on a regular basis (e.g. after each five to ten new accuracy measurements).

8.9 To determine acceptable accuracy and precision limits for surrogate standards the following procedure should be performed.

8.9.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

8.9.2 Once a minimum of thirty samples of the same matrix have been analyzed, calculate the average percent recovery (p) and standard deviation of the percent recovery (s) for each of the surrogates.

8.9.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

Upper Control Limit (UCL) = p + 3s
Lower Control Limit (LCL) = p - 3s

8.9.4 For aqueous and soil matrices, these laboratory established surrogate control limits should, if applicable, be compared with the control limits listed in Table 8. The limits given in Table 8 are multi-laboratory performance based limits for soil and aqueous samples, and therefore, the single-laboratory limits established in Step 8.9.3 must fall within those given in Table 8 for these matrices.

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

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration".

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

8.10 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column or a different ionization mode using a mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 This method was tested by 15 laboratories using organic-free reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5-600 µg/L. Single operator precision, overall 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.

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 624," October 26, 1984.

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5. Budde, W.L. and J.W. Eichelberger, "Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories," EPA-600/4-79-020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, April 1980.

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

8. "Interlaboratory Method Study for EPA Method 624-Purgeables," Final Report for EPA Contract 68-03-3102.

9. "Method Performance Data for Method 624," Memorandum from R. Slater and T. Pressley, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, January 17, 1984.

10. Gebhart, J.E.; Lucas, S.V.; Naber, S.J.; Berry, A.M.; Danison, T.H.; Burkholder, H.M. "Validation of SW-846 Methods 8010, 8015, and 8020"; U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Old 45268, July 1987, Contract No. 68-03-1760.

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TABLE 1.
RETENTION TIMES AND CHARACTERISTIC IONS FOR VOLATILE COMPOUNDS

Compound	Retention Time (minutes)	Primary Ion	Secondary Ion(s)
Ethylene oxide	1.30	44	44, 43, 42
Chloromethane	2.30	50	52, 49
Dichlorodifluoromethane	2.47	85	85, 87, 101, 103
Bromomethane	3.10	94	96, 79
Vinyl chloride	3.80	62	64, 61
Acetonitrile	3.97	41	41, 40, 39
Chloroethane	4.60	64	66, 49
Methyl iodide	5.37	142	142, 127, 141
Methylene chloride	6.40	84	49, 51, 86
Carbon disulfide	7.47	76	76, 78, 44
Trichlorofluoromethane	8.30	101	103, 66
Propionitrile	8.53	54	54, 52, 55, 40
Allyl chloride	8.83	76	76, 41, 39, 78
1,1-Dichloroethene	9.00	96	61, 98
Bromochloromethane (I.S.)	9.30	128	49, 130, 51
Allyl alcohol	9.77	57	57, 58, 39
trans-1,2-Dichloroethene	10.00	96	61, 98
1,2-Dichloroethane	10.10	62	64, 98
Propargyl alcohol	10.77	55	55, 39, 38, 53
Chloroform	11.40	83	85, 47
1,2-Dichloroethane-d_4(surr)	12.10	65	102
2-Butanone	12.20	72	43, 72
Methacrylonitrile	12.37	41	41, 67, 39, 52, 66
Dibromomethane	12.53	93	93, 174, 95, 172, 176
2-Chloroethanol	12.93	49	49, 44, 43, 51, 80
b-Propiolactone	13.00	42	42, 43, 44
Epichlorohydrin	13.10	57	57, 49, 62, 51
1,1,1-Trichloroethane	13.40	97	99, 117
Carbon tetrachloride	13.70	117	119, 121
1,4-Dioxane	13.70	88	88, 58, 43, 57
Isobutyl alcohol	13.80	43	43, 41, 42, 74
Bromodichloromethane	14.30	83	85, 129
Chloroprene	14.77	53	53, 88, 90, 51
1,2:3,4-Diepoxybutane	14.87	55	55, 57, 56
1,2-Dichloropropane	15.70	63	62, 41
Chloral hydrate (b)	15.77	82	44, 84, 86, 111
cis-1,3-Dichloropropene	15.90	75	77, 39
Bromoacetone	16.33	136	43, 136, 138, 93, 95
Trichloroethene	16.50	130	95, 97, 132
Benzene	17.00	78	52, 71
trans-1,3-Dichloropropene	17.20	75	77, 39
1,1,2-Trichloroethane	17.20	97	83, 85, 99
3-Chloropropionitrile	17.37	54	54, 49, 89, 91
1,2-Dibromoethane	18.40	107	107, 109, 93, 188
Pyridine	18.57	79	79, 52, 51, 50

TABLE 1.
(Continued)

Compound	Retention Time (minutes)	Primary Ion	Secondary Ion(s)
2-Chloroethyl vinyl ether	18.60	63	65,106
2-Hydroxypropionitrile	18.97	44	44,43,42,53
1,4-Difluorobenzene (I.S.)	19.60	114	63,88
Malononitrile	19.60	66	66,39,65,38
Methyl methacrylate	19.77	69	69,41,100,39
Bromoform	19.80	173	171,175,252
1,1,1,2-Tetrachloroethane	20.33	131	131,133,117,119,95
1,3-Dichloro-2-propanol	21.83	79	79,43,81,49
1,1,2,2-Tetrachloroethane	22.10	83	85,131,133
Tetrachloroethene	22.20	164	129,131,166
1,2,3-Trichloropropane	22.20	75	75,77,110,112,97
1,4-Dichloro-2-butene	22.73	75	75,53,77,124,89
n-Propylamine	23.00	59	59,41,39
2-Picoline	23.20	93	93,66,92,78
Toluene	23.50	92	91,65
Ethyl methacrylate	23.53	69	69,41,99,86,114
Chlorobenzene	24.60	112	114,77
Pentachloroethane[a]	24.83	167	167,130,132,165,169
Ethylbenzene	26.40	106	91
1,2-Dibromo-3-chloropropane	27.23	157	157,75,155,77
4-Bromofluorobenzene (surr.)	28.30	95	174,176
Benzyl chloride	29.50	91	91,126,65,128
Styrene	30.83	104	104,103,78,51,77
bis-(2-Chloroethyl) sulfide(b)	33.53	109	111, 158, 160
Acetone	--	43	58
Acrolein	--	56	55,58
Acrylonitrile	--	53	52,51
Chlorobenzene-d_5 (I.S.)	--	117	82,119
Chlorodibromomethane	--	129	208,206
1,1-Dichloroethane	--	63	65,83
Ethanol	--	31	45,27,46
2-Hexanone	--	43	58,57, 100
Iodomethane	--	142	127,141
4-Methyl-2-pentanone	--	43	58,57,100
Toluene-d_8 (surr.)	--	98	70,100
Vinyl acetate	--	43	86
Xylene (Total)	--	106	91

a The base peak at m/e 117 was not used due to an interference at that mass with a nearly coeluting internal standard, chlorobenzene-d_5.

b Response factor judged to be too low (less than 0.02) for practical use.

TABLE 2.
ESTIMATED QUANTITATION LIMITS (EQL) FOR VOLATILE ORGANICS[a]

Volatiles	Estimated Quantitation Limits[b] Ground water µg/L	Low Soil/Sediment µg/kg
Acetone	100	100
Acetonitrile	100	100
Allyl chloride	5	5
Benzene	5	5
Benzyl chloride	100	100
Bromodichloromethane	5	5
Bromoform	5	5
Bromomethane	10	10
2-Butanone	100	100
Carbon disulfide	100	100
Carbon tetrachloride	5	5
Chlorobenzene	5	5
Chlorodibromomethane	5	5
Chloroethane	10	10
2-Chloroethyl vinyl ether	10	10
Chloroform	5	5
Chloromethane	10	10
Chloroprene	5	5
1,2-Dibromo-3-chloropropane	100	100
1,2-Dibromoethane	5	5
Dibromomethane	5	5
1,4-Dichloro-2-butene	100	100
Dichlorodifluoromethane	5	5
1,1-Dichloroethane	5	5
1,2-Dichloroethane	5	5
1,1 Dichloroethene	5	5
trans-1,2-Dichloroethene	5	5
1,2-Dichloropropane	5	5
cis-1,3-Dichloropropene	5	5
trans-1,3-Dichloropropene	5	5
Ethylbenzene	5	5
Ethyl methacrylate	5	5
2-Hexanone	50	50
Isobutyl alcohol	100	100
Methacrylonitrile	100	100
Methylene chloride	5	5
Methyl iodide	5	5
Methyl methacrylate	5	50
4-Methyl-2-pentanone	50	50
Pentachloroethane	10	10

TABLE 2.
(Continued)

Volatiles	Estimated Quantitation Limits[b] Ground water µg/L	Low Soil/Sediment µg/kg
Propionitrile	100	100
Styrene	5	5
1,1,1,2-Tetrachloroethane	5	5
1,1,2,2-Tetrachloroethane	5	5
Tetrachloroethene	5	5
Toluene	5	5
1,1,1-Trichloroethane	5	5
1,1,2-Trichloroethane	5	5
Trichloroethene	5	5
1,2,3-Trichloropropane	5	5
Vinyl acetate	50	50
Vinyl chloride	10	10
Xylene (Total)	5	5

a Sample EQLs are highly matrix dependent. The EQLs listed herein are provided for guidance and may not always be achievable. See the following information for further guidance on matrix dependent EQLs.

b 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 percent dry weight of each sample.

Other Matrices	Factor[c]
Water miscible liquid waste	50
High-concentration soil and sludge	125
Non-water miscible waste	500

[c]EQL = [EQL for low soil sediment (Table 2)] X [Factor]. For non-aqueous samples, the factor is on a wet weight basis.

TABLE 3.
BFB KEY ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5 to 9% of mass 176

TABLE 4.
QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS
OF HIGH-CONCENTRATION SOILS/SEDIMENTS

Approximate Concentration Range	Volume of Methanol Extract[a]
500- 10,000 µg/kg	100 µL
1,000- 20,000 µg/kg	50 µL
5,000-100,000 µg/kg	10 µL
25,000-500,000 µg/kg	100 µL of 1/50 dilution[b]

Calculate appropriate dilution factor for concentrations exceeding this table.

a The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5 mL syringe whatever volume of methanol is necessary to maintain a volume of 100 µL added to the syringe.

b Dilute and aliquot of the methanol extract and then take 100 µL for analysis.

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

Bromochloromethane	1,4-Difluorobenzene
Acetone	Benzene
Acrolein	Bromodichloromethane
Acrylonitrile	Bromoform
Bromomethane	2-Butanone
Carbon disulfide	Carbon tetrachloride
Chloroethane	Chlorodibromomethane
Chloroform	2-Chloroethyl vinyl ether
Chloromethane	Dibromomethane
Dichlorodifluoromethane	1,4-Dichloro-2-butene
1,1-Dichloroethane	1,2-Dichloropropane
1,2-Dichloroethane	cis-1,3-Dichloropropene
1,2-Dichloroethane-d_4 (surrogate)	trans-1,3-Dichloropropene
1,1-Dichloroethene	1,1,1-Trichloroethane
trans-1,2-Dichloroethene	1,1,2-Trichloroethane
Iodomethane	Trichloroethene
Methylene chloride	Vinyl acetate
Trichlorofluoromethane	
Vinyl chloride	

Chlorobenzene-d_5
Bromofluorobenzene (surrogate)
Chlorobenzene
Ethylbenzene
Ethyl methacrylate
2-Hexanone
4-Methyl-2-pentanone
Styrene
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
Toluene-d_8 (surrogate)
1,2,3-Trichloropropane
Xylene

TABLE 6.
CALIBRATION AND QC ACCEPTANCE CRITERIA[a]

Parameter	Range for Q (µg/L)	Limit for s (µg/L)	Range for x (µg/L)	Range p,p_s (%)
Benzene	12.8-27.2	6.9	15.2-26.0	37-151
Bromodichloromethane	13.1-26.9	6.4	10.1-28.0	35-155
Bromoform	14.2-25.8	5.4	11.4-31.1	45-169
Bromomethane	2.8-37.2	17.9	D-41.2	D-242
Carbon tetrachloride	14.6-25.4	5.2	17.2-23.5	70-140
Chlorobenzene	13.2-26.8	6.3	16.4-27.4	37-160
2-Chloroethylvinyl ether	D-44.8	25.9	D-50.4	D-305
Chloroform	13.5-26.5	6.1	13.7-24.2	51-138
Chloromethane	D-40.8	19.8	D-45.9	D-273
Dibromochloromethane	13.5-26.5	6.1	13.8-26.6	53-149
1,2-Dichlorobenzene	12.6-27.4	7.1	11.8-34.7	18-190
1,3-Dichlorobenzene	14.6-25.4	5.5	17.0-28.8	59-156
1,4-Dichlorobenzene	12.6-27.4	7.1	11.8-34.7	18-190
1,1-Dichloroethane	14.5-25.5	5.1	14.2-28.4	59-155
1,2-Dichloroethane	13.6-26.4	6.0	14.3-27.4	49-155
1,1-Dichloroethene	10.1-29.9	9.1	3.7-42.3	D-234
trans-1,2-Dichloroethene	13.9-26.1	5.7	13.6-28.4	54-156
1,2-Dichloropropane	6.8-33.2	13.8	3.8-36.2	D-210
cis-1,3-Dichloropropene	4.8-35.2	15.8	1.0-39.0	D-227
trans-1,3-Dichloropropene	10.0-30.0	10.4	7.6-32.4	17-183
Ethyl benzene	11.8-28.2	7.5	17.4-26.7	37-162
Methylene chloride	12.1-27.9	7.4	D-41.0	D-221
1,1,2,2-Tetrachloroethane	12.1-27.9	7.4	13.5-27.2	46-157
Tetrachloroethene	14.7-25.3	5.0	17.0-26.6	64-148
Toluene	14.9-25.1	4.8	16.6-26.7	47-150
1,1,1-Trichloroethane	15.0-25.0	4.6	13.7-30.1	52-162
1,1,2-Trichloroethane	14.2-25.8	5.5	14.3-27.1	52-150
Trichloroethene	13.3-26.7	6.6	18.5-27.6	71-157
Trichlorofluoromethane	9.6-30.4	10.0	8.9-31.5	17-181
Vinyl chloride	0.8-39.2	20.0	D-43.5	D-251

Q = Concentration measured in QC check sample, in µg/L.
$\underline{s}$ = 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 624 and were calculated assuming a QC check sample concentration of 20 µg/L. These criteria are based directly upon 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]

Parameter	Accuracy, as recovery, x′ (μg/L)	Single analyst precision, s_r' (μg/L)	Overall precision, S′ (μg/L)
Benzene	0.93C+2.00	0.26$\bar{x}$-1.74	0.25$\bar{x}$-1.33
Bromodichloromethane	1.03C-1.58	0.15$\bar{x}$+0.59	0.20$\bar{x}$+1.13
Bromoform	1.18C-2.35	0.12$\bar{x}$+0.34	0.17$\bar{x}$+1.38
Bromomethane	1.00C	0.43$\bar{x}$	0.58$\bar{x}$
Carbon tetrachloride	1.10C-1.68	0.12$\bar{x}$+0.25	0.11$\bar{x}$+0.37
Chlorobenzene	0.98C+2.28	0.16$\bar{x}$-0.09	0.26$\bar{x}$-1.92
Chloroethane	1.18C+0.81	0.14$\bar{x}$+2.78	0.29$\bar{x}$+1.75
2-Chloroethylvinyl ether[a]	1.00C	0.62$\bar{x}$	0.84$\bar{x}$
Chloroform	0.93C+0.33	0.16$\bar{x}$+0.22	0.18$\bar{x}$+0.16
Chloromethane	1.03C-1.81	0.37$\bar{x}$+2.14	0.58$\bar{x}$+0.43
Dibromochloromethane	1.01C-0.03	0.17$\bar{x}$-0.18	0.17$\bar{x}$+0.49
1,2-Dichlorobenzene[b]	0.94C+4.47	0.22$\bar{x}$-1.45	0.30$\bar{x}$-1.20
1,3-Dichlorobenzene	1.06C+1.68	0.14$\bar{x}$-0.48	0.18$\bar{x}$-0.82
1,4-Dichlorobenzene[b]	0.94C+4.47	0.22$\bar{x}$-1.45	0.30$\bar{x}$-1.20
1,1-Dichloroethane	1.05C+0.36	0.13$\bar{x}$-0.05	0.16$\bar{x}$+0.47
1,2-Dichloroethane	1.02C+0.45	0.17$\bar{x}$-0.32	0.21$\bar{x}$-0.38
1,1-Dichloroethene	1.12C+0.61	0.17$\bar{x}$+1.06	0.43$\bar{x}$-0.22
trans-1,2,-Dichloroethene	1.05C+0.03	0.14$\bar{x}$+0.09	0.19$\bar{x}$+0.17
1,2-Dichloropropane[a]	1.00C	0.33$\bar{x}$	0.45$\bar{x}$
cis-1,3-Dichloropropene[a]	1.00C	0.38$\bar{x}$	0.52$\bar{x}$
trans-1,3-Dichloropropene[a]	1.00C	0.25$\bar{x}$	0.34$\bar{x}$
Ethyl benzene	0.98C+2.48	0.14$\bar{x}$+1.00	0.26$\bar{x}$-1.72
Methylene chloride	0.87C+1.88	0.15$\bar{x}$+1.07	0.32$\bar{x}$+4.00
1,1,2,2-Tetrachloroethane	0.93C+1.76	0.16$\bar{x}$+0.69	0.20$\bar{x}$+0.41
Tetrachloroethene	1.06C+0.60	0.13$\bar{x}$-0.18	0.16$\bar{x}$-0.45
Toluene	0.98C+2.03	0.15$\bar{x}$-0.71	0.22$\bar{x}$-1.71
1,1,1-Trichloroethane	1.06C+0.73	0.12$\bar{x}$-0.15	0.21$\bar{x}$-0.39
1,1,2-Trichloroethane	0.95C+1.71	0.14$\bar{x}$+0.02	0.18$\bar{x}$+0.00
Trichloroethene	1.04C+2.27	0.13$\bar{x}$+0.36	0.12$\bar{x}$+0.59
Trichlorofluoromethane	0.99C+0.39	0.33$\bar{x}$-1.48	0.34$\bar{x}$-0.39
Vinyl chloride	1.00C	0.48x	0.65x

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.

a Estimates based upon the performance in a single laboratory.

b Due to chromatographic resolution problems, performance statements for these isomers are based upon the sums of their concentrations.

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

Surrogate Compound	Low/High Water	Low/High Soil/Sediment
4-Bromofluorobenzene	86-115	74-121
1,2-Dichloroethane-d_4	76-114	70-121
Toluene-d_8	88-110	81-117

FIGURE 1.
PURGING CHAMBER

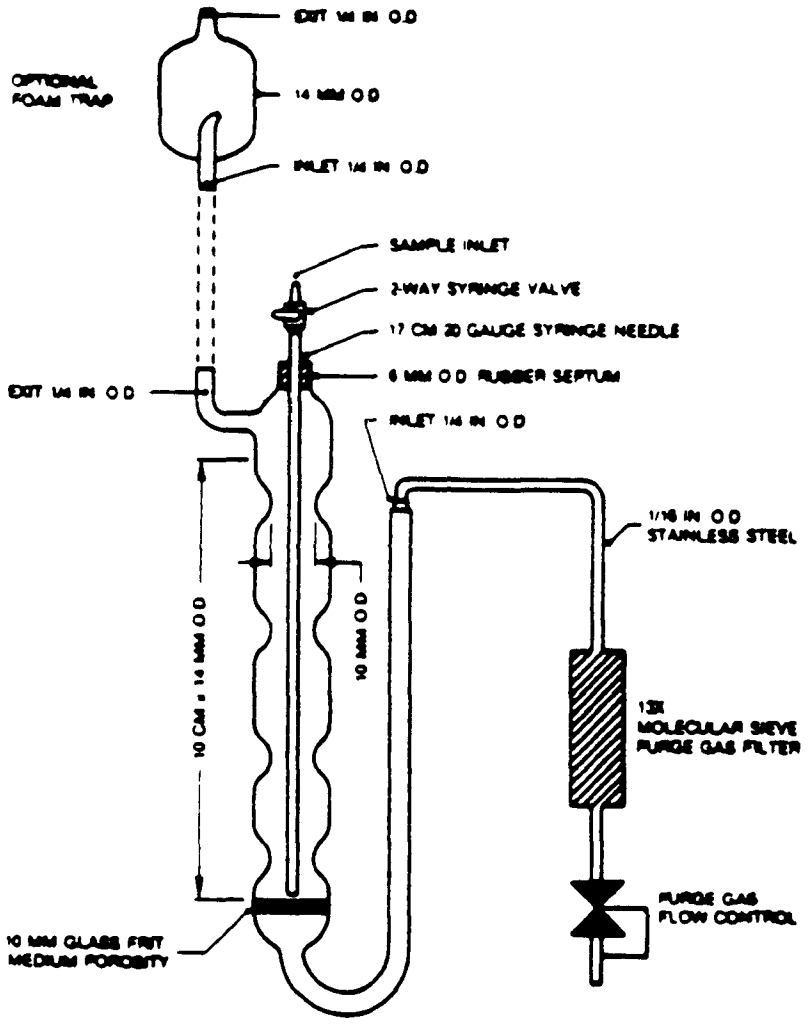


FIGURE 2.
TRAP PACKINGS AND CONSTRUCTION TO INCLUDE
DESORB CAPABILITY FOR METHOD 8240B

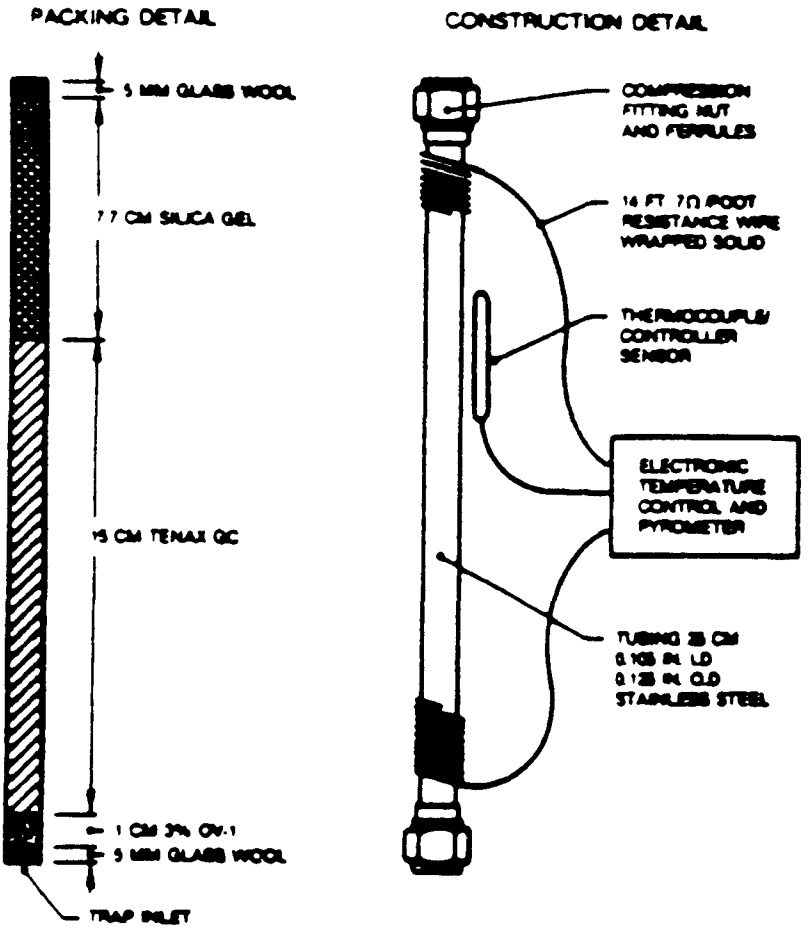


FIGURE 3.
SCHEMATIC OF PURGE-AND-TRAP DEVICE - PURGE MODE FOR METHOD 8240B

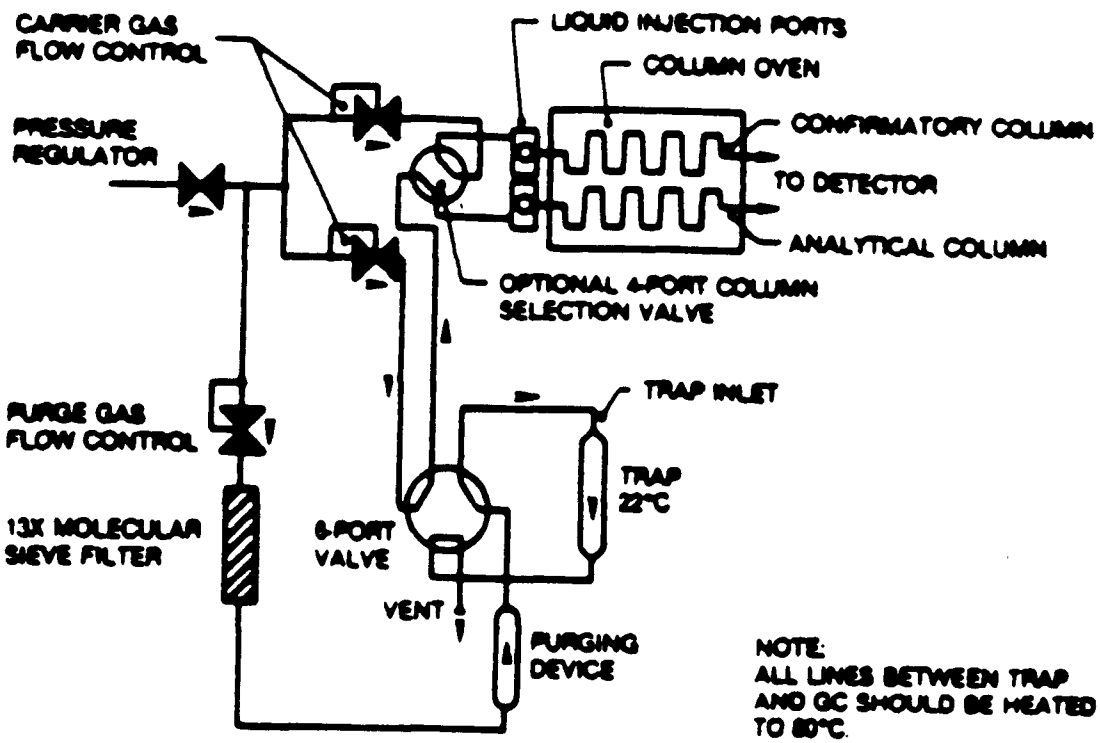


FIGURE 4.
SCHEMATIC OF PURGE-AND-TRAP DEVICE - DESORB MODE FOR METHOD 8240B

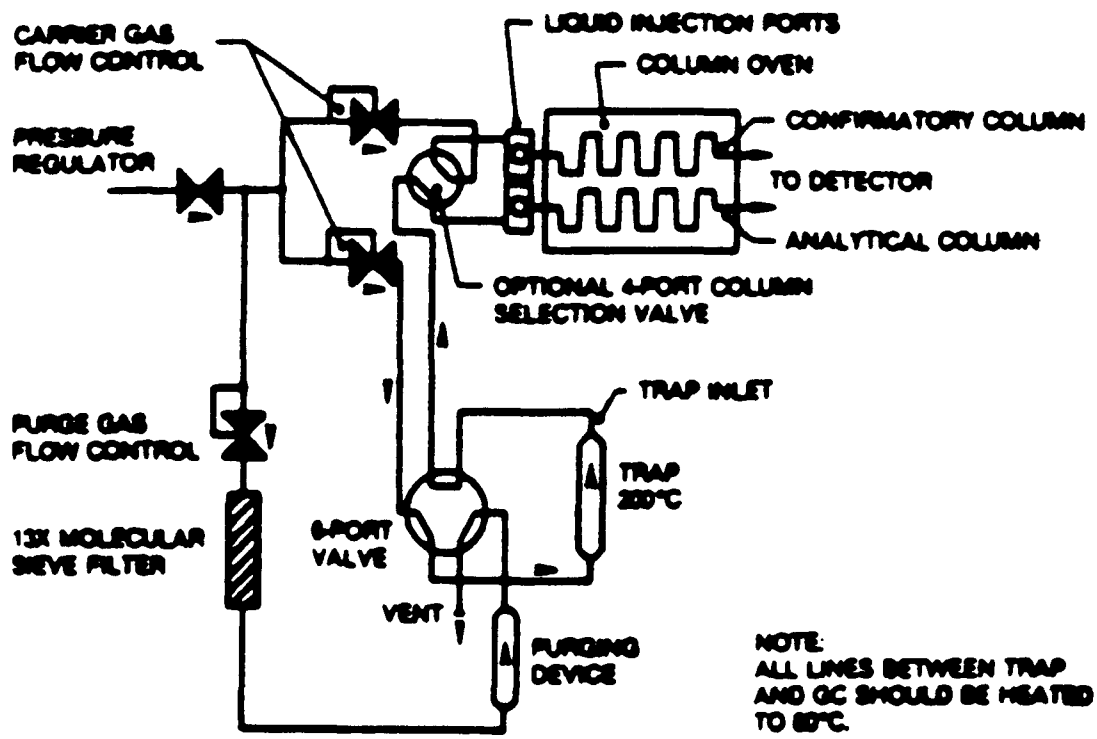
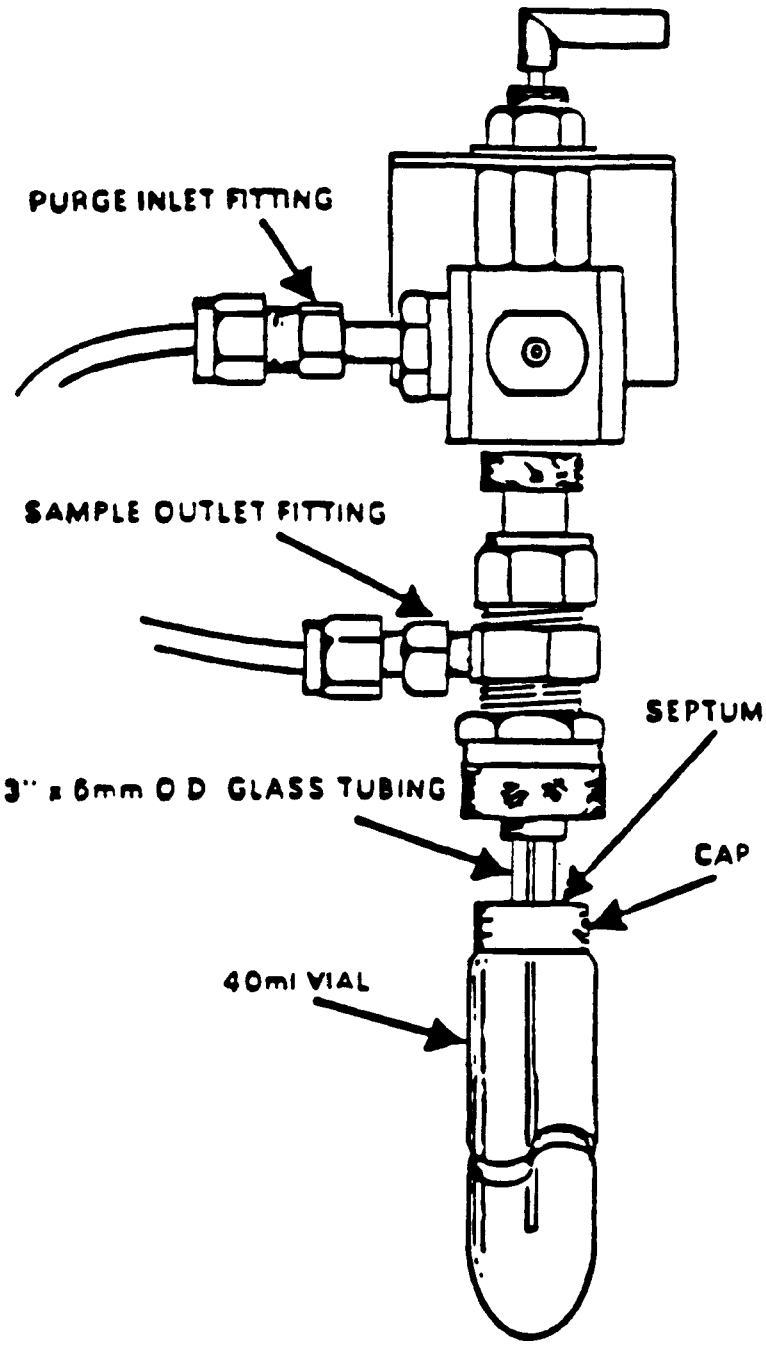
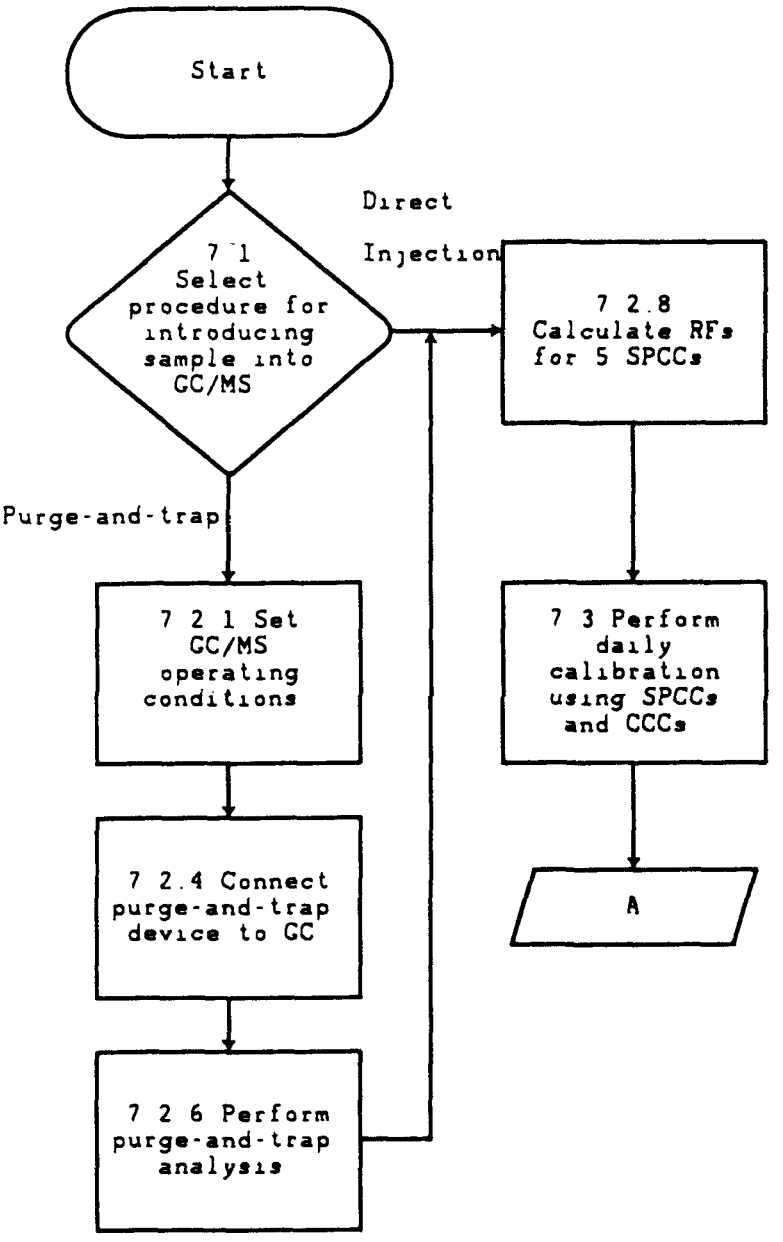
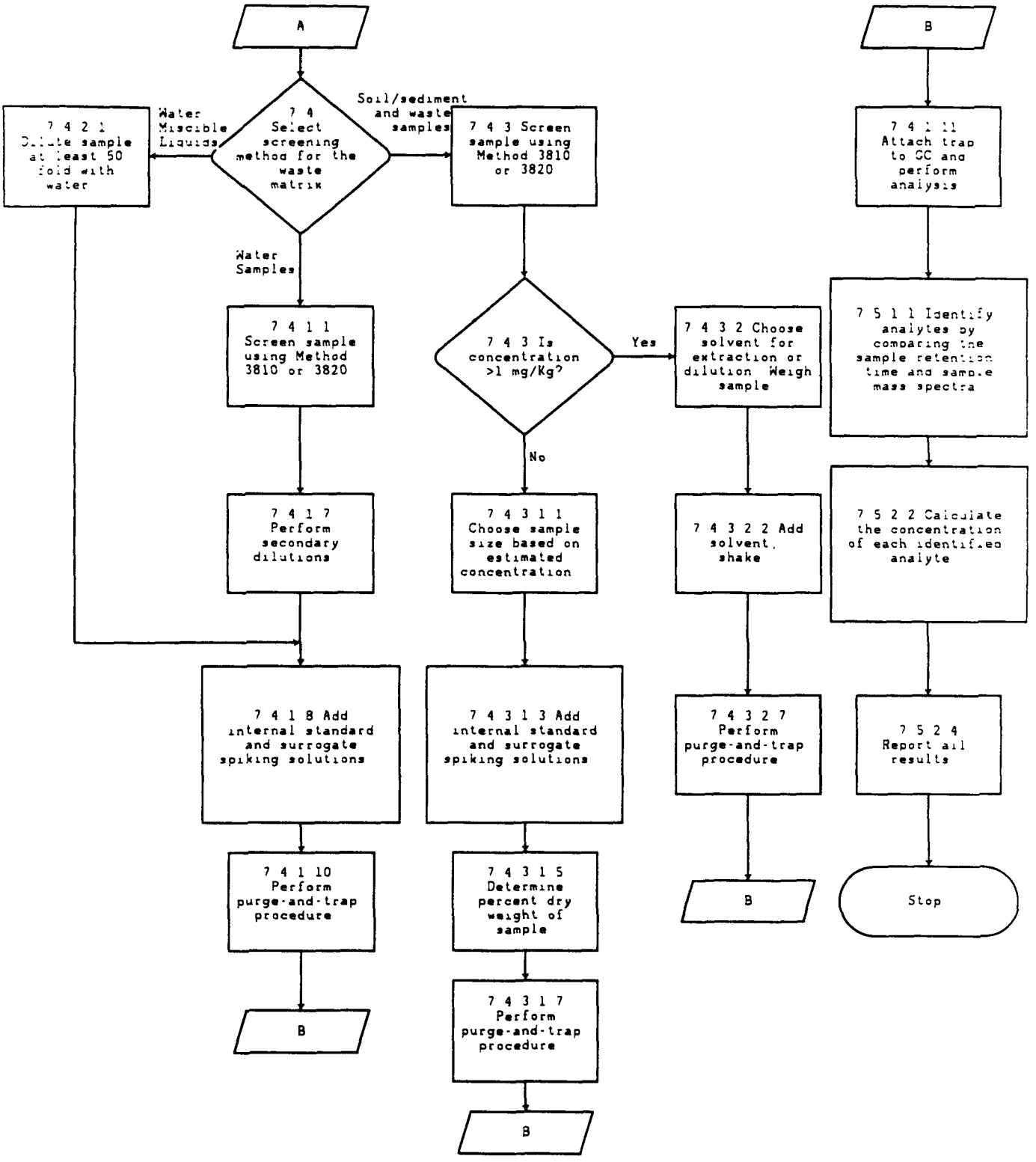


FIGURE 5.
LOW SOILS IMPINGER




Start
7 1 Select procedure for introducing sample into GC/MS
Direct Injection
Purge-and-trap
7 2 8 Calculate RFs for 5 SPCCs
7 2 1 Set GC/MS operating conditions
7 3 Perform daily calibration using SPCCs and CCCs
7 2 4 Connect purge-and-trap device to GC
A
7 2 6 Perform purge-and-trap analysis


A
7 4 Select screening method for the waste matrix
Water Miscible Liquids
Soil/sediment and waste samples
7 4 2 1 Dilute sample at least 50 fold with water
7 4 3 Screen sample using Method 3810 or 3820
Water Samples
7 4 1 1 Screen sample using Method 3810 or 3820
7 4 3 Is concentration >1 mg/Kg?
Yes
No
7 4 3 2 Choose solvent for extraction or dilution Weigh sample
7 4 1 7 Perform secondary dilutions
7 4 3 1 1 Choose sample size based on estimated concentration
7 4 3 2 2 Add solvent, shake
7 4 1 8 Add internal standard and surrogate spiking solutions
7 4 3 1 3 Add internal standard and surrogate spiking solutions
7 4 3 2 7 Perform purge-and-trap procedure
7 4 1 10 Perform purge-and-trap procedure
7 4 3 1 5 Determine percent dry weight of sample
7 4 3 1 7 Perform purge-and-trap procedure
B
B
B
B
B
7 4 1 11 Attach trap to GC and perform analysis
7 5 1 1 Identify analytes by comparing the sample retention time and sample mass spectra
7 5 2 2 Calculate the concentration of each identified analyte
7 5 2 4 Report all results
Stop

SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

1.0 SCOPE AND APPLICATION

1.1 Method 8250 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
Aldrin	309-00-2	X	X	X	X	X
4-Aminobiphenyl	92-67-1	X	ND	ND	ND	X
Aniline	62-53-3	X	X	ND	X	X
Anthracene	120-12-7	X	X	X	X	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
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
Benzyl alcohol	100-51-6	X	X	ND	X	X
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
Butyl benzyl phthalate	85-68-7	X	X	X	X	X

Compounds	CAS No[a]	Appropriate Preparation Techniques 3510	3520	3540	3550	3580
Chlordane	57-74-9	X	X	X	X	X
4-Chloroaniline	106-47-8	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
4-Chloro-3-methylphenol	59-50-7					
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
4,4′-DDD	72-54-8	X	X	X	X	X
4,4′-DDT	50-29-3	X	X	X	X	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
Di-n-butyl phthalate	84-74-2	X	X	X	X	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)	3855-82-1	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
Dieldrin	60-57-1	X	X	X	X	X
Diethyl phthalate	84-66-2	X	X	X	X	X
Dimethylaminoazobenzene	60-11-7	X	ND	ND	ND	X
7,12-Dimethylbenz(a)-anthracene	57-97-6	CP(45)	ND	ND	ND	CP
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
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
Diphenylamine	122-39-4	X	X	X	X	X
1,2-Diphenylhydrazine	122-66-7	X	X	X	X	X
Di-n-octyl phthalate	117-84-0	X	X	X	X	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
Ethyl methanesulfonate	62-50-0	X	ND	ND	ND	X
Fluoranthene	206-44-0	X	X	X	X	X
Fluorene	86-73-7	X	X	X	X	X

Compounds	CAS No[a]	Appropriate Preparation Techniques				
		3510	3520	3540	3550	3580
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
Indeno(1,2,3-cd)pyrene	193-39-5	X	X	X	X	X
Isophorone	78-59-1	X	X	X	X	X
Methoxychlor	72-43-5	X	ND	ND	ND	X
3-Methylcholanthrene	56-49-5	X	ND	ND	ND	X
Methyl methanesulfonate	66-27-3	X	ND	ND	ND	X
2-Methylnaphthalene	91-57-6	X	X	ND	X	X
2-Methylphenol	95-48-7	X	ND	ND	ND	X
4-Methylphenol	106-44-5	X	ND	ND	ND	X
Naphthalene	91-20-3	X	X	X	X	X
Naphthalene-d_8 (I.S.)	1146-65-2	X	X	X	X	X
1-Naphthylamine	134-32-7	OS(44)	ND	ND	ND	X
2-Naphthylamine	91-59-8	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
Nitrobenzene	98-95-3	X	X	X	X	X
Nitrobenzene-d_5 (surr.)	4165-60-0	X	X	X	X	X
2-Nitrophenol	88-75-5	X	X	X	X	X
4-Nitrophenol	100-02-7	X	X	X	X	X
N-Nitrosodibutylamine	924-16-3	X	ND	ND	ND	X
N-Nitrosodimethylamine	62-75-9	X	X	X	X	X
N-Nitrosodiphenylamine	86-30-6	X	X	X	X	X
N-Nitrosodi-n-propylamine	621-64-7	X	X	X	X	X
N-Nitrosopiperidine	100-75-4	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.)	198-55-0	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
Phenol	108-95-2	DC(28)	X	X	X	X
Phenol-d_6 (surr.)	13127-88-3	DC(28)	X	X	X	X
2-Picoline	109-06-8	ND	ND	ND	ND	ND
Pronamide	23950-58-5	X	ND	ND	ND	X
Pyrene	129-00-0	X	X	X	X	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

Compounds	CAS No[a]	Appropriate Preparation Techniques 3510	3520	3540	3550	3580
Toxaphene	8001-35-2	X	X	X	X	X
2,4,6-Tribromophenol(surr.)	118-79-6	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

a Chemical Abstract Service Registry Number.

CP = Nonreproducible chromatographic performance.
DC = Unfavorable distribution coefficient (number in parenthesis is percent recovery).
ND = Not determined.
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 8250 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 packed column. 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 and are not being determined by Method 8080. 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 8250 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.

4.1.2 Columns

4.1.2.1 For base/neutral compound detection - 2 m x 2 mm ID stainless or glass, packed with 3% SP-2250-DB on 100/120 mesh Supelcoport or equivalent.

4.1.2.2 For acid compound detection - 2 m x 2 mm ID glass, packed with 1% SP-1240-DA on 100/120 mesh Supelcoport or equivalent.

4.1.3 Mass spectrometer - Capable of scanning from 35 to 500 amu every 1 second 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. GC-to-MS interfaces constructed entirely of glass or glass-lined materials are recommended. Glass may be deactivated by silanizing with dichlorodimethylsilane.

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/NIH Mass Spectral Library should also be available.

4.2 Syringe - 10 μL.

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 or crimp tops. 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 200 mg 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 - Calibration standards at a minimum of five concentrations 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 standards in all matrix spikes. Take into account all dilutions of sample extracts.

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[a]
Phthalate esters	3610, 3620, 3640
Nitrosamines	3610, 3620, 3640
Organochlorine pesticides & PCBs	3620, 3640, 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 basic, neutral, and acidic Priority Pollutants	3640

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

7.3 Recommended GC/MS operating conditions

Electron energy:	70 volts (nominal)
Mass range:	35-500 amu
Scan time:	1 sec/scan
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:	Helium at 30 mL/min

Conditions for base/neutral analysis (3% SP-2250-DB):

Initial column temperature and hold time:	50°C for 4 minutes
Column temperature program:	50-300°C at 8°C/min
Final column temperature hold:	300°C for 20 minutes

Conditions for acid analysis (1% SP-1240-DA):

Initial column temperature and hold time:	70°C for 2 minutes
Column temperature program:	70-200°C at 8°C/min
Final column temperature hold:	200°C for 20 minutes

7.4 Initial calibration

7.4.1 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.

7.4.2 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).

7.4.3 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). 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_x	=	Concentration of the compound being measured (ng/μL).
C_{is}	=	Concentration of the specific internal standard (ng/μL).

7.4.4 A system performance check must be performed to ensure that minimum average response factors 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-dinitrophenol; and 4-nitrophenol. The minimum acceptable average RF for these compounds 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.

7.4.4.1 The percent relative standard deviation (%RSD = 100[SD/RF]) should be less than 15% 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.

7.4.4.2 If the %RSD of any CCC is 30% or greater, then the chromatographic system is too reactive for analysis to begin. Clean or replace to injector liner and/or capillary column, then repeat the calibration procedure beginning with Section 7.5.

7.4.5 Linearity - If the %RSD of any compound is 15% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation (Section 7.7.2).

7.4.5.1 If the %RSD of any compound is greater than 15%, construct calibration curves of area ratio (A/Ais) versus concentration using first or second order regression fit of the five calibration points. The analyst should select the regression order which introduces the least calibration error into the quantitation (Sections 7.7.2.2 and 7.7.2.3). If the %RSD is <15%, use of calibration curves is a recommended alternative to average response factor calibration, and a useful diagnostic of standard preparation accuracy and absorption activity in the chromatographic system.

7.5 Daily GC/MS calibration

7.5.1 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.

7.5.2 A calibration standard(s) at mid-concentration containing all semivolatile analytes, including all required surrogates, must be analyzed every 12 hours during analysis. Compare the instrument response factor from the standards every 12 hours with the SPCC (Section 7.4.3) and CCC (Section 7.4.4) criteria.

7.5.3 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.

7.5.4 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 drift using:

$$\% \text{ Drift} = \frac{C_I - C_c}{C_I} \times 100$$

where:

C_I = Calibration Check Compound standard concentration.
C_c = Measured concentration using selected quantitation method.

If the percent difference for each CCC is less than 20%, the initial calibration is assumed to be valid. If the criterion is not met (> 20% drift) 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. If the CCCs are not analytes required by the permit, then all required analytes must meet the 20% drift criterion.

7.5.5 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 daily calibration (Section 7.4), 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.

7.6 GC/MS analysis

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

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

7.6.3 Analyze the 1 mL extract by GC/MS using the appropriate column (as specified in Section 4.1.2). The recommended GC/MS operating conditions to be used are specified in Section 7.3.

7.6.4 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.

7.6.5 Perform all qualitative and quantitative measurements as described in Section 7.7. Store the extracts at 4°C, protected from light in screw-cap vials equipped with unpierced Teflon lined septa.

7.7 Data interpretation

7.7.1 Qualitative analysis

7.7.1.1 The qualitative identification of compounds determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met.

7.7.1.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.7.1.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

7.7.1.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.7.1.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.7.1.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.7.1.2 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 $\pm$ 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 sample the 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.

7.7.2 Quantitative Analysis

7.7.2.1 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.

7.7.2.2 If the %RSD of a compound's relative response factor is 15% or less, then the concentration in the extract may be determined using the average response factor ($\overline{RF}$) from initial calibration data (7.4.5.2) and the following equation:.

$$C_{ex}\ (mg/L) = \frac{(A_x \times C_{is})}{(A_{is} \times \overline{RF})}$$

where C_{ex} is the concentration of the compound in the extract, and the other terms are as defined in Section 7.4.3.

7.7.2.3 Alternatively, the regression line fitted to the initial calibration (Section 7.4.6.1) may be used for determination of the extract concentration.

7.7.2.4 Compute the concentration of the analyte in the sample using the equations in Sections 7.7.2.4.1 and 7.7.2.4.2.

7.7.2.4.1 The concentration of the analyte in the liquid phase of the sample is calculated using the concentration of the analyte in the extract and the volume of liquid extracted, as follows:

$$\text{Concentration in liquid } (\mu g/L) = \frac{(C_{ex} \times V_{ex})}{V_o}$$

where:

V_{ex} = extract volume, in mL
V_o = volume of liquid extracted, in L.

7.7.2.4.2 The concentration of the analyte in the solid phase of the sample is calculated using the concentration of the pollutant in the extract and the weight of the solids, as follows:

$$\text{Concentration in solid } (\mu g/kg) = \frac{(C_{ex} \times V_{ex})}{W_s}$$

where:

V_{ex} = extract volume, in mL
W_s = sample weight, in kg.

7.7.2.5 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.

7.7.2.6 Quantitation of multicomponent compounds (e.g. Aroclors) is beyond the scope of Method 8250A. Normally, quantitation is performed using a GC/ECD by Method 8080.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document quality data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.2 Before processing any samples, the analyst should demonstrate, through the analysis of a reagent water blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent water blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

8.3 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g. column changed), recalibration of the system must take place.

8.4 Required instrument QC is found in the following section:

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

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

8.4.3 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 hr.

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

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

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

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

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

8.5.5 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 of interest 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 analyzed.

8.5.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Step 8.5.6.1 or 8.5.6.2.

8.5.6.1 Locate and correct the source of the problem and repeat the test for all analytes of interest beginning with Section 8.5.2.

8.5.6.2 Beginning with Section 8.5.2, 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 8.5.2.

8.6 The laboratory must, on an ongoing basis, analyze a reagent blank, a matrix spike, and a matrix spike/duplicate for each analytical batch (up to a maximum of 20 samples/batch) to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.6.1 The concentration of the spike in the sample should be determined as follows:

8.6.1.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.6.2, whichever concentration would be larger.

8.6.1.2 If the concentration of a specific analyte in the sample is not being checked against a limit specific to that analyte, the spike should be at 100 µg/L or 1 to 5 times higher than the background concentration determined in Section 8.6.2, whichever concentration would be larger.

8.6.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be at (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or 100 µg/L.

8.6.2 Analyze one sample aliquot to determine the background concentration (B) of each analyte. If necessary, prepare a new QC check sample concentrate (Section 8.5.1) appropriate for the background concentration in the sample. Spike a second sample aliquot with 1.00 mL of the QC reference sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as 100(A-B)%/T, where T is the known true value of the spike.

8.6.3 Compare the percent recovery (p) for each analyte with the corresponding QC acceptance criteria found in Table 6. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than 100 µg/L, the analyst must use either the QC acceptance criteria presented in Table 6, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of an analyte: (1) Calculate accuracy (x') using the equation found in Table 7, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 7, substituting x' for $\bar{x}$; (3) calculate the range for recovery at the spike concentration as $(100x'/T) \pm 2.44(100S'/T)\%$.

8.6.4 If any individual p falls outside the designated range for recovery, that analyte has failed the acceptance criteria. A check standard containing each analyte that failed the criteria must be analyzed as described in Section 8.7.

8.7 If any analyte fails the acceptance criteria for recovery in Section 8.6, a QC check standard containing each analyte that failed must be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC check standard will depend upon the number of analytes being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of analytes in Table 6 must be measured in the sample in Step 8.6, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spiked sample.

8.7.1 Prepare the QC reference sample by adding 1.0 mL of the QC check sample concentrate (Step 8.5.1 or 8.6.2) to 1 L of reagent water. The QC check standard needs only to contain the analytes that failed criteria in the test in Section 8.6.

8.7.2 Analyze the QC check standard to determine the concentration measured (A) of each analyte. Calculate each percent recovery (P_s) as 100(A/T)%, where T is the true value of the standard concentration.

8.7.3 Compare the percent recovery (P_s) for each analyte with the corresponding QC acceptance criteria found in Table 6. Only analytes that failed the test in Section 8.6 need to be compared with these criteria. If the recovery of any such analyte falls outside the designated range, the laboratory performance for that analyte is judged to be out of control, and the problem must be immediately identified and corrected. The result for that analyte in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.8 As part of the QC program for the laboratory, method accuracy for each matrix studied must be assessed and records must be maintained. After the analysis of five spiked samples (of the same matrix) as in Section 8.6, calculate the average percent recovery ($\bar{p}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{p} - 2s_p$ to $\bar{p} + 2s_p$. If $\bar{p}$ = 90% and s_p = 10%, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each analyte on a regular basis (e.g. after each five to ten new accuracy measurements).

8.9 To determine acceptable accuracy and precision limits for surrogate standards the following procedure should be performed.

8.9.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

8.9.2 Once a minimum of thirty samples of the same matrix have been analyzed, calculate the average percent recovery (P) and standard deviation of the percent recovery (s) for each of the surrogates.

8.9.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

Upper Control Limit (UCL) = P + 3s
Lower Control Limit (LCL) = P - 3s

8.9.4 For aqueous and soil matrices, these laboratory established surrogate control limits should, if applicable, be compared with the control limits listed in Table 8. The limits given in Table 8 are multi-laboratory performance based limits for soil and aqueous samples, and therefore, the single-laboratory limits established in Step 8.9.3 must fall within those given in Table 8 for these matrices.

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

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration".

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

8.10 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column or mass spectrometry using other ionization modes must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 Method 8250 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.

10.0 REFERENCES

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

TABLE 1.
CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS

Compound	Retention Time (min)	Method detection limit (µg/L)	Primary Ion	Secondary Ion(s)
Acenaphthene	17.8	1.9	154	153, 152
Acenaphthene-d_{10} (I.S.)	--	--	164	162, 160
Acenaphthylene	17.4	3.5	152	151, 153
Acetophenone	--	--	105	77, 51
Aldrin	24.0	1.9	66	263, 220
4-Aminobiphenyl	--	--	169	168, 170
Aniline	--	--	93	66, 65
Anthracene	22.8	1.9	178	176, 179
Aroclor-1016[b]	18-30	--	222	260, 292
Aroclor-1221[b]	15-30	30	190	224, 260
Aroclor-1232[b]	15-32	--	190	224, 260
Aroclor-1242[b]	15-32	--	222	256, 292
Aroclor-1248[b]	12-34	--	292	362, 326
Aroclor-1254[b]	22-34	36	292	362, 326
Aroclor-1260[b]	23-32	--	360	362, 394
Benzidine[a]	28.8	44	184	92, 185
Benzoic acid	--	--	122	105, 77
Benzo(a)anthracene	31.5	7.8	228	229, 226
Benzo(b)fluoranthene	34.9	4.8	252	253, 125
Benzo(k)fluoranthene	34.9	2.5	252	253, 125
Benzo(g,h,i)perylene	45.1	4.1	276	138, 277
Benzo(a)pyrene	36.4	2.5	252	253, 125
Benzyl alcohol	--	--	108	79, 77
α-BHC[a]	21.1	--	183	181, 109
ß-BHC	23.4	4.2	181	183, 109
δ-BHC	23.7	3.1	183	181, 109
γ-BHC (Lindane)[a]	22.4	--	183	181, 109
Bis(2-chloroethoxy)methane	12.2	5.3	93	95, 123
Bis(2-chloroethyl) ether	8.4	5.7	93	63, 95
Bis(2-chloroisopropyl) ether	9.3	5.7	45	77, 121
Bis(2-ethylhexyl) phthalate	30.6	2.5	149	167, 279
4-Bromophenyl phenyl ether	21.2	1.9	248	250, 141
Butyl benzyl phthalate	29.9	2.5	149	91, 206
Chlordane[b]	19-30	--	373	375, 377
4-Chloroaniline	--	--	127	129
1-Chloronaphthalene	--	--	162	127, 164
2-Chloronaphthalene	15.9	1.9	162	127, 164
4-Chloro-3-methylphenol	13.2	3.0	107	144, 142
2-Chlorophenol	5.9	3.3	128	64, 130
4-Chlorophenyl phenyl ether	19.5	4.2	204	206, 141
Chrysene	31.5	2.5	228	226, 229
Chrysene-d_{12} (I.S.)	--	--	240	120, 236
4,4'-DDD	28.6	2.8	235	237, 165
4,4'-DDT	29.3	4.7	235	237, 165

TABLE 1.
(Continued)

Compound	Retention Time (min)	Method detection limit (µg/L)	Primary Ion	Secondary Ion(s)
Dibenz(a,j)acridine	--	--	279	280, 277
Dibenz(a,h)anthracene	43.2	2.5	278	139, 279
Dibenzofuran	--	--	168	139
Di-n-butyl phthalate	24.7	2.5	149	150, 104
1,2-Dichlorobenzene	8.4	1.9	146	148, 111
1,3-Dichlorobenzene	7.4	1.9	146	148, 111
1,4-Dichlorobenzene	7.8	4.4	146	148, 111
1,4-Dichlorobenzene-d_4 (I.S.)	--	--	152	150, 115
3,3'-Dichlorobenzidine	32.2	16.5	252	254, 126
2,4-Dichlorophenol	9.8	2.7	162	164, 98
2,6-Dichlorophenol	--	--	162	164, 98
Dieldrin	27.2	2.5	79	263, 279
Diethyl phthalate	20.1	1.9	149	177, 150
p-Dimethylaminoazobenzene	--	--	120	225, 77
7,12-Dimethylbenz(a)anthracene	--	--	256	241, 257
α-,α-Dimethylphenethylamine	--	--	58	91, 42
2,4-Dimethylphenol	9.4	2.7	122	107, 121
Dimethyl phthalate	18.3	1.6	163	194, 164
4,6-Dinitro-2-methylphenol	16.2	24	198	51, 105
2,4-Dinitrophenol	15.9	42	184	63, 154
2,4-Dinitrotoluene	19.8	5.7	165	63, 89
2,6-Dinitrotoluene	18.7	1.9	165	63, 89
Diphenylamine	--	--	169	168, 167
1,2-Diphenylhydrazine	--	--	77	105, 182
Di-n-octyl phthalate	32.5	2.5	149	167, 43
Endosulfan I[a]	26.4	--	195	339, 341
Endosulfan II[a]	28.6	--	337	339, 341
Endosulfan sulfate	29.8	5.6	272	387, 422
Endrin[a]	27.9	--	263	82, 81
Endrin aldehyde	--	--	67	345, 250
Endrin ketone	--	--	317	67, 319
Ethyl methanesulfonate	--	--	79	109, 97
Fluoranthene	26.5	2.2	202	101, 203
Fluorene	19.5	1.9	166	165, 167
2-Fluorobiphenyl (surr.)	--	--	172	171
2-Fluorophenol (surr.)	--	--	112	64
Heptachlor	23.4	1.9	100	272, 274
Heptachlor epoxide	25.6	2.2	353	355, 351
Hexachlorobenzene	21.0	1.9	284	142, 249
Hexachlorobutadiene	11.4	0.9	225	223, 227
Hexachlorocyclopentadiene[a]	13.9	--	237	235, 272
Hexachloroethane	8.4	1.6	117	201, 199
Indeno(1,2,3-cd)pyrene	42.7	3.7	276	138, 227
Isophorone	11.9	2.2	82	95, 138
Methoxychlor	--	--	227	228

TABLE 1.
(Continued)

Compound	Retention Time (min)	Method detection limit (µg/L)	Primary Ion	Secondary Ion(s)
3-Methylcholanthrene	--	--	268	253, 267
Methyl methanesulfonate	--	--	80	79, 65
2-Methylnaphthalene	--	--	142	141
2-Methylphenol	--	--	108	107, 79
4-Methylphenol	--	--	108	107, 79
Naphthalene	12.1	1.6	128	129, 127
Naphthalene-d_8 (I.S.)	--	--	136	68
1-Naphthylamine	--	--	143	115, 116
2-Naphthylamine	--	--	143	115, 116
2-Nitroaniline	--	--	65	92, 138
3-Nitroaniline	--	--	138	108, 92
4-Nitroaniline	--	--	138	108, 92
Nitrobenzene	11.1	1.9	77	123, 65
Nitrobenzene-d_5 (surr.)	--	--	82	128, 54
2-Nitrophenol	6.5	3.6	139	109, 65
4-Nitrophenol	20.3	2.4	139	109, 65
N-Nitroso-di-n-butylamine	--	--	84	57, 41
N-Nitrosodimethylamine[a]	--	--	42	74, 44
N-Nitrosodiphenylamine[a]	20.5	1.9	169	168, 167
N-Nitroso-di-N-propylamine	--	--	70	130, 42
N-Nitrosopiperidine	--	--	42	114, 55
Pentachlorobenzene	--	--	250	252, 248
Pentachloronitrobenzene	--	--	295	237, 142
Pentachlorophenol	17.5	3.6	266	264, 268
Perylene-d_{12} (I.S.)	--	--	264	260, 265
Phenacetin	--	--	108	109, 179
Phenanthrene	22.8	5.4	178	179, 176
Phenanthrene-d_{10} (I.S.)	--	--	188	94, 80
Phenol	8.0	1.5	94	65, 66
Phenol-d_6 (surr.)	--	--	99	42, 71
2-Picoline	--	--	93	66, 92
Pronamide	--	--	173	175, 145
Pyrene	27.3	1.9	202	200, 203
Terphenyl-d_{14} (surr.)	--	--	244	122, 212
1,2,4,5-Tetrachlorobenzene	--	--	216	214, 218
2,3,4,6-Tetrachlorophenol	--	--	232	230, 131
Toxaphene[b]	25-34	--	159	231, 233
2,4,6-Tribromophenol (surr.)	--	--	330	332, 141
1,2,4-Trichlorobenzene	11.6	1.9	180	182, 145
2,4,5-Trichlorophenol	--	--	196	198, 200
2,4,6-Trichlorophenol	11.8	2.7	196	198, 200

[a]See Section 1.3
[b]These compounds are mixtures of various isomers.

TABLE 2.
DETERMINATION OF ESTIMATED QUANTITATION LIMITS (EQL)
FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-concentration soil by ultrasonic extraction with GPC cleanup	670
High-concentration soil and sludges by ultrasonic extraction	10,000
Non-water miscible waste	100,000

[a] Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

[b] EQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

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-Nitroso-di-n-phenylamine	Phenol
Di-n-octyl phthalate	Pentachlorophenol
Benzo(a)pyrene	2,4,6-Trichlorophenol

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

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 5.
SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES
ASSIGNED FOR QUANTITATION
(Continued)

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-Dimethylphenethylamine	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_8 (surr.)	1-Naphthylamine
N-Nitroso-di-n-propylamine	2-Nitrophenol	2-Naphthylamine
Phenol	N-Nitroso-di-n-butylamine	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-Tetrachloro-benzene

(surr.) = surrogate

TABLE 6.
QC ACCEPTANCE CRITERIA[a]

Compound	Test conc. (μg/L)	Limit for s (μg/L)	Range for $\bar{x}$ (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
Benzo(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
Butyl benzyl phthalate	100	23.4	D-139.9	D-152
ß-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-octyl phthalate	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
Hexachloroethane	100	24.5	55.2-100.0	40-113

TABLE 6.
QC ACCEPTANCE CRITERIA[a]
(Continued)

Compound	Test conc. (µg/L)	Limit for s (µg/L)	Range for $\bar{x}$ (µg/L)	Range p, p_s (%)
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-Nitroso-di-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]

Parameter	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
Benzo(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
Butyl benzyl phthalate	0.66C-1.68	0.18$\bar{x}$+0.94	0.53$\bar{x}$+0.92
ß-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
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

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

Parameter	Accuracy, as recovery, x′ (μg/L)	Single analyst precision, s_r' (μg/L)	Overall precision, S′ (μg/L)
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-Nitroso-di-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.

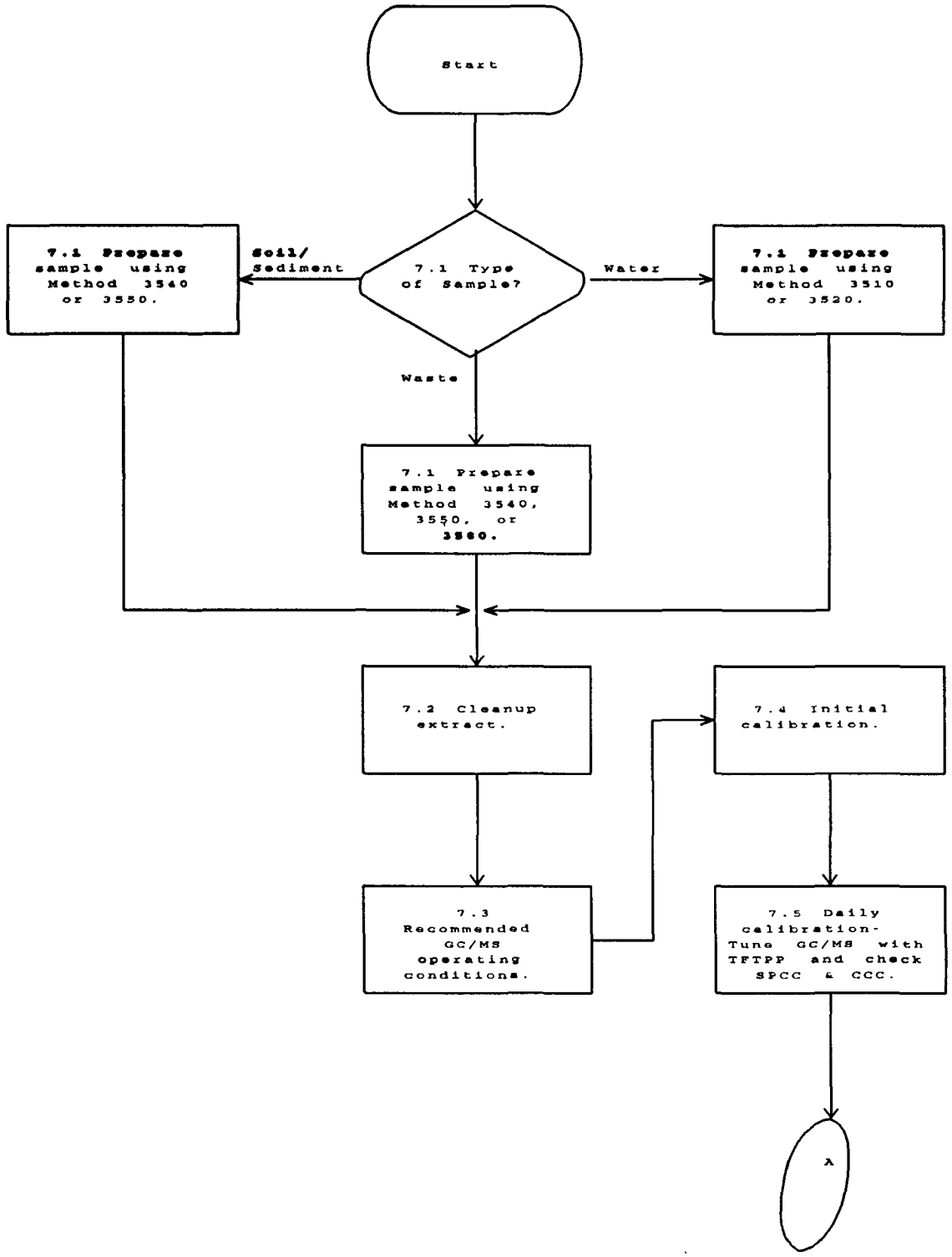
S′ = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{x}$, in μg/L.

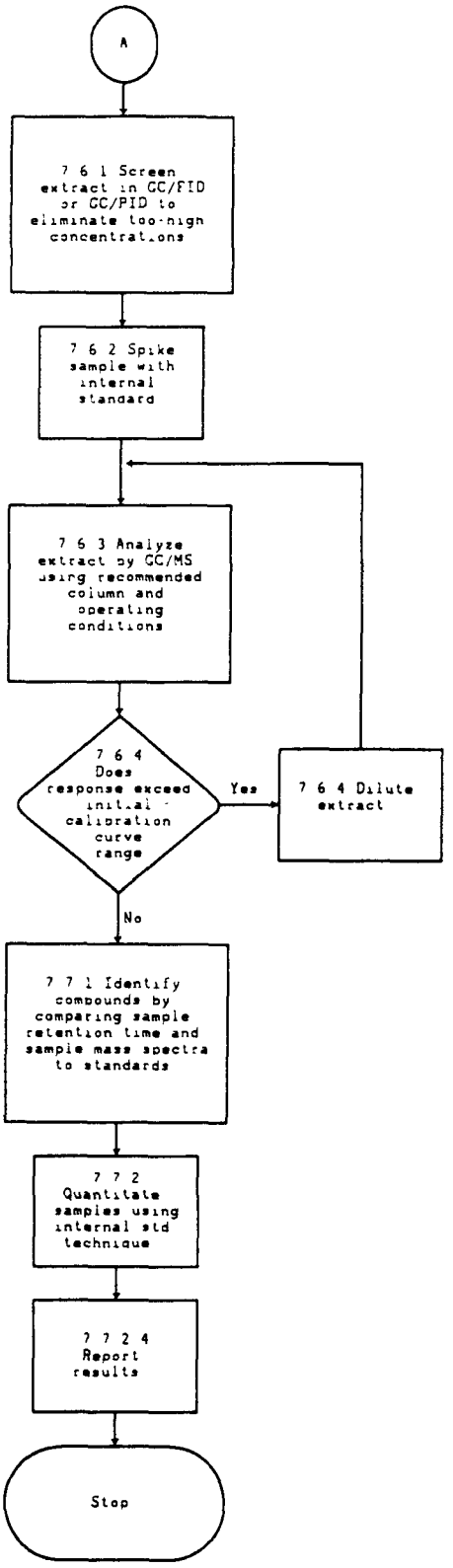
C = True value for the concentration, in μg/L.

$\bar{x}$ = 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/Medium Water	Low/Medium 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


Start
7.1 Type of Sample?
Soil/ Sediment
Water
Waste
7.1 Prepare sample using Method 3540 or 3550.
7.1 Prepare sample using Method 3510 or 3520.
7.1 Prepare sample using Method 3540, 3550, or 3580.
7.2 Cleanup extract.
7.4 Initial calibration.
7.3 Recommended GC/MS operating conditions.
7.5 Daily calibration- Tune GC/MS with TFTPP and check SPCC & CCC.
A


A
7 6 1 Screen extract in GC/FID or GC/PID to eliminate too-high concentrations
7 6 2 Spike sample with internal standard
7 6 3 Analyze extract by GC/MS using recommended column and operating conditions
7 6 4 Does response exceed initial calibration curve range
Yes
7 6 4 Dilute extract
No
7 7 1 Identify compounds by comparing sample retention time and sample mass spectra to standards
7 7 2 Quantitate samples using internal std technique
7 7 2 4 Report results
Stop

METHOD 8260A

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

1.0 SCOPE AND APPLICATION

1.1 Method 8260 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including ground water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. The following compounds can be determined by this method:

Analyte	CAS No.[b]	Appropriate Technique	
		Purge-and-Trap	Direct Injection
Acetone	67-64-1	pp	a
Acetonitrile	75-05-8	pp	a
Acrolein	107-02-8	pp	a
Acrylonitrile	107-13-1	pp	a
Allyl alcohol	107-18-6	ht	a
Allyl chloride	107-05-1	a	a
Benzene	71-43-2	a	a
Benzyl chloride	100-44-7	a	a
Bromoacetone	598-31-2	pp	a
Bromochloromethane (I.S.)	74-97-5	a	a
Bromodichloromethane	75-27-4	a	a
4-Bromofluorobenzene (surr.)	460-00-4	a	a
Bromoform	75-25-2	a	a
Bromomethane	74-83-9	a	a
n-Butanol	71-36-3	ht	a
2-Butanone (MEK)	78-93-3	pp	a
Carbon disulfide	75-15-0	pp	a
Carbon tetrachloride	56-23-5	a	a
Chloral hydrate	302-17-0	pp	a
Chlorobenzene	108-90-7	a	a
2-Chloro-1,3-butadiene	126-99-8	a	a
Chlorodibromomethane	124-48-1	a	a
Chloroethane	75-00-3	a	a
2-Chloroethanol	107-03-3	pp	a
bis-(2-Chloroethyl) sulfide	505-60-2	pp	a
2-Chloroethyl vinyl ether	110-75-8	a	a
Chloroform	67-66-3	a	a
Chloromethane	74-87-3	a	a
Chloroprene	126-99-8	a	pc
3-Chloropropene	107-05-1	a	a
3-Chloropropionitrile	542-76-7	i	pc

Analyte	CAS No.[b]	Appropriate Technique: Purge-and-Trap	Appropriate Technique: Direct Injection
1,2-Dibromo-3-chloropropane	96-12-8	pp	a
1,2-Dibromoethane	106-93-4	a	a
Dibromomethane	74-95-3	a	a
1,2-Dichlorobenzene	95-50-1	a	a
1,3-Dichlorobenzene	541-73-1	a	a
1,4-Dichlorobenzene	106-46-7	a	a
cis-1,4-Dichloro-2-butene	1476-11-5	a	a
trans-1,4-Dichloro-2-butene	110-57-6	pp	a
Dichlorodifluoromethane	75-71-8	a	a
1,1-Dichloroethane	75-34-3	a	a
1,2-Dichloroethane	107-06-2	a	a
1,1-Dichloroethene	75-35-4	a	a
trans-1,2-Dichloroethene	156-60-5	a	a
1,2-Dichloropropane	78-87-5	a	a
1,3-Dichloro-2-propanol	96-23-1	pp	a
cis-1,3-Dichloropropene	10061-01-5	a	a
trans-1,3-Dichloropropene	10061-02-6	a	a
1,2,3,4-Diepoxybutane	1464-53-5	a	a
Diethyl ether	60-29-7	a	a
1,4-Difluorobenzene (I.S.)	540-36-3	a	a
1,4-Dioxane	123-91-1	pp	a
Epichlorohydrin	106-89-8	i	a
Ethanol	64-17-5	i	a
Ethyl acetate	141-78-6	i	a
Ethylbenzene	100-41-4	a	a
Ethylene oxide	75-21-8	pp	a
Ethyl methacrylate	97-63-2	a	a
Hexachlorobutadiene	87-68-3	a	a
Hexachloroethane	67-72-1	i	a
2-Hexanone	591-78-6	pp	a
2-Hydroxypropionitrile	78-97-7	i	pc
Iodomethane	74-88-4	a	a
Isobutyl alcohol	78-83-1	pp	a
Isopropylbenzene	98-82-8	a	a
Malononitrile	109-77-3	pp	a
Methacrylonitrile	126-98-7	pp	a
Methanol	67-56-1	i	a
Methylene chloride	75-09-2	a	a
Methyl iodide	74-88-4	a	a
Methyl methacrylate	80-62-6	a	a
4-Methyl-2-pentanone (MIBK)	108-10-1	pp	a
Naphthalene	91-20-3	a	a
Nitrobenzene	98-95-3	a	a
2-Nitropropane	79-46-9	a	a
Pentachloroethane	76-01-7	i	a
2-Picoline	109-06-8	pp	a
Propargyl alcohol	107-19-7	pp	a

Analyte	CAS No.[b]	Appropriate Technique: Purge-and-Trap	Appropriate Technique: Direct Injection
ß-Propiolactone	57-57-8	pp	a
Propionitrile (ethyl cyanide)	107-12-0	ht	pc
n-Propylamine	107-10-8	a	a
Pyridine	110-86-1	i	a
Styrene	100-42-5	a	a
1,1,1,2-Tetrachloroethane	630-20-6	a	a
1,1,2,2-Tetrachloroethane	79-34-5	a	a
Tetrachloroethene	127-18-4	a	a
Toluene	108-88-3	a	a
1,2,4-Trichlorobenzene	120-82-1	a	a
1,1,1-Trichloroethane	71-55-6	a	a
1,1,2-Trichloroethane	79-00-5	a	a
Trichloroethene	79-01-6	a	a
Trichlorofluoromethane	75-69-4	a	a
1,2,3-Trichloropropane	96-18-4	a	a
Vinyl acetate	108-05-4	a	a
Vinyl chloride	75-01-4	a	a
o-Xylene	95-47-6	a	a
m-Xylene	108-38-3	a	a
p-Xylene	106-42-3	a	a

a Adequate response by this technique.
b Chemical Abstract Services Registry Number.
ht Method analyte only when purged at 80°C
i Inappropriate technique for this analyte.
pc Poor chromatographic behavior.
pp Poor purging efficiency resulting in high EQLs.

1.2 Method 8260 can be used to quantitate most volatile organic compounds that have boiling points below 200°C and that are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique. However, for the more soluble compounds, quantitation limits are approximately ten times higher because of poor purging efficiency. Such compounds include low-molecular-weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. See Tables 1 and 2 for lists of analytes and retention times that have been evaluated on a purge-and-trap GC/MS system. Also, the method detection limits for 25 mL sample volumes are presented. The following analytes are also amenable to analysis by Method 8260:

Bromobenzene	1,3-Dichloropropane
n-Butylbenzene	2,2-Dichloropropane
sec-Butylbenzene	1,1-Dichloropropene
tert-Butylbenzene	Fluorobenzene
Chloroacetonitrile	p-Isopropyltoluene
1-Chlorobutane	Methyl acrylate

1-Chlorohexane	Methyl-t-butyl ether
2-Chlorotoluene	Pentafluorobenzene
4-Chlorotoluene	n-Propylbenzene
Crotonaldehyde	1,2,3-Trichlorobenzene
Dibromofluoromethane	1,2,4-Trimethylbenzene
cis-1,2-Dichloroethene	1,3,5-Trimethylbenzene

1.3 The estimated quantitation limit (EQL) of Method 8260 for an individual compound is somewhat instrument dependent. Using standard quadrupole instrumentation, limits should be approximately 5 µg/kg (wet weight) for soil/sediment samples, 0.5 mg/kg (wet weight) for wastes, and 5 µg/L for ground water (see Table 3). Somewhat lower limits may be achieved using an ion trap mass spectrometer or other instrumentation of improved design. No matter which instrument is used, EQLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

1.4 Method 8260 is based upon a purge-and-trap, gas chromatographic/mass spectrometric (GC/MS) procedure. This method is restricted to use by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

1.5 An additional method for sample introduction is direct injection. This technique has been tested for the analysis of waste oil diluted with hexadecane 1:1 (vol/vol) and may have application for the analysis of some alcohols and aldehydes in aqueous samples.

2.0 SUMMARY OF METHOD

2.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by direct injection (in limited applications). Purged sample components are trapped in a tube containing suitable sorbent materials. When purging is complete, the sorbent tube is heated and backflushed with helium to desorb trapped sample components. The analytes are desorbed directly to a large bore capillary or cryofocussed on a capillary precolumn before being flash evaporated to a narrow bore capillary for analysis. The column is temperature programmed to separate the analytes which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph. Wide bore capillary columns require a jet separator, whereas narrow bore capillary columns can be directly interfaced to the ion source.

2.2 If the above sample introduction techniques are not applicable, a portion of the sample is dispersed in solvent to dissolve the volatile organic constituents. A portion of the solution is combined with organic-free reagent water in the purge chamber. It is then analyzed by purge-and-trap GC/MS following the normal water method.

2.3 Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron

impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard with a five-point calibration curve.

2.4 The method includes specific calibration and quality control steps that replace the general requirements in Method 8000.

3.0 INTERFERENCES

3.1 Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of calibration and reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter (Figure 1). Subtracting blank values from sample results is not permitted. If reporting values not corrected for blanks result in what the laboratory feels is a false positive for a sample, this should be fully explained in text accompanying the uncorrected data.

3.2 Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. The preventive technique is rinsing of the purging apparatus and sample syringes with two portions of organic-free reagent water between samples. After analysis of a sample containing high concentrations of volatile organic compounds, one or more calibration blanks should be analyzed to check for cross contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds or high concentrations of compounds being determined, it may be necessary to wash the purging device with a soap solution, rinse it with organic-free reagent water, and then dry the purging device in an oven at 105°C. In extreme situations, the whole purge and trap device may require dismantling and cleaning. Screening of the samples prior to purge and trap GC/MS analysis is highly recommended to prevent contamination of the system. This is especially true for soil and waste samples. Screening may be accomplished with an automated headspace technique or by Method 3820 (Hexadecane Extraction and Screening of Purgeable Organics).

3.2.1 The low purging efficiency of many analytes from a 25 mL sample often results in significant concentrations remaining in the sample purge vessel after analysis. After removal of the analyzed sample aliquot and three rinses of the purge vessel with analyte free water, it is required that the empty vessel be subjected to a heated purge cycle prior to the analysis of another sample in the same purge vessel to reduce sample to sample carryover.

3.3 Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride. Otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed

from stainless steel or copper tubing. Laboratory clothing worn by the analyst should be clean since clothing previously exposed to methylene chloride fumes during liquid/liquid extraction procedures can contribute to sample contamination.

3.4 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal into the sample during shipment and storage. A trip blank prepared from organic-free reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.5 Use of sensitive mass spectrometers to achieve lower detection level will increase the potential to detect laboratory contaminants as interferences.

3.6 Direct injection - Some contamination may be eliminated by baking out the column between analyses. Changing the injector liner will reduce the potential for cross-contamination. A portion of the analytical column may need to be removed in the case of extreme contamination. Use of direct injection will result in the need for more frequent instrument maintenance.

3.7 If hexadecane is added to samples or petroleum samples are analyzed, some chromatographic peaks will elute after the target analytes. The oven temperature program must include a post-analysis bake out period to ensure that semi-volatile hydrocarbons are volatilized.

4.0 APPARATUS AND MATERIALS

4.1 Purge-and-trap device - aqueous samples, described in Method 5030.

4.2 Purge-and-trap device - solid samples, described in Method 5030.

4.3 Injection port liners (HP catalogue #18740-80200, or equivalent) are modified for direct injection analysis by placing a 1-cm plug of pyrex wool approximately 50-60 mm down the length of the injection port towards the oven. An 0.53 mm id column is mounted 1 cm into the liner from the oven side of the injection port, according to manufacturer's specifications.

Figure 1 Modified Injector

4.4 Gas chromatography/mass spectrometer/data system

4.4.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection or interface to purge-and-trap apparatus. The system includes all required accessories, including syringes, analytical columns, and

gases. The GC should be equipped with variable constant differential flow controllers so that the column flow rate will remain constant throughout desorption and temperature program operation. For some column configurations, the column oven must be cooled to < 30°C, therefore, a subambient oven controller may be required. The capillary column should be directly coupled to the source.

4.4.1.1 Capillary precolumn interface when using cryogenic cooling - This device interfaces the purge and trap concentrator to the capillary gas chromatograph. The interface condenses the desorbed sample components and focuses them into a narrow band on an uncoated fused silica capillary precolumn. When the interface is flash heated, the sample is transferred to the analytical capillary column.

4.4.1.1.1 During the cryofocussing step, the temperature of the fused silica in the interface is maintained at -150°C under a stream of liquid nitrogen. After the desorption period, the interface must be capable of rapid heating to 250°C in 15 seconds or less to complete the transfer of analytes.

4.4.2 Gas chromatographic columns

4.4.2.1 Column 1 - 60 m x 0.75 mm ID capillary column coated with VOCOL (Supelco), 1.5 μm film thickness, or equivalent.

4.4.2.2 Column 2 - 30 - 75 m x 0.53 mm ID capillary column coated with DB-624 (J&W Scientific), Rt_x-502.2 (RESTEK), or VOCOL (Supelco), 3 μm film thickness, or equivalent.

4.4.2.3 Column 3 - 30 m x 0.25 - 0.32 mm ID capillary column coated with 95% dimethyl - 5% diphenyl polysiloxane (DB-5, Rt_x-5, SPB-5, or equivalent), 1 μm film thickness.

4.4.3 Mass spectrometer - Capable of scanning from 35 to 300 amu every 2 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 p-Bromofluorobenzene (BFB) which meets all of the criteria in Table 4 when 5-50 ng of the GC/MS tuning standard (BFB) is injected through the GC. To ensure sufficient precision of mass spectral data, the desirable MS scan rate allows acquisition of at least five spectra while a sample component elutes from the GC.

4.4.3.1 The ion trap mass spectrometer may be used if it is capable of axial modulation to reduce ion-molecule reactions and can produce electron impact-like spectra that match those in the EPA/NIST Library. The mass spectrometer must be capable of producing a mass spectrum for BFB which meets all of the criteria in Table 3 when 5 or 50 ng are introduced.

4.4.4 GC/MS interface - Two alternatives are used to interface the GC to the mass spectrometer.

4.4.4.1 Direct coupling by inserting the column into the mass spectrometer is generally used for 0.25-0.32 mm id columns.

4.4.4.2 A separator including an all transfer line and glass enrichment device or split interface is used with an 0.53 mm column.

4.4.4.3 Any enrichment device or transfer line can be used if all of the performance specifications described in Section 8 (including acceptable calibration at 50 ng or less) can be achieved. GC-to-MS interfaces constructed entirely of glass or of glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

4.4.5 Data system - A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting 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.

4.5 Microsyringes - 10, 25, 100, 250, 500, and 1,000 µL.

4.6 Syringe valve - Two-way, with Luer ends (three each), if applicable to the purging device.

4.7 Syringes - 5, 10, or 25 mL, gas-tight with shutoff valve.

4.8 Balance - Analytical, 0.0001 g, and top-loading, 0.1 g.

4.9 Glass scintillation vials - 20 mL, with Teflon lined screw-caps or glass culture tubes with Teflon lined screw-caps.

4.10 Vials - 2 mL, for GC autosampler.

4.11 Disposable pipets - Pasteur.

4.12 Volumetric flasks, Class A - 10 mL and 100 mL, with ground-glass stoppers.

4.13 Spatula - Stainless steel.

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 Methanol, CH_3OH - Pesticide quality or equivalent, demonstrated to be free of analytes. Store apart from other solvents.

5.4 Reagent Hexadecane - Reagent hexadecane is defined as hexadecane in which interference is not observed at the method detection limit of compounds of interest.

5.4.1 In order to demonstrate that all interfering volatiles have been removed from the hexadecane, a direct injection blank must be analyzed.

5.5 Polyethylene glycol, $H(OCH_2CH_2)_nOH$ - Free of interferences at the detection limit of the target analytes.

5.6 Hydrochloric acid (1:1 v/v), HCl - Carefully add a measured volume of concentrated HCl to an equal volume of organic-free reagent water.

5.7 Stock solutions - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol, using assayed liquids or gases, as appropriate.

5.7.1 Place about 9.8 mL of methanol in a 10 mL tared ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.7.2 Add the assayed reference material, as described below.

5.7.2.1 Liquids - Using a 100 μL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.7.2.2 Gases - To prepare standards for any compounds that boil below 30°C (e.g. bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5 mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared by using a lecture bottle equipped with a Hamilton Lecture Bottle Septum (#86600). Attach Teflon tubing to the side arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.7.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. 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.

5.7.4 Transfer the stock standard solution into a bottle with a Teflon lined screw-cap. Store, with minimal headspace, at -10°C to -20°C and protect from light.

5.7.5 Prepare fresh standards for gases weekly or sooner if comparison with check standards indicates a problem. Reactive compounds such as 2-chloroethyl vinyl ether and styrene may need to be prepared more frequently. All other standards must be replaced after two months, or sooner if comparison with check standards indicates a problem. Both gas and liquid standards must be monitored closely by comparison to the initial calibration curve and by comparison to QC check standards. It may be necessary to replace the standards more frequently if either check exceeds a 25% drift.

5.7.6 Optionally calibration using a certified gaseous mixture can be accomplished daily utilizing commercially available gaseous analyte mixture of bromomethane, chloromethane, chloroethane, vinyl chloride, dichlorodifluoromethane and trichlorofluoromethane in nitrogen. These mixtures of documented quality are stable for as long as six months without refrigeration. (VOA-CYL III, RESTEK Corporation, Cat. #20194 or equivalent).

5.7.6.1 Preparation of Calibration Standards From a Gas Mixture

5.7.6.1.1 Before removing the cylinder shipping cap, be sure the valve is completely closed (turn clockwise). The contents are under pressure and should be used in a well-ventilated area.

5.7.6.1.2 Wrap the pipe thread end of the Luer fitting with Teflon tape. Remove the shipping cap from the cylinder and replace it with the Luer fitting.

5.7.6.1.3 Transfer half the working standard containing other analytes, internal standards, and surrogates to the purge apparatus.

5.7.6.1.4 Purge the Luer fitting and stem on the gas cylinder prior to sample removal using the following sequence:

a) Connect either the 100 µL or 500 µL Luer syringe to the inlet fitting of the cylinder.

b) Make sure the on/off valve on the syringe is in the open position.

c) Slowly open the valve on the cylinder and withdraw a full syringe volume.

d) **Be sure to close the valve on the cylinder before you withdraw the syringe from the Luer fitting.**

e) Expel the gas from the syringe into a well-ventilated area.

f) Repeat steps a through e one more time to fully purge the fitting.

5.7.6.1.5 Once the fitting and stem have been purged, quickly withdraw the volume of gas you require using steps 5.6.6.1.4(a) through (d). Be sure to close the valve on the cylinder and syringe before you withdraw the syringe from the Luer fitting.

5.7.6.1.6 Open the syringe on/off valve for 5 seconds to reduce the syringe pressure to atmospheric pressure. The pressure in the cylinder is ~30psi.

5.7.6.1.7 The gas mixture should be quickly transferred into the reagent water through the female Luer fitting located above the purging vessel.

NOTE: Make sure the arrow on the 4-way valve is pointing toward the female Luer fitting when transferring the sample from the syringe. **Be sure to switch the 4-way valve back to the closed position before removing the syringe from the luer fitting.**

5.7.6.1.8 Transfer the remaining half of the working standard into the purging vessel. This procedure insures that the total volume of gas mix is flushed into the purging vessel, with none remaining in the valve or lines.

5.7.6.1.9 Concentration of each compound in the cylinder is typically 0.0025 µg/µL.

5.7.6.1.10 The following are the recommended gas volumes spiked in to 5 mLs of water to produce a typical 5-point calibration:

Gas Volume	Calibration Concentration
40 µL	20 µg/L
100 µL	50 µg/L
200 µL	100 µg/L
300 µL	150 µg/L
400 µL	200 µg/L

5.7.6.1.11 The following are the recommended gas volumes spiked in to 25-mls of water to produce a typical 5-point calibration:

Gas Volume	Calibration Concentration
10 µL	1 µg/L
20 µL	2 µg/L
50 µL	5 µg/L
100 µL	10 µg/L
250 µL	25 µg/L

5.8 Secondary dilution standards - Using stock standard solutions, prepare in methanol, secondary dilution standards containing the compounds of interest, either singly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Store in a vial with no headspace for one week only.

5.9 Surrogate standards - The surrogates recommended are toluene-d_8, 4-bromofluorobenzene, and dibromofluoromethane. Other compounds may be used as surrogates, depending upon the analysis requirements. A stock surrogate solution in methanol should be prepared as described above, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 50-250 µg/10 mL in methanol. Each water sample undergoing GC/MS analysis must be spiked with 10 µL of the surrogate spiking solution prior to analysis.

5.9.1 If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute surrogate solutions may be required.

5.10 Internal standards - The recommended internal standards are fluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected by GC/MS. Prepare internal standard stock and secondary dilution standards in methanol using the procedures described in Sections 5.7 and 5.8. It is recommended that the secondary dilution standard should be prepared at a concentration of 25 mg/L of each internal standard compound. Addition of 10 µL of this standard to 5.0 mL of sample or calibration standard would be the equivalent of 50 µg/L.

5.10.1 If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute internal standard solutions may be required. Area counts of the internal standard peaks should be between 50-200% of the area of the target analytes in the mid-point calibration analysis.

5.11 4-Bromofluorobenzene (BFB) standard - A standard solution containing 25 ng/µL of BFB in methanol should be prepared.

5.11.1 If a more sensitive mass spectrometer is employed to achieve lower detection levels, a more dilute BFB standard solution may be required.

5.12 Calibration standards - Calibration standards at a minimum of five concentrations should be prepared from the secondary dilution of stock standards (see Sections 5.7 and 5.8). Prepare these solutions in organic-free reagent water. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to

the expected 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). Calibration standards must be prepared daily.

5.13 Matrix spiking standards - Matrix spiking standards should be prepared from volatile organic compounds which will be representative of the compounds being investigated. At a minimum, the matrix spike should include 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. It is desirable to perform a matrix spike using compounds found in samples. Some permits may require spiking specific compounds of interest, especially if they are polar and would not be represented by the above listed compounds. The standard should be prepared in methanol, with each compound present at a concentration of 250 µg/10.0 mL.

5.13.1 If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute matrix spiking solutions may be required.

5.14 Great care must be taken to maintain the integrity of all standard solutions. It is recommended all standards in methanol be stored at -10°C to -20°C in amber bottles with Teflon lined screw-caps.

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 Three alternate methods are provided for sample introduction. All internal standards, surrogates, and matrix spikes (when applicable) must be added to samples before introduction.

7.1.1 Direct injection - in very limited application, (e.g., volatiles in waste oil or aqueous process wastes) direct injection of aqueous samples or samples diluted according to Method 3585 may be appropriate. Direct injection has been used for the analysis of volatiles in waste oil (diluted 1:1 with hexadecane) and for determining if the sample is ignitable (aqueous injection, Methods 1010 or 1020). Direct injection is only permitted for the determination of volatiles at the TCLP regulatory limits, at concentrations in excess of 10,000 µg/L, or for water-soluble compounds that do not purge.

7.1.2 Purge-and-trap for aqueous samples, see Method 5030 for details.

7.1.3 Purge-and-trap for solid samples, see Method 5030 for details.

7.2 Chromatographic conditions

7.2.1 General:

Injector temperature:	200-225°C
Transfer line temperature:	250-300°C

7.2.2 Column 1 (A sample chromatogram is presented in Figure 5)

Carrier gas (He) flow rate:	15 mL/min
Initial temperature:	10°C, hold for 5 minutes
Temperature program:	6°C/min to 160°C
Final temperature:	160°C, hold until all expected compounds have eluted.

7.2.3 Column 2, Cryogenic cooling (A sample chromatogram is presented in Figure 6)

Carrier gas (He) flow rate:	15 mL/min
Initial temperature:	10°C, hold for 5 minutes
Temperature program:	6°C/min to 160°C
Final temperature:	160°C, hold until all expected compounds have eluted.

7.2.4 Column 2, Non-cryogenic cooling (A sample chromatogram is presented in Figure 7). It is recommended that carrier gas flow and split and make-up gases be set using performance of standards as guidance. Set the carrier gas head pressure to ≈ 10 psi and the split to ≈ 30 mL/min. Optimize the make-up gas flow for the separator (approximately 30 mL/min) by injecting BFB, and determining the optimum response when varying the make-up gas. This will require several injections of BFB. Next, make several injections of the volatile working standard with all analytes of interest. Adjust the carrier and split to provide optimum chromatography and response. This is an especially critical adjustment for the volatile gas analytes. The head pressure should optimize between 8-12 psi and the split between 20-60 mL/min. The use of the splitter is important to minimize the effect of water on analyte response, to allow the use of a larger volume of helium during trap desorption, and to slow column flow.

Initial temperature:	45°C, hold for 2 minutes
Temperature program:	8°C/min to 200°C
Final temperature:	200°C, hold for 6 minutes.

A trap preheated to 150°C prior to trap desorption is required to provide adequate chromatography of the gas analytes.

7.2.5 Column 3 (A sample chromatogram is presented in Figure 8)

Carrier gas (He) flow rate:	4 mL/min
Initial temperature:	10°C, hold for 5 minutes
Temperature program:	6°C/min to 70°C, then 15°C/min to 145°C
Final temperature:	145°C, hold until all expected compounds have eluted.

7.2.6 Direct injection - Column 4

Carrier gas (He) flow rate:	4 mL/min
Column:	J&W DB-24, 70m x 0.53 mm
Initial temperature:	40°C, hold for 3 minutes
Temperature program:	8°C/min
Final temperature:	260°C, hold until all expected compounds have eluted.
Column Bake out (direct inj):	75 minutes
Injector temperature:	200-225°C
Transfer line temperature:	250-300°C

7.3 Initial calibration - the recommended MS operating conditions

Mass range:	35-260 amu	
Scan time:	0.6-2 sec/scan	
Source temperature:	According to manufacturer's specifications	
Ion trap only:	Axial modulation	4.0 volts
	Manifold set	220°C
	Emission current	30 amps

7.3.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 4 for a 5-50 ng injection or purging of 4-bromofluorobenzene (2 μL injection of the BFB standard). Analyses must not begin until these criteria are met.

7.3.2 Set up the purge-and-trap system as outlined in Method 5030 if purge-and-trap analysis is to be utilized. A set of at least five calibration standards containing the method analytes is needed. One calibration standard should contain each analyte at a concentration approaching but greater than the method detection limit (Table 1) for that compound; the other calibration standards should contain analytes at concentrations that define the range of the method. Calibration should be done using the sample introduction technique that will be used for samples. For Method 5030, the purging efficiency for 5 mL of water is greater than for 25 mL. Therefore, develop the standard curve with whichever volume of sample that will be analyzed.

7.3.2.1 To prepare a calibration standard for purge-and-trap or aqueous direct injection, add an appropriate volume of a secondary dilution standard solution to an aliquot of organic-free reagent water in a volumetric flask. Use a microsyringe and rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask. Aqueous standards are not stable and should be prepared daily. Transfer 5.0 mL (or 25 mL if lower detection limits are required) of each standard to a gas tight syringe along with 10 μL of internal standard. Then transfer the contents to a purging device or syringe. Perform purge-and-trap or direct injection as outlined in Method 5030.

7.3.2.2 To prepare a calibration standard for direct injection analysis of oil, dilute standards in hexadecane.

7.3.3 Tabulate the area response of the characteristic ions (see Table 5) against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard that has a retention time closest to the compound being measured (Section 7.6.2). The RF is calculated 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.
C_x = Concentration of the compound being measured.

7.3.4 The average RRF must be calculated and recorded for each compound. A system performance check should be made before this calibration curve is used. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum average relative response factor. These compounds are chloromethane; 1,1-dichloroethane; bromoform; 1,1,2,2-tetrachloroethane; and chlorobenzene. These compounds are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system. Examples of these occurrences are:

7.3.4.1 Chloromethane - This compound is the most likely compound to be lost if the purge flow is too fast.

7.3.4.2 Bromoform - This compound is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio relative to m/z 95 may improve bromoform response.

7.3.4.3 Tetrachloroethane and 1,1-dichloroethane - These compounds are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.3.5 Using the RRFs from the initial calibration, calculate and record the percent relative standard deviation (%RSD) for all compounds. The percent RSD is calculated as follows:

$$\% \; RSD = \frac{SD}{\overline{RF_x}} \times 100\%$$

where:

RSD = Relative standard deviation.
RF_x = mean of 5 initial RRFs for a compound.
SD = standard deviation of average RRFs for a compound.

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(x_i - \bar{x})^2}{N - 1}}$$

The percent relative standard deviation should be less than 15% for each compound. However, the %RSD for each individual Calibration Check Compound (CCC) must be less than 30%. The CCCs are:

1,1-Dichloroethene,
Chloroform,
1,2-Dichloropropane,
Toluene,
Ethylbenzene, and
Vinyl chloride.

7.3.5.1 If a %RSD greater than 30 percent is measured for any CCC, then corrective action to eliminate a system leak and/or column reactive sites is required before reattempting calibration.

7.3.6 Linearity - If the %RSD of any compound is 15% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation.

7.3.6.1 If the %RSD of any compound is greater than 15%, construct calibration curves of area ratio (A/A_{is}) versus concentration using first or higher order regression fit of the five calibration points. The analyst should select the regression order which introduces the least calibration error into the quantitation. If the %RSD is <15%, use of calibration curves is a recommended alternative to average response factor calibration, and a useful diagnostic of standard preparation accuracy and absorption activity in the chromatographic system.

7.3.7 These curves are verified each shift by purging a performance standard. Recalibration is required only if calibration and on-going performance criteria cannot be met.

7.4 GC/MS calibration verification

7.4.1 Prior to the analysis of samples, inject or purge 5-50 ng of the 4-bromofluorobenzene standard following Method 5030. The resultant mass spectra for the BFB must meet all of the criteria given in Table 4 before sample analysis begins. These criteria must be demonstrated each 12-hour shift.

7.4.2 The initial calibration curve (Section 7.3) for each compound of interest must be checked and verified once every 12 hours during analysis with the introduction technique used for samples. This is accomplished by analyzing a calibration standard that is at a concentration near the midpoint concentration for the working range of the GC/MS by checking the SPCC and CCC.

7.4.3 System Performance Check Compounds (SPCCs) - A system performance check must be made each 12 hours. If the SPCC criteria are met, a comparison of relative response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum relative response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. 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.

7.4.3.1 The minimum relative response factor for volatile SPCCs are as follows:

Chloromethane	0.1
1,1-Dichloroethane	0.1
Bromoform	0.25
Chlorobenzene	0.3
1,1,2,2-Tetrachloroethane	0.3

7.4.4 Calibration Check Compounds (CCCs) - After the system performance check is met, CCCs listed in Section 7.3.8 are used to check the validity of the initial calibration.

Calculate the percent drift using the following equation:

$$\% \text{ Drift} = (C_I - C_c)/C_I \times 100$$

where:

C_I = Calibration Check Compound standard concentration.
C_c = Measured concentration using selected quantitation method.

If the percent drift for each CCC is less than 20%, the initial calibration is assumed to be valid. If the criterion is not met (> 20% drift), 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 quantitative sample analysis begins. If the CCCs are not required analytes by the permit, then all required analytes must meet the 20% drift criterion.

7.4.5 The internal standard responses and retention times in the check calibration 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. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning are necessary.

7.4.6 For compounds which exhibit linearity of response, the RRF of the daily check standard may be used for quantitation, provided the criteria for SPCCs and CCCs are satisfied.

7.5 GC/MS analysis

7.5.1 It is highly recommended that the extract be screened on a headspace-GC/FID (Methods 3810/8015), headspace-GC/PID/ELCD (Methods 3810/8021), or waste dilution-GC/PID/ELCD (Methods 3585/8021) using the same type of capillary column. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds. Use of screening is particularly important when this method is used to achieve low detection levels.

7.5.2 All samples and standard solutions must be allowed to warm to ambient temperature before analysis. Set up the purge-and-trap system as outlined in Method 5030 if purge-and-trap introduction will be used.

7.5.3 BFB tuning criteria and GC/MS calibration verification criteria must be met before analyzing samples.

7.5.3.1 Remove the plunger from a 5 mL syringe and attach a closed syringe valve. If lower detection limits are required, use a 25 mL syringe. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL.

7.5.4 The process of taking an aliquot destroys the validity of aqueous and soil samples for future analysis; therefore, if there is only one VOA vial, the analyst should prepare a second aliquot for analysis at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. For aqueous samples, filling one 20 mL syringe would require the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

7.5.4.1 The following procedure is appropriate for diluting aqueous purgeable samples. All steps must be performed without delays until the diluted sample is in a gas-tight syringe.

7.5.4.1.1 Dilutions may be made in volumetric flasks (10 to 100 mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

7.5.4.1.2 Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask selected and add slightly less than this quantity of organic-free reagent water to the flask.

7.5.4.1.3 Inject the proper aliquot of sample from the syringe into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with organic-free reagent water. Cap the flask, invert, and shake three times. Repeat above procedure for additional dilutions.

7.5.4.1.4 Fill a 5 mL syringe with the diluted sample.

7.5.4.2 Compositing aqueous samples prior to GC/MS analysis

7.5.4.2.1 Add 5 mL or equal larger amounts of each sample (up to 5 samples are allowed) to a 25 mL glass syringe. Special precautions must be made to maintain zero headspace in the syringe.

7.5.4.2.2 The samples must be cooled at 4°C during this step to minimize volatilization losses.

7.5.4.2.3 Mix well and draw out a 5 mL aliquot for analysis.

7.5.4.2.4 Follow sample introduction, purging, and desorption steps described in Method 5030.

7.5.4.2.5 If less than five samples are used for compositing, a proportionately smaller syringe may be used unless a 25 mL sample is to be purged.

7.5.5 Add 10.0 µL of surrogate spiking solution and 10 µL of internal standard spiking solution to each sample. The surrogate and internal standards may be mixed and added as a single spiking solution. The addition of 10 µL of the surrogate spiking solution to 5 mL of sample is equivalent to a concentration of 50 µg/L of each surrogate standard. The addition of 10 µL of the surrogate spiking solution to 5 g of sample is equivalent to a concentration of 50 µg/kg of each surrogate standard.

7.5.5.1 If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute surrogate and internal standard solutions may be required.

7.5.6 Perform purge-and-trap or direct injection by Method 5030. If the initial analysis of sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the

sample must be reanalyzed at a higher dilution. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion. When a sample is analyzed that has saturated ions from a compound, this analysis must be followed by a blank organic-free reagent water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until the blank analysis is demonstrated to be free of interferences.

7.5.6.1. All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve. Proceed to Sections 7.6.1 and 7.6.2 for qualitative and quantitative analysis.

7.5.7 For matrix spike analysis, add 10 µL of the matrix spike solution (Section 5.13) to the 5 mL of sample to be purged. Disregarding any dilutions, this is equivalent to a concentration of 50 µg/L of each matrix spike standard.

7.6 Data interpretation

7.6.1 Qualitative analysis

7.6.1.1 The qualitative identification of compounds determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met.

7.6.1.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.6.1.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

7.6.1.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.6.1.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times.

Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.6.1.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

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 type of analyses being conducted. 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 $\pm$ 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.

Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison

of sample with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

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.

7.6.2.2 When MS response is linear and passes through the origin, calculate the concentration of each identified analyte in the sample as follows:

Water

$$\text{concentration } (\mu g/L) = \frac{(A_x)(I_s)}{(A_{is})(\overline{RRF})(V_o)}$$

where:

A_x = Area of characteristic ion for compound being measured.
I_s = Amount of internal standard injected (ng).
A_{is} = Area of characteristic ion for the internal standard.
$\overline{RRF}$ = Relative Response factor for compound being measured.
V_o = Volume of water purged (mL), taking into consideration any dilutions made.

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

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

where:

A_x, I_s, A_{is}, $\overline{RRF}$, = Same as for water.
V_t = Volume of total extract (μL) (use 10,000 μL or a factor of this when dilutions are made).
V_i = Volume of extract added (μL) for purging.
W_s = Weight of sample extracted or purged (g).
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 formulae 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 RRF 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.

8.0 QUALITY CONTROL

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

8.2 Additional required instrument QC is found in the Sections 7.3 and 7.4:

8.2.1 The GC/MS system must be tuned to meet the BFB specifications.

8.2.2 There must be an initial calibration of the GC/MS system

8.2.3 The GC/MS system must meet the SPCC criteria and the CCC criteria, 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 10 mg/L or less 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 Prepare a QC reference sample to contain 20 µg/L or less of each analyte by adding 200 µL of QC reference sample concentrate to 100 mL of organic-free reagent water.

8.3.3 Four 5 mL aliquots of the well mixed QC reference sample are analyzed according to the method beginning in Section 7.5.1.

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 using the four results.

8.3.5 Tables 7 and 8 provide single laboratory recovery and precision data obtained for the method analytes from water. Similar results from dosed water should be expected by any experienced laboratory. Compare s and $\bar{x}$ (Section 8.3.4) for each analyte to the single laboratory recovery and precision data. Results are comparable if the calculated standard deviation of the recovery does not exceed 2.6 times the single laboratory RSD or 20%, whichever is greater, and the mean recovery lies within the interval $\bar{x} \pm 3S$ or $\bar{x} \pm 30\%$, whichever is greater.

NOTE: The large number of analytes in Tables 7 and 8 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 are not comparable to the data in Table 6 or 7, 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 are not comparable. 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.

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 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

9.2 This method has been tested in a single laboratory using spiked water. Using a wide-bore capillary column, water was spiked at concentrations between 0.5 and 10 µg/L. Single laboratory accuracy and precision data are

presented for the method analytes in Table 6. Calculated MDLs are presented in Table 1.

9.3 The method was tested using water spiked at 0.1 to 0.5 µg/L and analyzed on a cryofocussed narrow-bore column. The accuracy and precision data for these compounds are presented in Table 7. MDL values were also calculated from these data and are presented in Table 2.

9.4 Direct injection has been used for the analysis of waste motor oil samples using a wide-bore column. The accuracy and precision data for these compounds are presented in Table 10.

10.0 REFERENCES

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TABLE 1.
CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL)
FOR VOLATILE ORGANIC COMPOUNDS ON WIDE BORE CAPILLARY COLUMNS

ANALYTE	RETENTION TIME (minutes)			MDL[d] (µg/L)
	Column 1[a]	Column 2[b]	Column 2'[c]	
Dichlorodifluoromethane	1.35	0.70	3.13	0.10
Chloromethane	1.49	0.73	3.40	0.13
Vinyl Chloride	1.56	0.79	3.93	0.17
Bromomethane	2.19	0.96	4.80	0.11
Chloroethane	2.21	1.02	--	0.10
Trichlorofluoromethane	2.42	1.19	6.20	0.08
Acrolein	3.19			
Iodomethane	3.56			
Acetonitrile	4.11			
Carbon disulfide	4.11			
Allyl chloride	4.11			
Methylene chloride	4.40	2.06	9.27	0.03
1,1-Dichloroethene	4.57	1.57	7.83	0.12
Acetone	4.57			
trans-1,2-Dichloroethene	4.57	2.36	9.90	0.06
Acrylonitrile	5.00			
1,1-Dichloroethane	6.14	2.93	10.80	0.04
Vinyl acetate	6.43			
2,2-Dichloropropane	8.10	3.80	11.87	0.35
2-Butanone	--			
cis-1,2-Dichloroethene	8.25	3.90	11.93	0.12
Propionitrile	8.51			
Chloroform	9.01	4.80	12.60	0.03
Bromochloromethane	--	4.38	12.37	0.04
Methacrylonitrile	9.19			
1,1,1-Trichloroethane	10.18	4.84	12.83	0.08
Carbon tetrachloride	11.02	5.26	13.17	0.21
1,1-Dichloropropene	--	5.29	13.10	0.10
Benzene	11.50	5.67	13.50	0.04
1,2-Dichloroethane	12.09	5.83	13.63	0.06
Trichloroethene	14.03	7.27	14.80	0.19
1,2-Dichloropropane	14.51	7.66	15.20	0.04
Bromodichloromethane	15.39	8.49	15.80	0.08
Dibromomethane	15.43	7.93	15.43	0.24
Methyl methacrylate	15.50			
1,4-Dioxane	16.17			
2-Chloroethyl vinyl ether	--			
4-Methyl-2-pentanone	17.32			
trans-1,3-Dichloropropene	17.47	--	16.70	--
Toluene	18.29	10.00	17.40	0.11
cis-1,3-Dichloropropene	19.38	--	17.90	--
1,1,2-Trichloroethane	19.59	11.05	18.30	0.10
Ethyl methacrylate	20.01			

TABLE 1.
(Continued)

ANALYTE	RETENTION TIME (minutes) Column 1[a]	Column 2[b]	Column 2'[c]	MDL[d] (µg/L)
2-Hexanone	20.30			
Tetrachloroethene	20.26	11.15	18.60	0.14
1,3-Dichloropropane	20.51	11.31	18.70	0.04
Dibromochloromethane	21.19	11.85	19.20	0.05
1,2-Dibromoethane	21.52	11.83	19.40	0.06
1-Chlorohexane	--	13.29	--	0.05
Chlorobenzene	23.17	13.01	20.67	0.04
1,1,1,2-Tetrachloroethane	23.36	13.33	20.87	0.05
Ethylbenzene	23.38	13.39	21.00	0.06
p-Xylene	23.54	13.69	21.30	0.13
m-Xylene	23.54	13.68	21.37	0.05
o-Xylene	25.16	14.52	22.27	0.11
Styrene	25.30	14.60	22.40	0.04
Bromoform	26.23	14.88	22.77	0.12
Isopropylbenzene (Cumene)	26.37	15.46	23.30	0.15
cis-1,4-Dichloro-2-butene	27.12			
1,1,2,2-Tetrachloroethane	27.29	16.35	24.07	0.04
Bromobenzene	27.46	15.86	24.00	0.03
1,2,3-Trichloropropane	27.55	16.23	24.13	0.32
n-Propylbenzene	27.58	16.41	24.33	0.04
2-Chlorotoluene	28.19	16.42	24.53	0.04
trans-1,4-Dichloro-2-butene	28.26			
1,3,5-Trimethylbenzene	28.31	16.90	24.83	0.05
4-Chlorotoluene	28.33	16.72	24.77	0.06
Pentachloroethane	29.41			
1,2,4-Trimethylbenzene	29.47	17.70	31.50	0.13
sec-Butylbenzene	30.25	18.09	26.13	0.13
tert-Butylbenzene	30.59	17.57	26.60	0.14
p-Isopropyltoluene	30.59	18.52	26.50	0.12
1,3-Dichlorobenzene	30.56	18.14	26.37	0.12
1,4-Dichlorobenzene	31.22	18.39	26.60	0.03
Benzyl chloride	32.00			
n-Butylbenzene	32.23	19.49	27.32	0.11
1,2-Dichlorobenzene	32.31	19.17	27.43	0.03
1,2-Dibromo-3-chloropropane	35.30	21.08	--	0.26
1,2,4-Trichlorobenzene	38.19	23.08	31.50	0.04
Hexachlorobutadiene	38.57	23.68	32.07	0.11
Naphthalene	39.05	23.52	32.20	0.04
1,2,3-Trichlorobenzene	40.01	24.18	32.97	0.03

TABLE 1.
(Continued)

ANALYTE	RETENTION TIME (minutes)			MDL[d] (µg/L)
	Column 1[a]	Column 2[b]	Column 2'[c]	
INTERNAL STANDARDS/SURROGATES				
1,4-Difluorobenzene	13.26			
Chlorobenzene-d_5	23.10			
1,4-Dichlorobenzene-d_4	31.16			
4-Bromofluorobenzene	27.83	15.71	23.63	
1,2-Dichlorobenzene-d_4	32.30	19.08	27.25	
Dichloroethane-d_4	12.08			
Dibromofluoromethane	--			
Toluene-d_8	18.27			
Pentafluorobenzene	--			
Fluorobenzene	13.00	6.27	14.06	

[a] Column 1 - 60 meter x 0.75 mm ID VOCOL capillary. Hold at 10°C for 8 minutes, then program to 180°C at 4°/min.

[b] Column 2 - 30 meter x 0.53 mm ID DB-624 wide-bore capillary using cryogenic oven. Hold at 10°C for 5 minutes, then program to 160°C at 6°/min.

[c] Column 2' - 30 meter x 0.53 mm ID DB-624 wide-bore capillary, cooling GC oven to ambient temperatures. Hold at 10°C for 6 minutes, program to 70°C at 10°/min, program to 120°C at 5°/min, then program to 180°C at 8°/min.

[d] MDL based on a 25 mL sample volume.

TABLE 2.
CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL)
FOR VOLATILE ORGANIC COMPOUNDS ON NARROW BORE CAPILLARY COLUMNS

ANALYTE	RETENTION TIME (minutes) Column 3[a]	MDL[b] (µg/L)
Dichlorodifluoromethane	0.88	0.11
Chloromethane	0.97	0.05
Vinyl chloride	1.04	0.04
Bromomethane	1.29	0.06
Chloroethane	1.45	0.02
Trichlorofluoromethane	1.77	0.07
1,1-Dichloroethene	2.33	0.05
Methylene chloride	2.66	0.09
trans-1,2-Dichloroethene	3.54	0.03
1,1-Dichloroethane	4.03	0.03
cis-1,2-Dichloroethene	5.07	0.06
2,2-Dichloropropane	5.31	0.08
Chloroform	5.55	0.04
Bromochloromethane	5.63	0.09
1,1,1-Trichloroethane	6.76	0.04
1,2-Dichloroethane	7.00	0.02
1,1-Dichloropropene	7.16	0.12
Carbon tetrachloride	7.41	0.02
Benzene	7.41	0.03
1,2-Dichloropropane	8.94	0.02
Trichloroethene	9.02	0.02
Dibromomethane	9.09	0.01
Bromodichloromethane	9.34	0.03
Toluene	11.51	0.08
1,1,2-Trichloroethane	11.99	0.08
1,3-Dichloropropane	12.48	0.08
Dibromochloromethane	12.80	0.07
Tetrachloroethene	13.20	0.05
1,2-Dibromoethane	13.60	0.10
Chlorobenzene	14.33	0.03
1,1,1,2-Tetrachloroethane	14.73	0.07
Ethylbenzene	14.73	0.03
p-Xylene	15.30	0.06
m-Xylene	15.30	0.03
Bromoform	15.70	0.20
o-Xylene	15.78	0.06
Styrene	15.78	0.27
1,1,2,2-Tetrachloroethane	15.78	0.20
1,2,3-Trichloropropane	16.26	0.09
Isopropylbenzene	16.42	0.10

TABLE 2.
(Continued)

ANALYTE	RETENTION TIME (minutes) Column 3[a]	MDL[b] (µg/L)
Bromobenzene	16.42	0.11
2-Chlorotoluene	16.74	0.08
n-Propylbenzene	16.82	0.10
4-Chlorotoluene	16.82	0.06
1,3,5-Trimethylbenzene	16.99	0.06
tert-Butylbenzene	17.31	0.33
1,2,4-Trimethylbenzene	17.31	0.09
sec-Butylbenzene	17.47	0.12
1,3-Dichlorobenzene	17.47	0.05
p-Isopropyltoluene	17.63	0.26
1,4-Dichlorobenzene	17.63	0.04
1,2-Dichlorobenzene	17.79	0.05
n-Butylbenzene	17.95	0.10
1,2-Dibromo-3-chloropropane	18.03	0.50
1,2,4-Trichlorobenzene	18.84	0.20
Naphthalene	19.07	0.10
Hexachlorobutadiene	19.24	0.10
1,2,3-Trichlorobenzene	19.24	0.14

[a] Column 3 - 30 meter x 0.32 mm ID DB-5 capillary with 1 µm film thickness.

[b] MDL based on a 25 mL sample volume.

TABLE 3.
ESTIMATED QUANTITATION LIMITS FOR VOLATILE ANALYTES[a]

	Estimated Quantitation Limits		
	Ground water µg/L		Low Soil/Sediment[b] µg/kg
Volume of water purged	5 mL	25 mL	
All analytes in Table 1	5	1	5

[a] Estimated Quantitation Limit (EQL) - The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The EQL is generally 5 to 10 times the MDL. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes the EQL analyte concentration is selected for the lowest non-zero standard in the calibration curve. Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable. See the following information for further guidance on matrix-dependent EQLs.

[b] 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 percent dry weight in each sample.

Other Matrices	Factor[c]
Water miscible liquid waste	50
High-concentration soil and sludge	125
Non-water miscible waste	500

[c]EQL = [EQL for low soil sediment (Table 3)] X [Factor]. For non-aqueous samples, the factor is on a wet-weight basis.

TABLE 4.
BFB MASS - INTENSITY SPECIFICATIONS (4-BROMOFLUOROBENZENE)

Mass	Intensity Required (relative abundance)
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5 to 9% of mass 176

TABLE 5.
CHARACTERISTIC MASSES (M/Z) FOR PURGEABLE ORGANIC COMPOUNDS

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Acetone	58	43
Acetonitrile	41	41, 40, 39
Acrolein	56	55, 58
Acrylonitrile	53	52, 51
Allyl alcohol	57	57, 58, 39
Allyl chloride	76	76, 41, 39, 78
Benzene	78	-
Benzyl chloride	91	91, 126, 65, 128
Bromoacetone	136	43, 136, 138, 93, 95
Bromobenzene	156	77, 158
Bromochloromethane	128	49, 130
Bromodichloromethane	83	85, 127
Bromoform	173	175, 254
Bromomethane	94	96
iso-Butanol	74	43
n-Butanol	56	41
2-Butanone	72	43, 72
n-Butylbenzene	91	92, 134
sec-Butylbenzene	105	134
tert-Butylbenzene	119	91, 134
Carbon disulfide	76	78
Carbon tetrachloride	117	119
Chloral hydrate	82	44, 84, 86, 111
Chloroacetonitrile	48	75
Chlorobenzene	112	77, 114
1-Chlorobutane	56	49
Chlorodibromomethane	129	208, 206
Chloroethane	64	66
2-Chloroethanol	49	49, 44, 43, 51, 80
bis-(2-chloroethyl) sulfide	109	111, 158, 160
2-Chloroethyl vinyl ether	63	65, 106
Chloroform	83	85
Chloromethane	50	52
Chloroprene	53	53, 88, 90, 51
3-Chloropropionitrile	54	54, 49, 89, 91
2-Chlorotoluene	91	126
4-Chlorotoluene	91	126
1,2-Dibromo-3-chloropropane	75	155, 157
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109, 188
Dibromomethane	93	95, 174
1,2-Dichlorobenzene	146	111, 148
1,2-Dichlorobenzene-d_4	152	115, 150
1,3-Dichlorobenzene	146	111, 148

TABLE 5.
(continued)

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion(s)
1,4-Dichlorobenzene	146	111, 148
cis-1,4-Dichloro-2-butene	75	75, 53, 77, 124, 89
trans-1,4-Dichloro-2-butene	53	88, 75
Dichlorodifluoromethane	85	87
1,1-Dichloroethane	63	65, 83
1,2-Dichloroethane	62	98
1,1-Dichloroethene	96	61, 63
cis-1,2-Dichloroethene	96	61, 98
trans-1,2-Dichloroethene	96	61, 98
1,2-Dichloropropane	63	112
1,3-Dichloropropane	76	78
2,2-Dichloropropane	77	97
1,3-Dichloro-2-propanol	79	79, 43, 81, 49
1,1-Dichloropropene	75	110, 77
cis-1,3-Dichloropropene	75	77, 39
trans-1,3-Dichloropropene	75	77, 39
1,2,3,4-Diepoxybutane	55	55, 57, 56
Diethyl ether	74	45, 59
1,4-Dioxane	88	88, 58, 43, 57
Epichlorohydrin	57	57, 49, 62, 51
Ethanol	31	45, 27, 46
Ethyl acetate	88	43, 45, 61
Ethylbenzene	91	106
Ethylene oxide	44	44, 43, 42
Ethyl methacrylate	69	69, 41, 99, 86, 114
Hexachlorobutadiene	225	223, 227
Hexachloroethane	201	166, 199, 203
2-Hexanone	43	58, 57, 100
2-Hydroxypropionitrile	44	44, 43, 42, 53
Iodomethane	142	127, 141
Isobutyl alcohol	43	43, 41, 42, 74
Isopropylbenzene	105	120
p-Isopropyltoluene	119	134, 91
Malonitrile	66	66, 39, 65, 38
Methacrylonitrile	41	41, 67, 39, 52, 66
Methyl acrylate	55	85
Methyl-t-butyl ether	73	57
Methylene chloride	84	86, 49
Methyl ethyl ketone	72	43
Methyl iodide	142	142, 127, 141
Methyl methacrylate	69	69, 41, 100, 39
4-Methyl-2-pentanone	100	43, 58, 85
Naphthalene	128	-
Nitrobenzene	123	51, 77

TABLE 5.
(continued)

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion(s)
2-Nitropropane	46	-
2-Picoline	93	93, 66, 92, 78
Pentachloroethane	167	167, 130, 132, 165, 169
Propargyl alcohol	55	55, 39, 38, 53
β-Propiolactone	42	42, 43, 44
Propionitrile (ethyl cyanide)	54	54, 52, 55, 40
n-Propylamine	59	59, 41, 39
n-Propylbenzene	91	120
Pyridine	79	52
Styrene	104	78
1,2,3-Trichlorobenzene	180	182, 145
1,2,4-Trichlorobenzene	180	182, 145
1,1,1,2-Tetrachloroethane	131	133, 119
1,1,2,2-Tetrachloroethane	83	131, 85
Tetrachloroethene	164	129, 131, 166
Toluene	92	91
1,1,1-Trichloroethane	97	99, 61
1,1,2-Trichloroethane	83	97, 85
Trichloroethene	95	97, 130, 132
Trichlorofluoromethane	151	101, 153
1,2,3-Trichloropropane	75	77
1,2,4-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
Vinyl acetate	43	86
Vinyl chloride	62	64
o-Xylene	106	91
m-Xylene	106	91
p-Xylene	106	91
INTERNAL STANDARDS/SURROGATES		
1,4-Difluorobenzene	114	
Chlorobenzene-d_5	117	
1,4-Dichlorobenzene-d_4	152	115, 150
4-Bromofluorobenzene	95	174, 176
Dibromofluoromethane	113	
Dichloroethane-d_4	102	
Toluene-d_8	98	
Pentafluorobenzene	168	
Fluorobenzene	96	77

TABLE 6.
SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED WITH A WIDE BORE CAPILLARY COLUMN

Analyte	Conc. Range, µg/L	Number of Samples	Recovery[a] %	Standard Deviation of Recovery[b]	Percent Rel Std Dev.
Benzene	0.1 - 10	31	97	6.5	5.7
Bromobenzene	0.1 - 10	30	100	5.5	5.5
Bromochloromethane	0.5 - 10	24	90	5.7	6.4
Bromodichloromethane	0.1 - 10	30	95	5.7	6.1
Bromoform	0.5 - 10	18	101	6.4	6.3
Bromomethane	0.5 - 10	18	95	7.8	8.2
n-Butylbenzene	0.5 - 10	18	100	7.6	7.6
sec-Butylbenzene	0.5 - 10	16	100	7.6	7.6
tert-Butylbenzene	0.5 - 10	18	102	7.4	7.3
Carbon tetrachloride	0.5 - 10	24	84	7.4	8.8
Chlorobenzene	0.1 - 10	31	98	5.8	5.9
Chloroethane	0.5 - 10	24	89	8.0	9.0
Chloroform	0.5 - 10	24	90	5.5	6.1
Chloromethane	0.5 - 10	23	93	8.3	8.9
2-Chlorotoluene	0.1 - 10	31	90	5.6	6.2
4-Chlorotoluene	0.1 - 10	31	99	8.2	8.3
1,2-Dibromo-3-Chloropropane	0.5 - 10	24	83	16.6	19.9
Dibromochloromethane	0.1 - 10	31	92	6.5	7.0
1,2-Dibromoethane	0.5 - 10	24	102	4.0	3.9
Dibromomethane	0.5 - 10	24	100	5.6	5.6
1,2-Dichlorobenzene	0.1 - 10	31	93	5.8	6.2
1,3-Dichlorobenzene	0.5 - 10	24	99	6.8	6.9
1,4-Dichlorobenzene	0.2 - 20	31	103	6.6	6.4
Dichlorodifluoromethane	0.5 - 10	18	90	6.9	7.7
1,1-Dichlorobenzene	0.5 - 10	24	96	5.1	5.3
1,2-Dichlorobenzene	0.1 - 10	31	95	5.1	5.4
1,1-Dichloroethene	0.1 - 10	34	94	6.3	6.7
cis-1,2-Dichloroethene	0.5 - 10	18	101	6.7	6.7
trans-1,2-Dichloroethene	0.1 - 10	30	93	5.2	5.6
1,2-Dichloropropane	0.1 - 10	30	97	5.9	6.1
1,3-Dichloropropane	0.1 - 10	31	96	5.7	6.0
2,2-Dichloropropane	0.5 - 10	12	86	14.6	16.9
1,1-Dichloropropene	0.5 - 10	18	98	8.7	8.9
Ethylbenzene	0.1 - 10	31	99	8.4	8.6
Hexachlorobutadiene	0.5 - 10	18	100	6.8	6.8
Isopropylbenzene	0.5 - 10	16	101	7.7	7.6
p-Isopropyltoluene	0.1 - 10	23	99	6.7	6.7
Methylene chloride	0.1 - 10	30	95	5.0	5.3
Naphthalene	0.1 -100	31	104	8.6	8.2
n-Propylbenzene	0.1 - 10	31	100	5.8	5.8
Styrene	0.1 -100	39	102	7.3	7.2
1,1,1,2-Tetrachloroethane	0.5 - 10	24	90	6.1	6.8

TABLE 6.
(Continued)

Analyte	Conc. Range, µg/L	Number of Samples	Recovery[a] %	Standard Deviation of Recovery[b]	Percent Rel Std Dev.
1,1,2,2-Tetrachloroethane	0.1 - 10	30	91	5.7	6.3
Tetrachloroethene	0.5 - 10	24	89	6.0	6.8
Toluene	0.5 - 10	18	102	8.1	8.0
1,2,3-Trichlorobenzene	0.5 - 10	18	109	9.4	8.6
1,2,4-Trichlorobenzene	0.5 - 10	18	108	9.0	8.3
1,1,1-Trichloroethane	0.5 - 10	18	98	7.9	8.1
1,1,2-Trichloroethane	0.5 - 10	18	104	7.6	7.3
Trichloroethene	0.5 - 10	24	90	6.5	7.3
Trichlorofluoromethane	0.5 - 10	24	89	7.2	8.1
1,2,3-Trichloropropane	0.5 - 10	16	108	15.6	14.4
1,2,4-Trimethylbenzene	0.5 - 10	18	99	8.0	8.1
1,3,5-Trimethylbenzene	0.5 - 10	23	92	6.8	7.4
Vinyl chloride	0.5 - 10	18	98	6.5	6.7
o-Xylene	0.1 - 31	18	103	7.4	7.2
m-Xylene	0.1 - 10	31	97	6.3	6.5
p-Xylene	0.5 - 10	18	104	8.0	7.7

[a] Recoveries were calculated using internal standard method. Internal standard was fluorobenzene.

[b] Standard deviation was calculated by pooling data form three concentrations.

TABLE 7.
SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR
VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED
WITH A NARROW BORE CAPILLARY COLUMN

Analyte	Conc. µg/L	Number of Samples	Recovery[a] %	Standard Deviation of Recovery	Percent Rel Std Dev.
Benzene	0.1	7	99	6.2	6.3
Bromobenzene	0.5	7	97	7.4	7.6
Bromochloromethane	0.5	7	97	5.8	6.0
Bromodichloromethane	0.1	7	100	4.6	4.6
Bromoform	0.5	7	101	5.4	5.3
Bromomethane	0.5	7	99	7.1	7.2
n-Butylbenzene	0.5	7	94	6.0	6.4
sec-Butylbenzene	0.5	7	110	7.1	6.5
tert-Butylbenzene	0.5	7	110	2.5	2.3
Carbon tetrachloride	0.1	7	108	6.8	6.3
Chlorobenzene	0.1	7	91	5.8	6.4
Chloroethane	0.1	7	100	5.8	5.8
Chloroform	0.1	7	105	3.2	3.0
Chloromethane	0.5	7	101	4.7	4.7
2-Chlorotoluene	0.5	7	99	4.6	4.6
4-Chlorotoluene	0.5	7	96	7.0	7.3
1,2-Dibromo-3-chloropropane	0.5	7	92	10.0	10.9
Dibromochloromethane	0.1	7	99	5.6	5.7
1,2-Dibromoethane	0.5	7	97	5.6	5.8
Dibromomethane	0.5	7	93	5.6	6.0
1,2-Dichlorobenzene	0.1	7	97	3.5	3.6
1,3-Dichlorobenzene	0.1	7	101	6.0	5.9
1,4-Dichlorobenzene	0.1	7	106	6.5	6.1
Dichlorodifluoromethane	0.1	7	99	8.8	8.9
1,1-Dichloroethane	0.5	7	98	6.2	6.3
1,2-Dichloroethane	0.1	7	100	6.3	6.3
1,1-Dichloroethene	0.1	7	95	9.0	9.5
cis-1,2-Dichloroethene	0.1	7	100	3.7	3.7
trans-1,2-Dichloroethene	0.1	7	98	7.2	7.3
1,2-Dichloropropane	0.5	7	96	6.0	6.3
1,3-Dichloropropane	0.5	7	99	5.8	5.9
2,2-Dichloropropane	0.5	7	99	4.9	4.9
1,1-Dichloropropene	0.5	7	102	7.4	7.3
Ethylbenzene	0.5	7	99	5.2	5.3
Hexachlorobutadiene	0.5	7	100	6.7	6.7
Isopropylbenzene	0.5	7	102	6.4	6.3
p-Isopropyltoluene	0.5	7	113	13.0	11.5
Methylene chloride	0.5	7	97	13.0	13.4
Naphthalene	0.5	7	98	7.2	7.3
n-Propylbenzene	0.5	7	99	6.6	6.7

TABLE 7.
(Continued)

Analyte	Conc. µg/L	Number of Samples	Recovery[a] %	Standard Deviation of Recovery	Percent Rel Std Dev
Styrene	0.5	7	96	19.0	19.8
1,1,1,2-Tetrachloroethane	0.5	7	100	4.7	4.7
1,1,2,2-Tetrachloroethane	0.5	7	100	12.0	12.0
Tetrachloroethene	0.1	7	96	5.0	5.2
Toluene	0.5	7	100	5.9	5.9
1,2,3-Trichlorobenzene	0.5	7	102	8.9	8.7
1,2,4-Trichlorobenzene	0.5	7	91	16.0	17.6
1,1,1-Trichloroethane	0.5	7	100	4.0	4.0
1,1,2-Trichloroethane	0.5	7	102	4.9	4.8
Trichloroethene	0.1	7	104	2.0	1.9
Trichlorofluoromethane	0.1	7	97	4.6	4.7
1,2,3-Trichloropropane	0.5	7	96	6.5	6.8
1,2,4-Trimethylbenzene	0.5	7	96	6.5	6.8
1,3,5-Trimethylbenzene	0.5	7	101	4.2	4.2
Vinyl chloride	0.1	7	104	0.2	0.2
o-Xylene	0.5	7	106	7.5	7.1
m-Xylene	0.5	7	106	4.6	4.3
p-Xylene	0.5	7	97	6.1	6.3

[a] Recoveries were calculated using internal standard method. Internal standard was fluorobenzene.

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

Surrogate Compound	Low/High Water	Low/High Soil/Sediment
4-Bromofluorobenzene[a]	86-115	74-121
Dibromofluoromethane[a]	86-118	80-120
Toluene-d_8[a]	88-110	81-117
Dichloroethane-d_4[a]	80-120	80-120

[a] Single laboratory data for guidance only.

TABLE 9.
QUANTITY OF EXTRACT REQUIRED FOR ANALYSIS OF
HIGH-CONCENTRATION SAMPLES

Approximate Concentration Range	Volume of Extract[a]
500 - 10,000 µg/kg	100 µL
1,000 - 20,000 µg/kg	50 µL
5,000 - 100,000 µg/kg	10 µL
25,000 - 500,000 µg/kg	100 µL of 1/50 dilution[b]

Calculate appropriate dilution factor for concentrations exceeding this table.

[a] The volume of solvent added to 5 mL of water being purged should be kept constant. Therefore, add to the 5 mL syringe whatever volume of solvent is necessary to maintain a volume of 100 µL added to the syringe.

[b] Dilute an aliquot of the solvent extract and then take 100 µL for analysis.

TABLE 10
DIRECT INJECTION ANALYSIS OF NEW OIL AT 5 PPM

Compound	Recovery (%)	%RSD	Blank (ppm)	Spike (ppm)
Acetone	91	14.8	1.9	5.0
Benzene	86	21.3	0.1	0.5
n-Butanol*,**	107	27.8	0.5	5.0
iso-Butanol*,**	95	19.5	0.9	5.0
Carbon tetrachloride	86	44.7	0.0	0.5
Carbon disulfide**	53	22.3	0.0	5.0
Chlorobenzene	81	29.3	0.0	5.0
Chloroform	84	29.3	0.0	6.0
1,4-Dichlorobenzene	98	24.9	0.0	7.5
1,2-Dichloroethane	101	23.1	0.0	0.5
1,1-Dichloroethene	97	45.3	0.0	0.7
Diethyl ether	76	24.3	0.0	5.0
Ethyl acetate	113	27.4	0.0	5.0
Ethylbenzene	83	30.1	0.2	5.0
Hexachloroethane	71	30.3	0.0	3.0
Methylene chloride	98	45.3	0.0	5.0
Methyl ethyl ketone	79	24.6	0.4	5.0
MIBK	93	31.4	0.0	5.0
Nitrobenzene	89	30.3	0.0	2.0
Pyridine	31	35.9	0.0	5.0
Tetrachloroethene	82	27.1	0.0	0.7
Trichlorofluoromethane	76	27.6	0.0	5.0
1,1,2-Cl_3F_3ethane	69	29.2	0.0	5.0
Toluene	73	21.9	0.6	5.0
Trichloroethene	66	28.0	0.0	0.5
Vinyl chloride	63	35.2	0.0	0.2
o-Xylene	83	29.5	0.4	5.0
m/p-Xylene	84	29.5	0.6	10.0

* Alternate mass employed
** IS quantitation
Data is taken from Reference 9.

FIGURE 1.
PURGING DEVICE

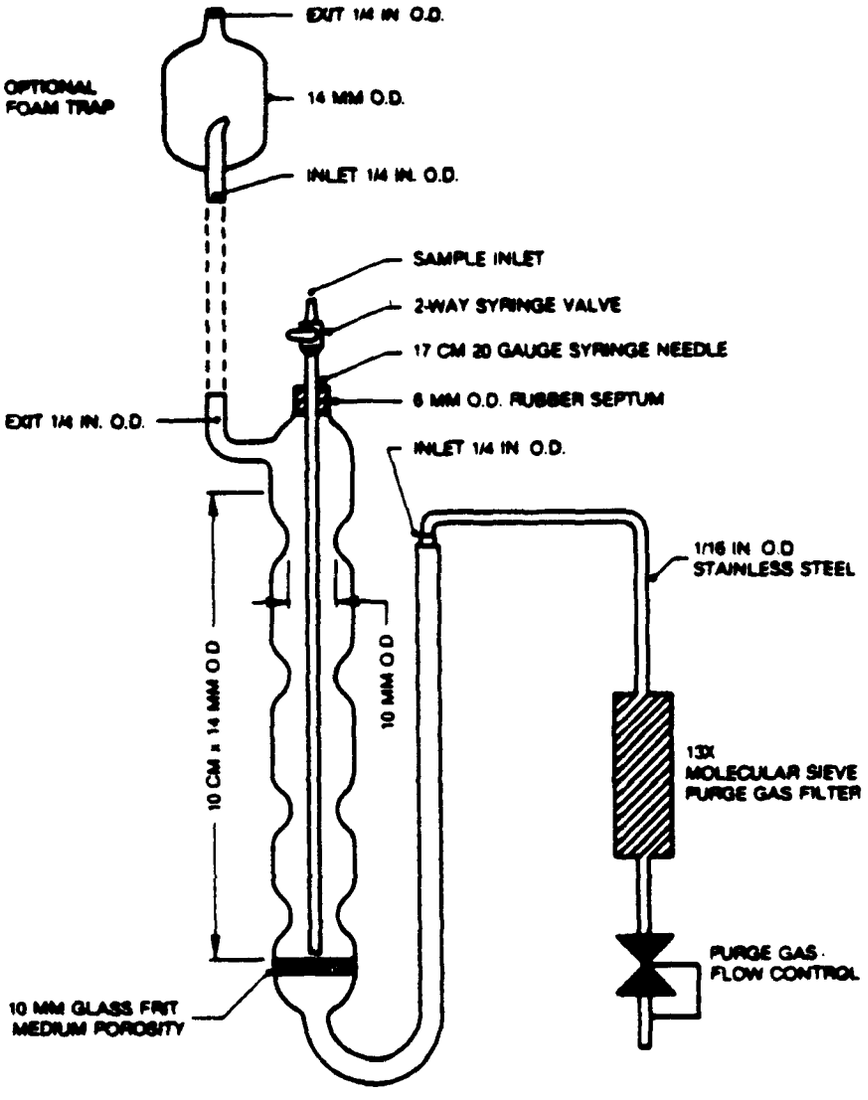


FIGURE 2.
TRAP PACKING AND CONSTRUCTION TO INCLUDE DESORB CAPABILITY

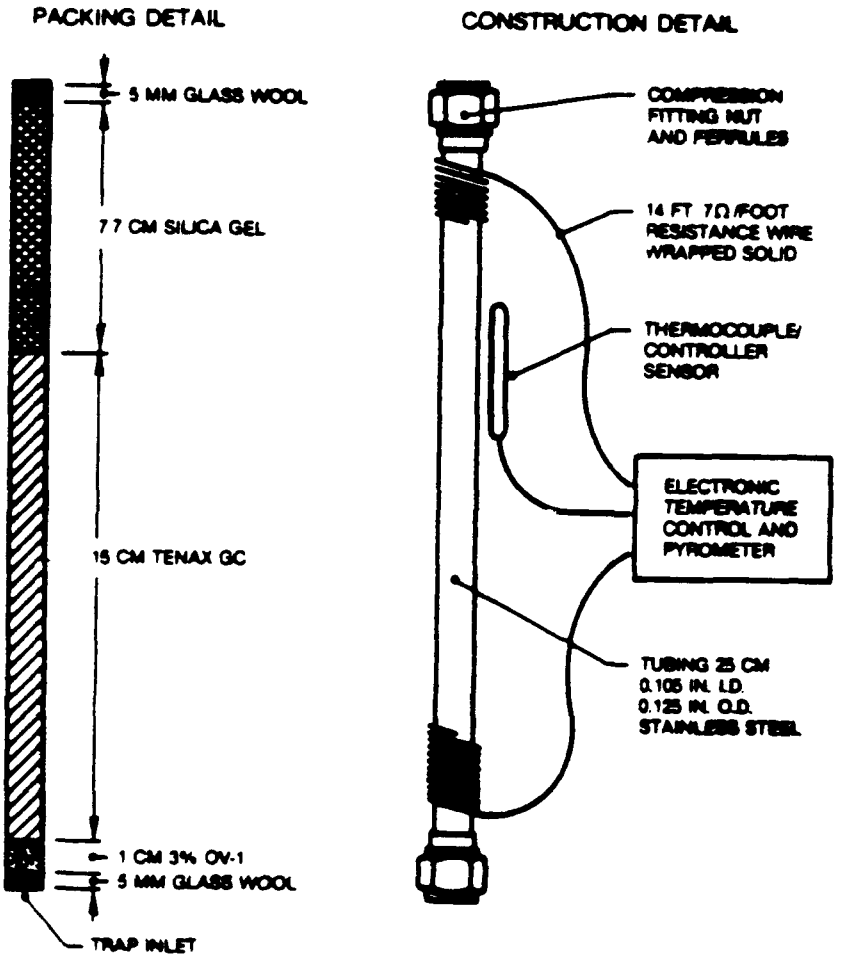


FIGURE 3.
SCHEMATIC OF PURGE-AND-TRAP DEVICE - PURGE MODE

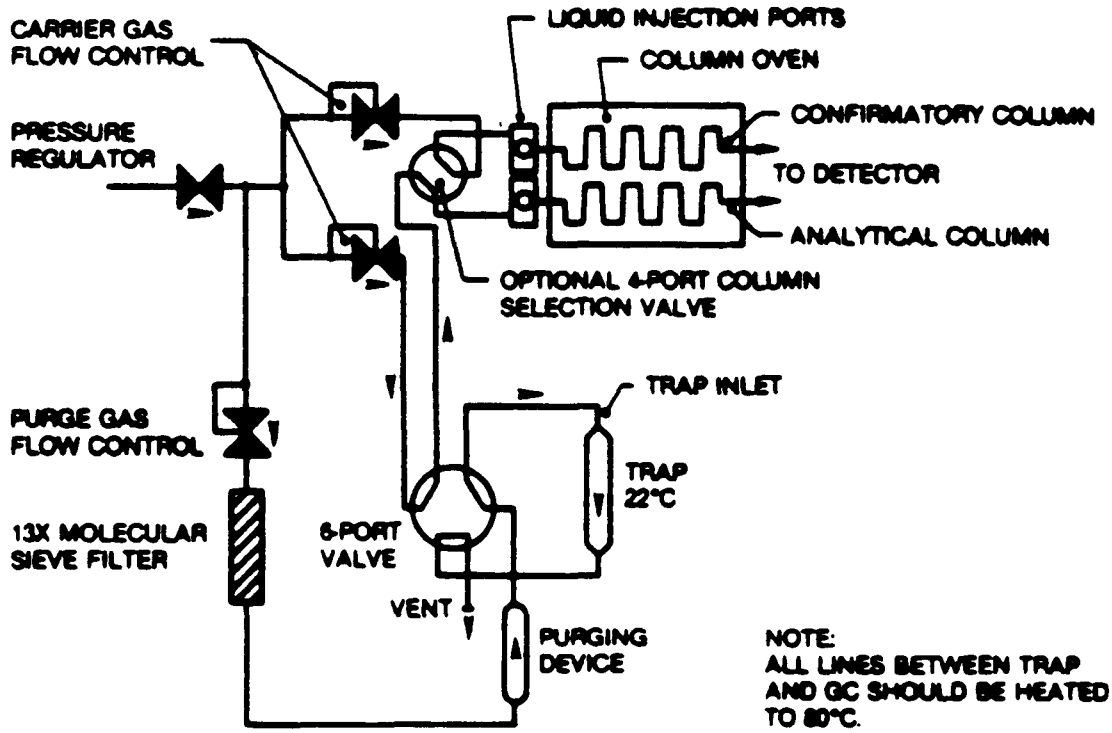


FIGURE 4.
SCHEMATIC OF PURGE-AND-TRAP DEVICE - DESORB MODE

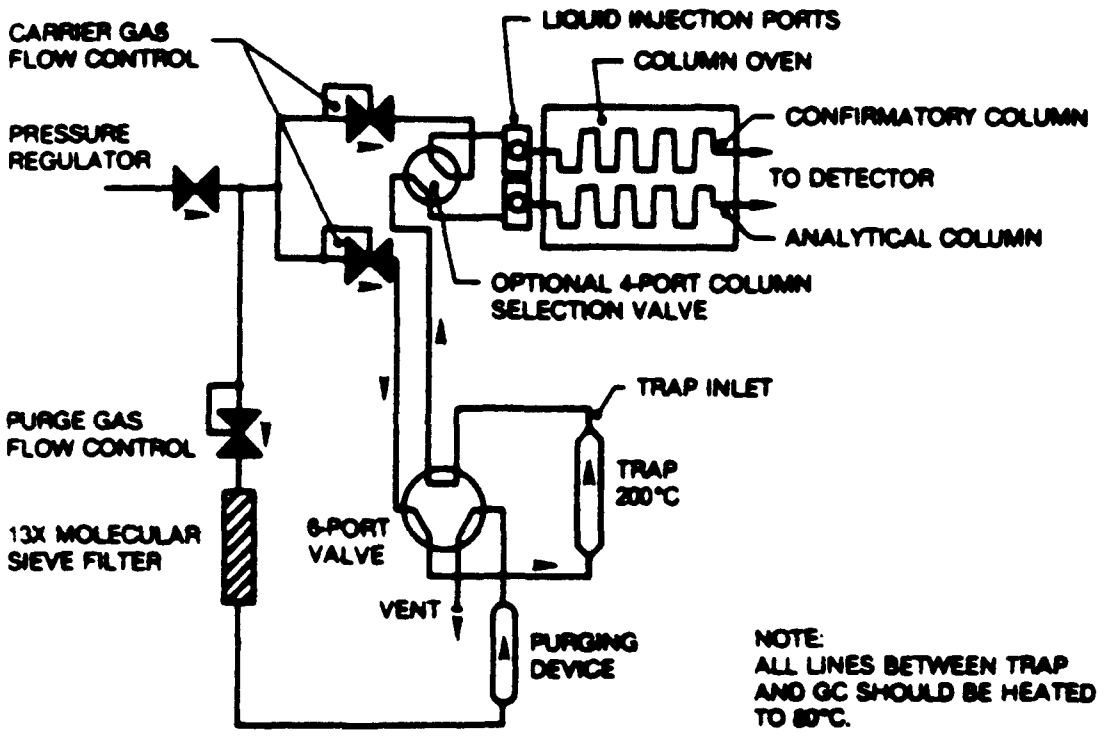


FIGURE 5.
GAS CHROMATOGRAM OF VOLATILE ORGANICS

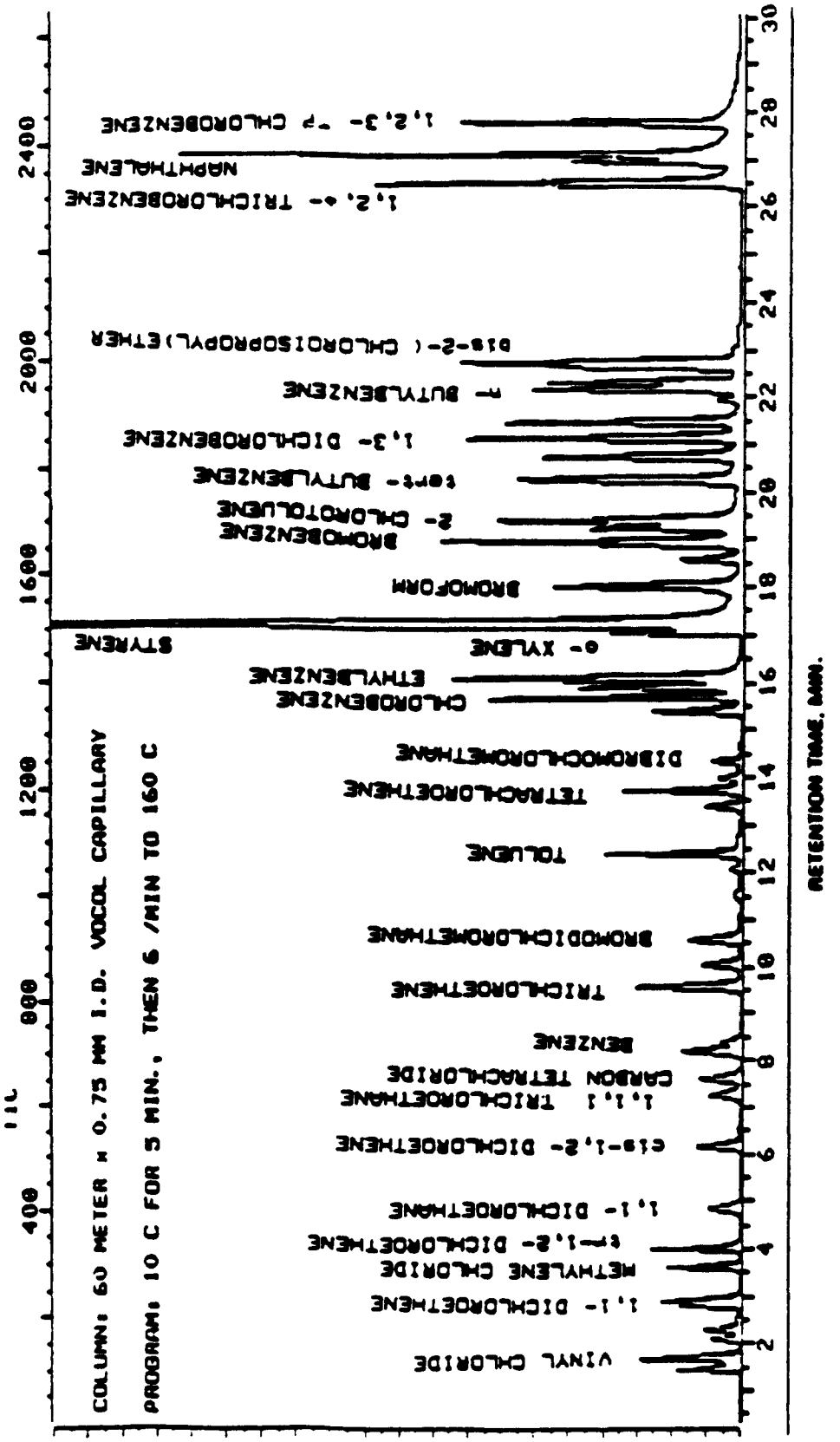


FIGURE 6.
GAS CHROMATOGRAM OF VOLATILE ORGANICS

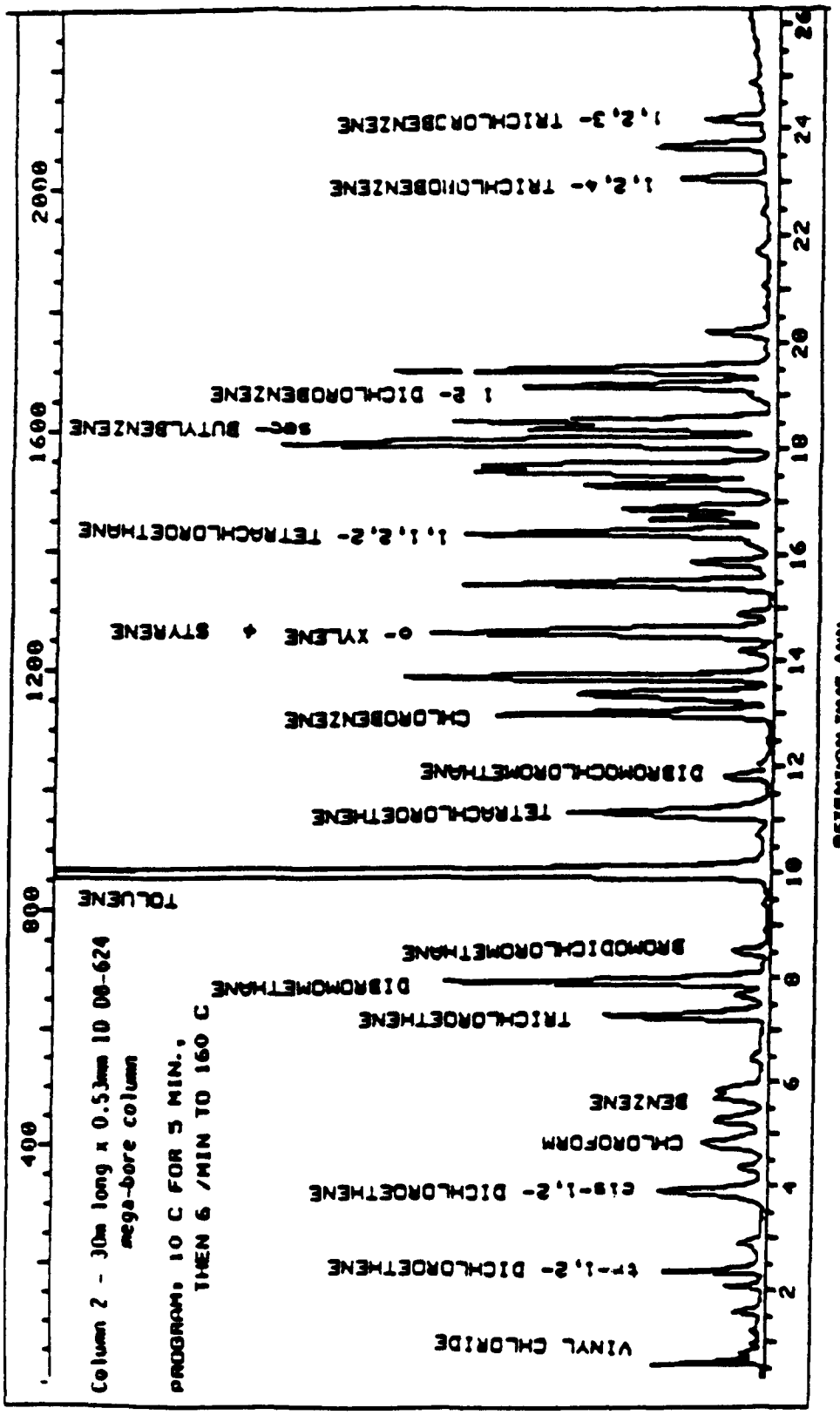


FIGURE 7.
GAS CHROMATOGRAM OF VOLATILE ORGANICS

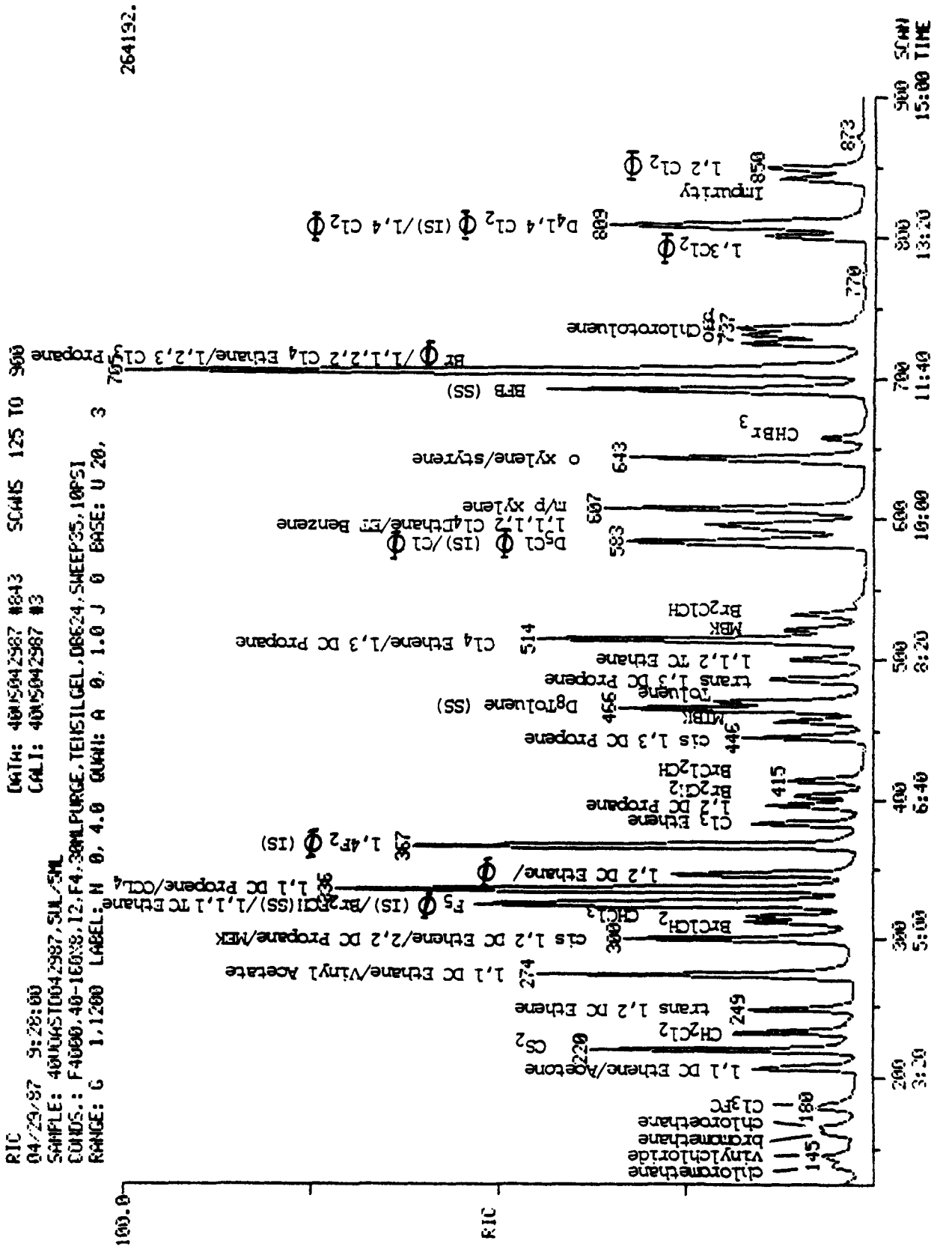


FIGURE 8.
GAS CHROMATOGRAM OF TEST MIXTURE

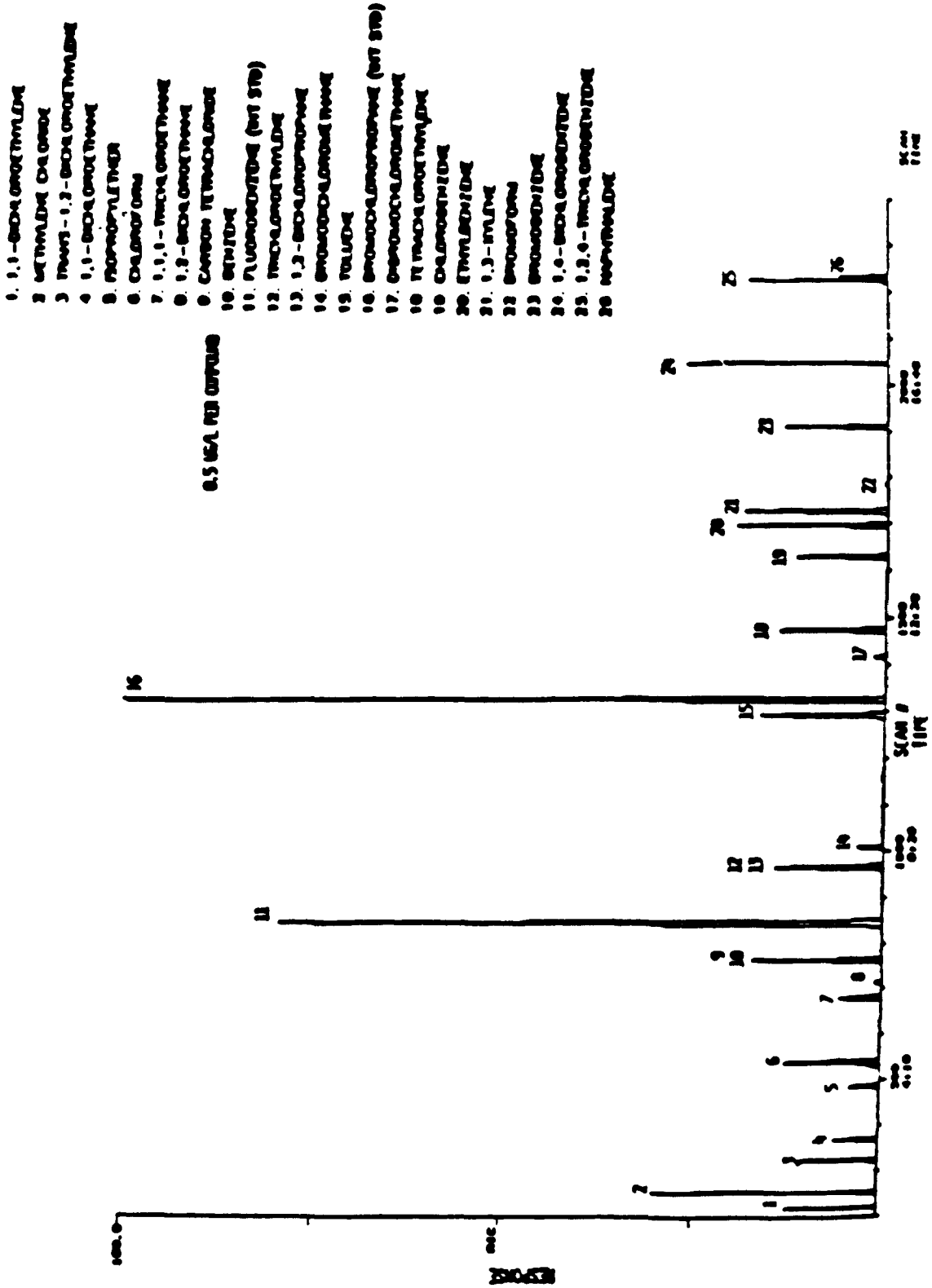
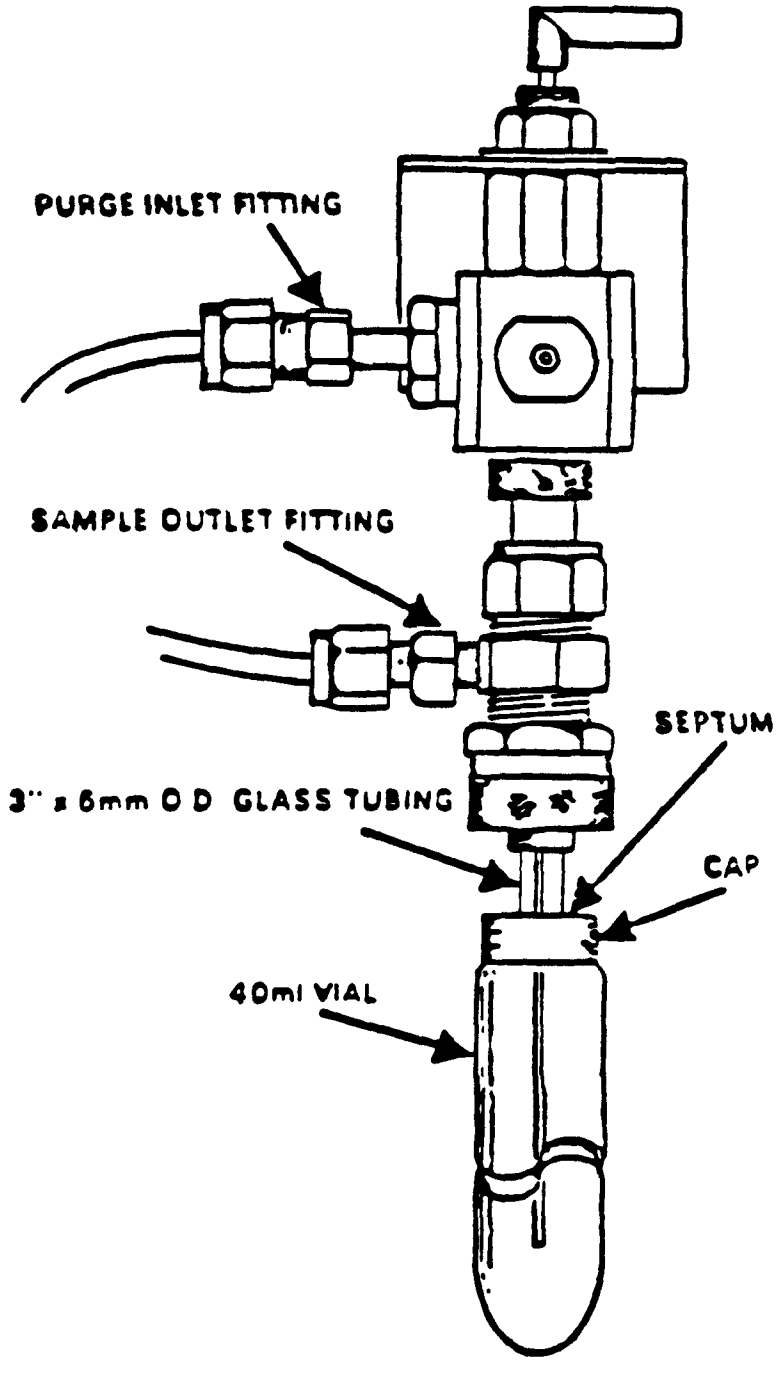
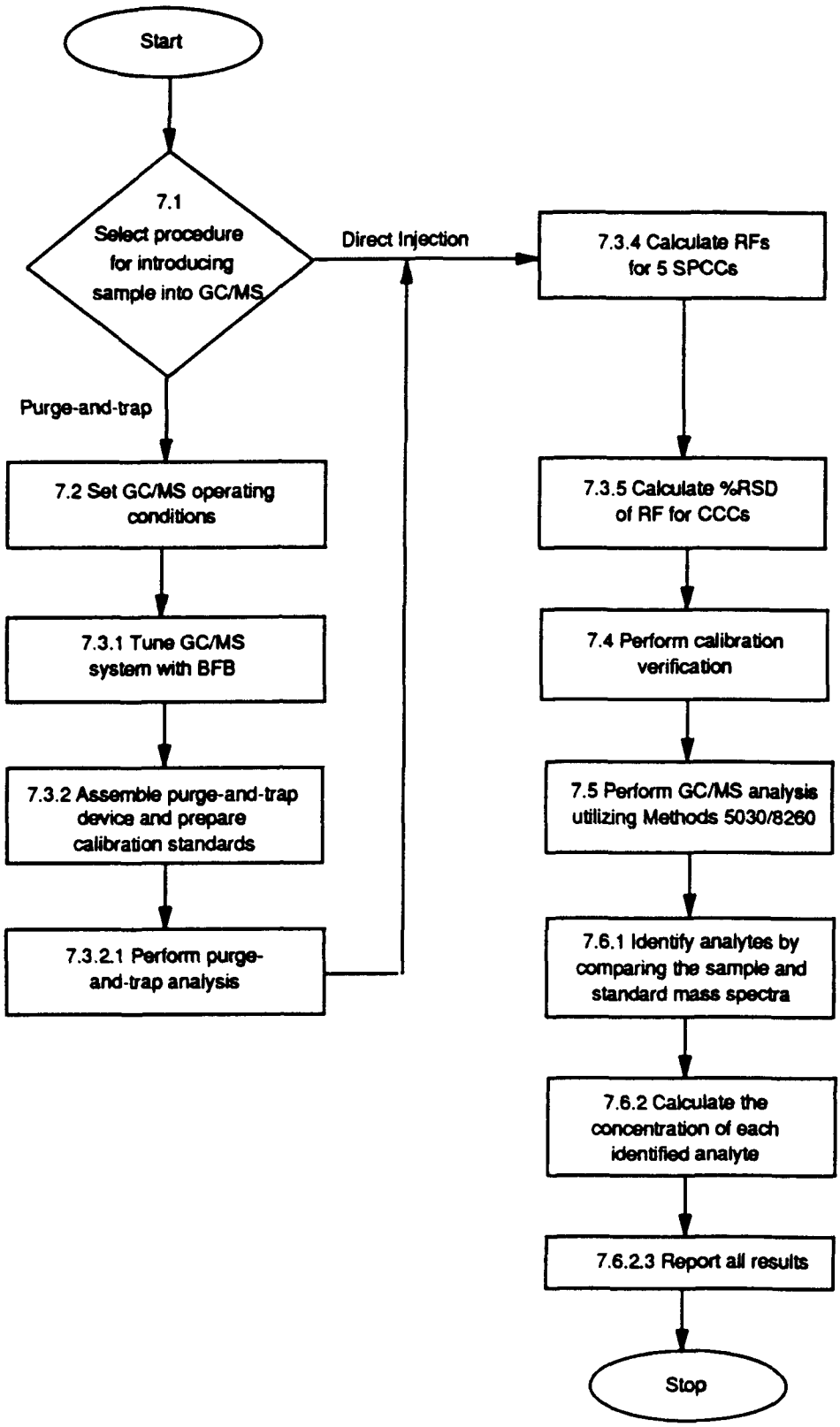


FIGURE 9.
LOW SOILS IMPINGER




Start
7.1
Select procedure for introducing sample into GC/MS
Direct Injection
Purge-and-trap
7.2 Set GC/MS operating conditions
7.3.1 Tune GC/MS system with BFB
7.3.2 Assemble purge-and-trap device and prepare calibration standards
7.3.2.1 Perform purge-and-trap analysis
7.3.4 Calculate RFs for 5 SPCCs
7.3.5 Calculate %RSD of RF for CCCs
7.4 Perform calibration verification
7.5 Perform GC/MS analysis utilizing Methods 5030/8260
7.6.1 Identify analytes by comparing the sample and standard mass spectra
7.6.2 Calculate the concentration of each identified analyte
7.6.2.3 Report all results
Stop

METHOD 8270B

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
3-Amino-9-ethylcarbazole	132-32-1	X	X	ND	ND	ND
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
2-sec-Butyl-4,6-dinitrophenol	88-85-7	X	ND	ND	ND	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-Chloro-1,2-phenylenediamine	95-83-0	X	X	ND	ND	ND
4-Chloro-1,3-phenylenediamine	5131-60-2	X	X	ND	ND	ND
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

Compounds	CAS No[a]	Appropriate Preparation Techniques 3510	3520	3540	3550	3580
Dibenzofuran	132-64-9	X	X	ND	X	X
Dibenzo(a,e)pyrene	192-65-4	ND	ND	ND	ND	X
1,2-Dibromo-3-chloropropane	96-12-8	X	X	ND	ND	ND
Di-n-butyl phthalate	84-74-2	X	X	X	X	X
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
Dihydrosaffrole	56312-13-1	ND	ND	ND	ND	ND
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
Dioxathion	78-34-2	ND	ND	ND	ND	ND
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

Compounds	CAS No[a]	Appropriate Preparation Techniques 3510	3520	3540	3550	3580
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
Ethyl methanesulfonate	62-50-0	X	ND	ND	ND	X
Ethyl parathion	56-38-2	X	X	ND	ND	ND
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
Hexamethylphosphoramide	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
4,4'-Methylenebis (N,N-dimethylaniline)	101-61-1	X	X	ND	ND	ND
Methyl methanesulfonate	66-27-3	X	ND	ND	ND	X
2-Methylnaphthalene	91-57-6	X	X	ND	X	X
2-Methyl-5-nitroaniline	99-55-8	X	X	ND	ND	ND
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

Compounds	CAS No[a]	Appropriate Preparation Techniques 3510	3520	3540	3550	3580
4-Methylphenol	106-44-5	X	ND	ND	ND	X
2-Methylpyridine	109-06-8	X	X	ND	ND	ND
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
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

Compounds	CAS No[a]	Appropriate Preparation Techniques 3510	3520	3540	3550	3580
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
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 dithiopyrophosphate	3689-24-5	X	X	ND	ND	ND
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
O,O,O-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 and for their qualitative and quantitative analysis by mass spectrometry.

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 - Appropriate sizes with ground glass stoppers.

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} (see Table 5). 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, 3541, 3550
Waste	3540, 3541, 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[a]
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

[a] 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 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 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.

7.3.4.1 The percent relative standard deviation (%RSD = 100[SD/RF]) should be less than 15% 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.

7.3.4.2 If the %RSD of any CCC is 30% or greater, then the chromatographic system is too reactive for analysis to begin. Clean or replace to injector liner and/or capillary column, then repeat the calibration procedure beginning with section 7.4.

7.3.5 Linearity - If the %RSD of any compound is 15% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation (Section 7.6.2).

7.3.5.1 If the %RSD of any compound is greater than 15%, construct calibration curves of area ratio (A/Ais) versus concentration using first or second order regression fit of the five calibration points. The analyst should select the regression order which introduces the least calibration error into the quantitation (Section 7.6.2.2 and 7.6.2.3). If the %RSD is <15%, use of calibration curves is a recommended alternative to average response factor calibration, and a useful diagnostic of standard preparation accuracy and absorption activity in the chromatographic system.

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 all semivolatile analytes, including all required surrogates, must be analyzed every 12 hours during analysis. Compare the instrument response factor from the standards every 12 hours with 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 drift using:

$$\% \text{ Drift} = \frac{C_I - C_c}{C_I} \times 100$$

where:

C_I = Calibration Check Compound standard concentration.
C_c = Measured concentration using selected quantitation method.

If the percent difference for each CCC is less than 20%, the initial calibration is assumed to be valid. If the criterion is not met (> 20% drift) 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. If the CCCs are not analytes required by the permit, then all required analytes must meet the 20% drift criterion.

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 The qualitative identification of compounds determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met.

7.6.1.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.6.1.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

7.6.1.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.6.1.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.6.1.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is

apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

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 $\pm$ 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.

7.6.2.2 If the %RSD of a compound's relative response factor is 15% or less, then the concentration in the extract may be determined using the average response factor ($\overline{RF}$) from initial calibration data (7.4.5.2) and the following equation:.

$$C_{ex}\ (mg/L) = \frac{(A_x \times C_{is})}{(A_{is} \times \overline{RF})}$$

where C_{ex} is the concentration of the compound in the extract, and the other terms are as defined in Section 7.4.3.

7.6.2.3 Alternatively, the regression line fitted to the initial calibration (Section 7.4.6.1) may be used for determination of the extract concentration.

7.6.2.4 Compute the concentration of the analyte in the sample using the equations in Sections 7.7.2.4.1 and 7.7.2.4.2.

7.6.2.4.1 The concentration of the analyte in the liquid phase of the sample is calculated using the concentration of the analyte in the extract and the volume of liquid extracted, as follows:

$$\text{Concentration in liquid } (\mu g/L) = \frac{(C_{ex} \times V_{ex})}{V_o}$$

where:

V_{ex} = extract volume, in mL
V_o = volume of liquid extracted, in L.

7.6.2.4.2 The concentration of the analyte in the solid phase of the sample is calculated using the concentration of the pollutant in the extract and the weight of the solids, as follows:

$$\text{Concentration in solid } (\mu g/kg) = \frac{(C_{ex} \times V_{ex})}{W_s}$$

where:

V_{ex} = extract volume, in mL
W_s = sample weight, in kg.

7.6.2.5 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.

7.6.2.6 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 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document quality data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control reference sample must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.2 Before processing any samples, the analyst should demonstrate, through the analysis of a reagent blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent blank should be processed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

8.3 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g. column changed), recalibration of the system must take place.

8.4 Required instrument QC is found in the following sections

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

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

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

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

8.5.1 A quality control (QC) reference sample concentrate is required containing each analyte at a concentration of 100 mg/L in acetone. 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.

8.5.2 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 water.

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

8.5.4 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.

8.5.5 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 analyzed.

8.5.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Step 8.5.6.1 or 8.5.6.2.

8.5.6.1 Locate and correct the source of the problem and repeat the test for all analytes of interest beginning with Step 8.5.2.

8.5.6.2 Beginning with Step 8.5.2, 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 Step 8.5.2.

8.6 The laboratory must, on an ongoing basis, analyze a reagent blank, a matrix spike, and a replicate for each analytical batch (up to a maximum of 20 samples/batch) to assess accuracy. For soil and waste samples where detectable amounts of organics are present, replicate samples may be appropriate in place of matrix spiked samples. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.6.1 The concentration of the spike in the sample should be determined as follows:

8.6.1.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Step 8.6.2, whichever concentration would be larger.

8.6.1.2 If the concentration of a specific analyte in a water sample is not being checked against a limit specific to that analyte, the spike should be at 100 µg/L or 1 to 5 times higher than

the background concentration determined in Step 8.6.2, whichever concentration would be larger. For other matrices, recommended spiking concentration is 20 times the EQL.

8.6.1.3 If it is impractical to determine background levels before spiking (e.g. maximum holding times will be exceeded), the spike concentration should be at (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or 100 µg/L. For other matrices, recommended spiking concentration is 20 times the EQL.

8.6.2 Analyze one sample aliquot to determine the background concentration (B) of each analyte. If necessary, prepare a new QC reference sample concentrate (Step 8.5.1) appropriate for the background concentration in the sample. Spike a second sample aliquot with 1.00 mL of the QC reference sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as 100(A-B)%/T, where T is the known true value of the spike.

8.6.3 Compare the percent recovery (p) for each analyte in a water sample with the corresponding QC acceptance criteria found in Table 6. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than 100 µg/L, the analyst must use either the QC acceptance criteria presented in Table 6, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of an analyte: (1) Calculate accuracy (x') using the equation found in Table 7, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 7, substituting x' for $\bar{x}$; (3) calculate the range for recovery at the spike concentration as $(100x'/T) \pm 2.44(100S'/T)\%$.

8.6.4 If any individual p falls outside the designated range for recovery, that analyte has failed the acceptance criteria. A check standard containing each analyte that failed the criteria must be analyzed as described in Step 8.7.

8.7 If any analyte in a water sample fails the acceptance criteria for recovery in Step 8.6, a QC reference sample containing each analyte that failed must be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC reference sample will depend upon the number of analytes being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of analytes in Table 6 must be measured in the sample in Step 8.6, the probability that the analysis of a QC reference sample will be required is high. In this case the QC reference sample should be routinely analyzed with the spiked sample.

8.7.1 Prepare the QC reference sample by adding 1.0 mL of the QC reference sample concentrate (Step 8.5.1 or 8.6.2) to 1 L of water. The QC reference sample needs only to contain the analytes that failed criteria in the test in Step 8.6.

8.7.2 Analyze the QC reference sample to determine the concentration measured (A) of each analyte. Calculate each percent recovery (p_s) as 100(A/T)%, where T is the true value of the standard concentration.

8.7.3 Compare the percent recovery (p_s) for each analyte with the corresponding QC acceptance criteria found in Table 6. Only analytes that failed the test in Step 8.6 need to be compared with these criteria. If the recovery of any such analyte falls outside the designated range, the laboratory performance for that analyte is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that analyte in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.8 As part of the QC program for the laboratory, method accuracy for each matrix studied must be assessed and records must be maintained. After the analysis of five spiked samples (of the same matrix) as in Step 8.6, calculate the average percent recovery ($\bar{p}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{p} - 2s_p$ to $\bar{p} + 2s_p$. If $\bar{p}$ = 90% and s_p = 10%, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each analyte on a regular basis (e.g. after each five to ten new accuracy measurements).

8.9 To determine acceptable accuracy and precision limits for surrogate standards the following procedure should be performed.

8.9.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

8.9.2 Once a minimum of thirty samples of the same matrix have been analyzed, calculate the average percent recovery (P) and standard deviation of the percent recovery (s) for each of the surrogates.

8.9.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

Upper Control Limit (UCL) = p + 3s
Lower Control Limit (LCL) = p - 3s

8.9.4 For aqueous and soil matrices, these laboratory established surrogate control limits should, if applicable, be compared with the control limits listed in Table 8. The limits given in Table 8 are multi-laboratory performance based limits for soil and aqueous samples, and therefore, the single-laboratory limits established in Step 8.9.3 must fall within those given in Table 8 for these matrices.

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

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.

- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration".

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

8.10 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or a mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

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.

9.2 Chromatograms from calibration standards analyzed with Day 0 and Day 7 samples were compared to detect possible deterioration of GC performance. These recoveries (using Method 3510 extraction) are presented in Table 9.

9.3 Method performance data (using Method 3541 Soxtec extraction) is presented in Table 10. Single laboratory accuracy and precision data were obtained for semivolatile organics in a clay soil by spiking at a concentration of 6 mg/kg for each compound. The spiking solution was mixed into the soil during addition and then allowed to equilibrate for approximately 1 hr prior to extraction. The spiked samples were then extracted by Method 3541 (Automated Soxhlet). Three determinations were performed and each extract was analyzed by gas chromatography/ mass spectrometry following Method 8270. The low recovery of the more volatile compounds is probably due to volatilization losses during equilibration. These data are listed in Table 11 and were taken from Reference 9.

10.0 REFERENCES

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

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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.

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9. Lopez-Avila, V. (W. Beckert, Project Officer); "Development of a Soxtec Extraction Procedure for Extraction of Organic Compounds from Soils and Sediments"; U.S. Environmental Protection Agency. Environmental Monitoring and Support Laboratory. Las Vegas, NV, October 1991; EPA 600/X-91/140.

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
Dihydrosaffrole	22.42	135	135,64,77
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
Dioxathion	25.25	97	97,125,270,153
Terbufos	25.35	231	231,57,97,153,103
α,α-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

TABLE 1.
(Continued)

Compound	Retention Time (min.)	Primary Ion	Secondary Ion(s)
Mexacarbate	26.02	165	165,150,134,164,222
4,4'-Oxydianiline	26.08	200	200,108,171,80,65
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

TABLE 1.
(Continued)

Compound	Retention Time (min.)	Primary Ion	Secondary Ion(s)
5,5-Diphenylhydantoin	33.40	180	180,104,252,223,209
Captafol	33.47	79	79,77,80,107
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

TABLE 1.
(Continued)

Compound	Retention Time (min.)	Primary Ion	Secondary Ion(s)
2-Fluorobiphenyl (surr.)	--	172	171
2-Fluorophenol (surr.)	--	112	64
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[1] 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[1] 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
Hexamethylphosphoramide	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[1] 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[1] 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
Hexachloroethan	Isophorone	2,6-Dinitrotoluene
Methyl methanesulfonate	2-Methylnaphthalene	Fluorene
2-Methylphenol	Naphthalene	2-Fluorobiphenyl (surr.)
4-Methylphenol	Nitrobenzene	Hexachlorocyclo-pentadiene
N-Nitrosodimethylamine	Nitrobenzene-d_8 (surr.)	1-Naphthylamine
N-Nitroso-di-n-propyl-amine	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
Fluoranthene	p-Dimethylaminoazobenzene	7,12-Dimethylbenz(a)anthracene
Hexachlorobenzene	Pyrene	Di-n-octyl phthalate
N-Nitrosodiphenylamine	Terphenyl-d_{14} (surr.)	Indeno(1,2,3-cd)pyrene
Pentachlorophenol		3-Methylcholanthrene
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 $\bar{x}$ (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

TABLE 7.
(Continued)

Compound	Accuracy, as recovery, x' (μg/L)	Single analyst precision, s_r' (μg/L)	Overall precision, S' (μg/L)
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
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

TABLE 9.
EXTRACTION EFFICIENCY AND AQUEOUS STABILITY RESULTS

COMPOUND	PERCENT RECOVERY ON DAY 0 AVG.	RSD	PERCENT RECOVERY ON DAY 7 AVG.	RSD
3-Amino-9-ethylcarbazole	80	8	73	3
4-Chloro-1,2-phenylenediamine	91	1	108	4
4-Chloro-1,3-phenylenediamine	84	3	70	3
1,2-Dibromo-3-chloropropane	97	2	98	5
2-sec-Butyl-4,6-dinitrophenol	99	3	97	6
Ethyl parathion	100	2	103	4
4,4'-Methylenebis(N,N-dimethylaniline)	108	4	90	4
2-Methyl-5-nitroaniline	99	10	93	4
2-Methylpyridine	80	4	83	4
Tetraethyl dithiopyrophosphate	92	7	70	1

Data from Reference 8.

TABLE 10.
AVERAGE PERCENT RECOVERIES AND PERCENT RSDs FOR THE TARGET COMPOUNDS FROM SPIKED CLAY SOIL AND TOPSOIL BY SOXTEC EXTRACTION WITH HEXANE-ACETONE (1:1)[a]

Cmpd #	Compound name	Clay Soil		Topsoil	
		Average percent recovery	Percent RSD	Average percent recovery	Percent RSD
1	1,3-Dichlorobenzene	0	--	0	--
2	1,2-Dichlorobenzene	0	--	0	--
3	Nitrobenzene	0	--	0	--
4	Benzal chloride	0	--	0	--
5	Benzotrichloride	0	--	0	--
6	4-Chloro-2-nitrotoluene	0	--	0	--
7	Hexachlorocyclopentadiene	4.1	15	7.8	23
8	2,4-Dichloronitrobenzene	35.2	7.6	21.2	15
9	3,4-Dichloronitrobenzene	34.9	15	20.4	11
10	Pentachlorobenzene	13.7	7.3	14.8	13
11	2,3,4,5-Tetrachloronitrobenzene	55.9	6.7	50.4	6.0
12	Benefin	62.6	4.8	62.7	2.9
13	alpha-BHC	58.2	7.3	54.8	4.8
14	Hexachlorobenzene	26.9	13	25.1	5.7
15	delta-BHC	95.8	4.6	99.2	1.3
16	Heptachlor	46.9	9.2	49.1	6.3
17	Aldrin	97.7	12	102	7.4
18	Isopropalin	102	4.3	105	2.3
19	Heptachlor epoxide	90.4	4.4	93.6	2.4
20	trans-Chlordane	90.1	4.5	95.0	2.3
21	Endosulfan I	96.3	4.4	101	2.2
22	Dieldrin	129	4.7	104	1.9
23	2,5-Dichlorophenyl-4'-nitrophenyl ether	110	4.1	112	2.1
24	Endrin	102	4.5	106	3.7
25	Endosulfan II	104	4.1	105	0.4
26	p,p'-DDT	134	2.1	111	2.0
27	2,3,6-Trichlorophenyl-4'nitrophenyl ether	110	4.8	110	2.8
28	2,3,4-Trichlorophenyl-4'-nitrophenyl ether	112	4.4	112	3.3
29	Mirex	104	5.3	108	2.2

[a] The operating conditions for the Soxtec apparatus were as follows: immersion time 45 min; extraction time 45 min; the sample size was 10 g; the spiking concentration was 500 ng/g, except for the surrogate compounds at 1000 ng/g, compounds 23, 27, and 28 at 1500 ng/g, compound 3 at 2000 ng/g, and compounds 1 and 2 at 5000 ng/g.

TABLE 11.
SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR THE EXTRACTION OF SEMIVOLATILE ORGANICS FROM SPIKED CLAY BY METHOD 3541 (AUTOMATED SOXHLET)[a]

Compound number	Compound name	Average percent recovery	Percent RSD
1	Phenol	47.8	5.6
2	Bis(2-chloroethyl)ether	25.4	13
3	2-Chlorophenol	42.7	4.3
4	Benzyl alcohol	55.9	7.2
5	2-Methylphenol	17.6	6.6
6	Bis(2-chloroisopropyl)ether	15.0	15
7	4-Methylphenol	23.4	6.7
8	N-Nitroso-di-n-propylamine	41.4	6.2
9	Nitrobenzene	28.2	7.7
10	Isophorone	56.1	4.2
11	2-Nitrophenol	36.0	6.5
12	2,4-Dimethylphenol	50.1	5.7
13	Benzoic acid	40.6	7.7
14	Bis(2-chloroethoxy)methane	44.1	3.0
15	2,4-Dichlorophenol	55.6	4.6
16	1,2,4-Trichlorobenzene	18.1	31
17	Naphthalene	26.2	15
18	4-Chloroaniline	55.7	12
19	4-Chloro-3-methylphenol	65.1	5.1
20	2-Methylnaphthalene	47.0	8.6
21	Hexachlorocyclopentadiene	19.3	19
22	2,4,6-Trichlorophenol	70.2	6.3
23	2,4,5-Trichlorophenol	26.8	2.9
24	2-Chloronaphthalene	61.2	6.0
25	2-Nitroaniline	73.8	6.0
26	Dimethyl phthalate	74.6	5.2
27	Acenaphthylene	71.6	5.7
28	3-Nitroaniline	77.6	5.3
29	Acenaphthene	79.2	4.0
30	2,4-Dinitrophenol	91.9	8.9
31	4-Nitrophenol	62.9	16
32	Dibenzofuran	82.1	5.9
33	2,4-Dinitrotoluene	84.2	5.4
34	2,6-Dinitrotoluene	68.3	5.8
35	Diethyl phthalate	74.9	5.4
36	4-Chlorophenyl-phenyl ether	67.2	3.2
37	Fluorene	82.1	3.4
38	4-Nitroaniline	79.0	7.9
39	4,6-Dinitro-2-methylphenol	63.4	6.8
40	N-Nitrosodiphenylamine	77.0	3.4
41	4-Bromophenyl-phenyl ether	62.4	3.0

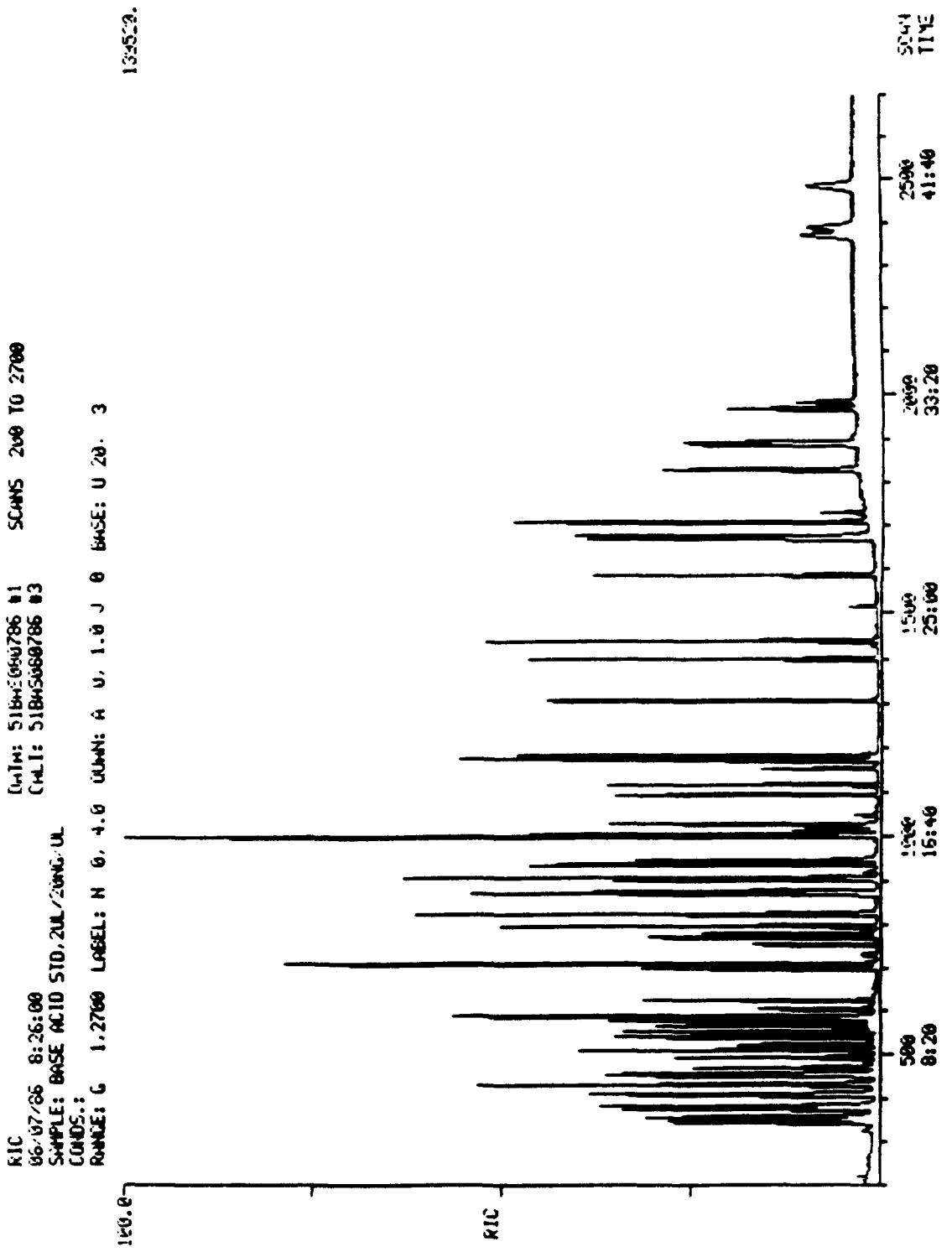
Table 11. (Continued)

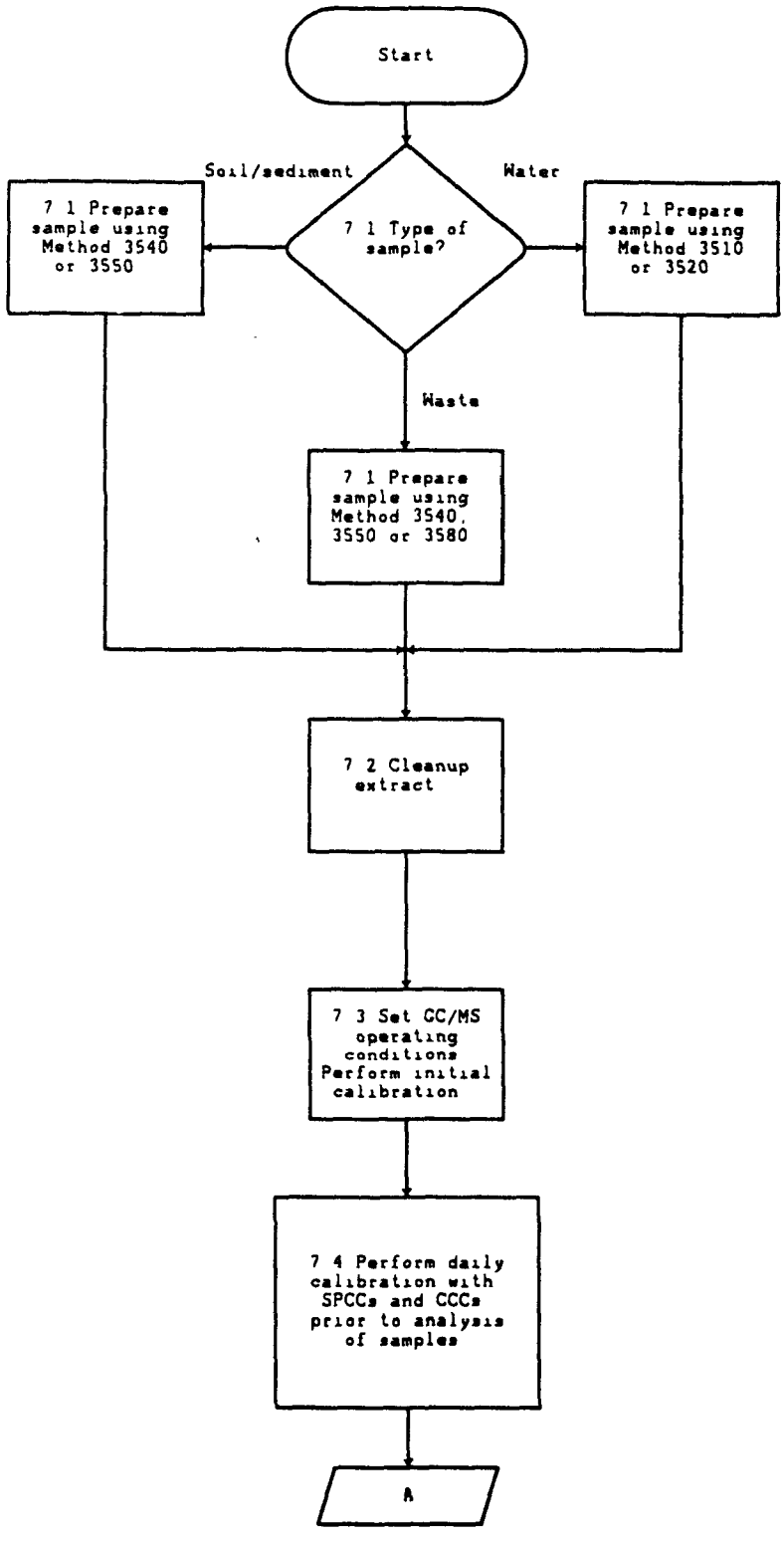
Compound number	Compound name	Average percent recovery	Percent RSD
42	Hexachlorobenzene	72.6	3.7
43	Pentachlorophenol	62.7	6.1
44	Phenanthrene	83.9	5.4
45	Anthracene	96.3	3.9
46	Di-n-butyl phthalate	78.3	40
47	Fluoranthene	87.7	6.9
48	Pyrene	102	0.8
49	Butylbenzyl phthalate	66.3	5.2
50	3,3'-Dichlorobenzidine	25.2	11
51	Benzo(a)anthracene	73.4	3.8
52	Bis(2-ethylhexyl) phthalate	77.2	4.8
53	Chrysene	76.2	4.4
54	Di-n-octyl phthalate	83.1	4.8
55	Benzo(b)fluoranthene	82.7	5.0
56	Benzo(k)fluoranthene	71.7	4.1
57	Benzo(a)pyrene	71.7	4.1
58	Indeno(1,2,3-cd)pyrene	72.2	4.3
59	Dibenzo(a,h)anthracene	66.7	6.3
60	Benzo(g,h,i)perylene	63.9	8.0
61	1,2-Dichlorobenzene	0	--
62	1,3-Dichlorobenzene	0	--
63	1,4-Dichlorobenzene	0	--
64	Hexachloroethane	0	--
65	Hexachlorobutadiene	0	--

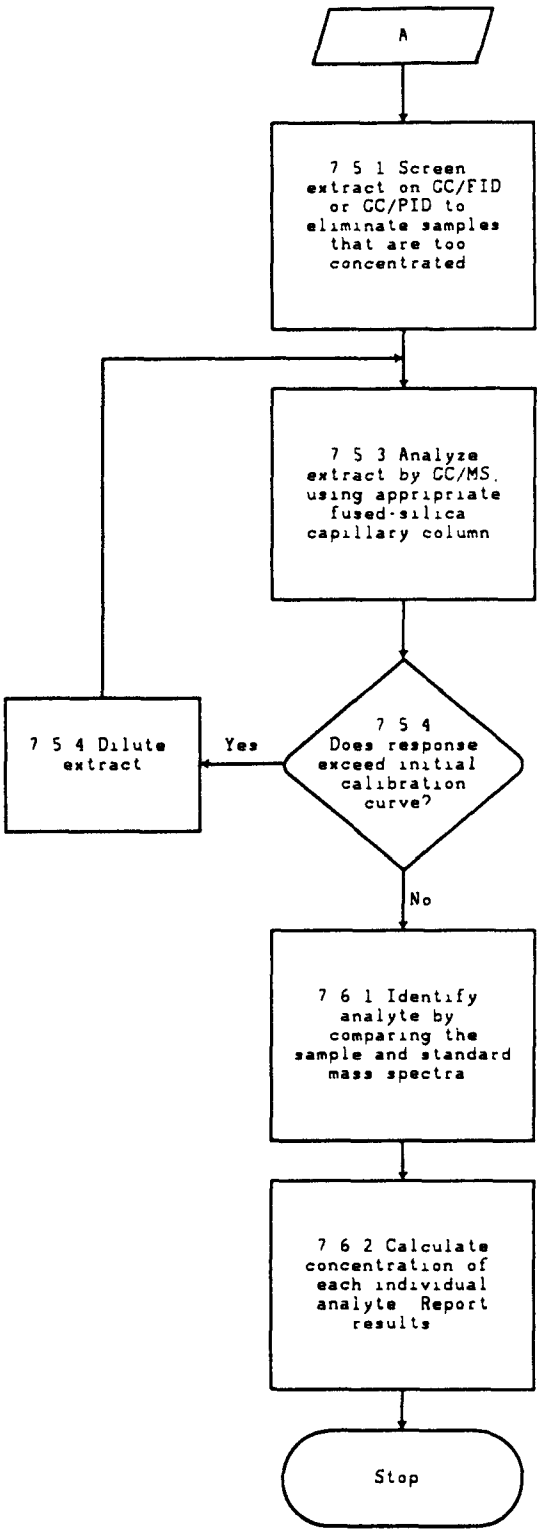
[a] Number of determinations was three. The operating conditions for the Soxtec apparatus were as follows: immersion time 45 min; extraction time 45 min; the sample size was 10 g clay soil; the spike concentration was 6 mg/kg per compound. The sample was allowed to equilibrate 1 hour after spiking.

Data taken from Reference 9.

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




Start
7 1 Type of sample?
Soil/sediment
Water
Waste
7 1 Prepare sample using Method 3540 or 3550
7 1 Prepare sample using Method 3510 or 3520
7 1 Prepare sample using Method 3540, 3550 or 3580
7 2 Cleanup extract
7 3 Set GC/MS operating conditions Perform initial calibration
7 4 Perform daily calibration with SPCCs and CCCs prior to analysis of samples
A


A
7 5 1 Screen extract on GC/FID or GC/PID to eliminate samples that are too concentrated
7 5 3 Analyze extract by GC/MS, using appripriate fused-silica capillary column
7 5 4 Does response exceed initial calibration curve?
Yes
7 5 4 Dilute extract
No
7 6 1 Identify analyte by comparing the sample and standard mass spectra
7 6 2 Calculate concentration of each individual analyte Report results
Stop

POLYCHLORINATED DIBENZODIOXINS (PCDDs) AND POLYCHLORINATED DIBENZOFURANS (PCDFs)BY HIGH-RESOLUTION GAS CHROMATOGRAPHY/HIGH-RESOLUTION MASS SPECTROMETRY (HRGC/HRMS)

1.0 SCOPE AND APPLICATION

1.1 This method provides procedures for the detection and quantitative measurement of polychlorinated dibenzo-p-dioxins (tetra- through octachlorinated homologues; PCDDs), and polychlorinated dibenzofurans (tetra- through octachlorinated homologues; PCDFs) in a variety of environmental matrices and at part-per-trillion (ppt) to part-per-quadrillion (ppq) concentrations. The following compounds can be determined by this method:

Compound Name
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)
1,2,3,7,8-Pentachlorodibenzo-p-dioxin (PeCDD)
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin (HxCDD)
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin (HxCDD)
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin (HxCDD)
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin (HpCDD)
2,3,7,8-Tetrachlorodibenzofuran (TCDF)
1,2,3,7,8-Pentachlorodibenzofuran (PeCDF)
2,3,4,7,8-Pentachlorodibenzofuran (PeCDF)
1,2,3,6,7,8-Hexachlorodibenzofuran (HxCDF)
1,2,3,7,8,9-Hexachlorodibenzofuran (HxCDF)
1,2,3,4,7,8-Hexachlorodibenzofuran (HxCDF)
2,3,4,6,7,8-Hexachlorodibenzofuran (HxCDF)
1,2,3,4,6,7,8-Heptachlorodibenzofuran (HpCDF)
1,2,3,4,7,8,9-Heptachlorodibenzofuran (HpCDF)

1.2 The analytical method calls for the use of high-resolution gas chromatography and high-resolution mass spectrometry (HRGC/HRMS) on purified sample extracts. Table 1 lists the various sample types covered by this analytical protocol, the 2,3,7,8-TCDD-based method calibration limits (MCLs), and other pertinent information. Samples containing concentrations of specific congeneric analytes (PCDDs and PCDFs) considered within the scope of this method that are greater than ten times the upper MCLs must be analyzed by a protocol designed for such concentration levels, e.g., Method 8280. An optional method for reporting the analytical results using a 2,3,7,8-TCDD toxicity equivalency factor (TEF) is described.

1.3 The sensitivity of this method is dependent upon the level of interferences within a given matrix. The calibration range of the method for a 1 L water sample is 10 to 2000 ppq for TCDD/TCDF and PeCDD/PeCDF, and 1.0 to 200 ppt for a 10 g soil, sediment, fly ash, or tissue sample for the same analytes

(Table 1). Analysis of a one-tenth aliquot of the sample permits measurement of concentrations up to 10 times the upper MCL. The actual limits of detection and quantitation will differ from the lower MCL, depending on the complexity of the matrix.

1.4 This method is designed for use by analysts who are experienced with residue analysis and skilled in HRGC/HRMS.

1.5 Because of the extreme toxicity of many of these compounds, the analyst must take the necessary precautions to prevent exposure to materials known or believed to contain PCDDs or PCDFs. It is the responsibility of the laboratory personnel to ensure that safe handling procedures are employed. Section 11 of this method discusses safety procedures.

2.0 SUMMARY OF METHOD

2.1 This procedure uses matrix specific extraction, analyte specific cleanup, and HRGC/HRMS analysis techniques.

2.2 If interferences are encountered, the method provides selected cleanup procedures to aid the analyst in their elimination. A simplified analysis flow chart is presented at the end of this method.

2.3 A specified amount (see Table 1) of soil, sediment, fly ash, water, sludge (including paper pulp), still bottom, fuel oil, chemical reactor residue, fish tissue, or human adipose tissue is spiked with a solution containing specified amounts of each of the nine isotopically ($^{13}C_{12}$) labeled PCDDs/PCDFs listed in Column 1 of Table 2. The sample is then extracted according to a matrix specific extraction procedure. Aqueous samples that are judged to contain 1 percent or more solids, and solid samples that show an aqueous phase, are filtered, the solid phase (including the filter) and the aqueous phase extracted separately, and the extracts combined before extract cleanup. The extraction procedures are:

a) Toluene:Soxhlet extraction for soil, sediment, fly ash and paper pulp samples;

b) Methylene chloride:liquid-liquid extraction for water samples;

c) Toluene:Dean-Stark extraction for fuel oil and aqueous sludge samples;

d) Toluene extraction for still bottom samples;

e) Hexane/methylene chloride:Soxhlet extraction or methylene chloride:Soxhlet extraction for fish tissue samples; and

f) Methylene chloride extraction for human adipose tissue samples.

g) As an option, all solid samples (wet or dry) can be extracted with toluene using a Soxhlet/Dean Stark extraction system.

The decision for the selection of an extraction procedure for chemical reactor residue samples is based on the appearance (consistency, viscosity) of the samples. Generally, they can be handled according to the procedure used for still bottom (or chemical sludge) samples.

2.4 The extracts are submitted to an acid-base washing treatment and dried. Following a solvent exchange step, the extracts are cleaned up by column chromatography on alumina, silica gel, and AX-21 activated carbon on Celite 545® (or equivalent).

2.4.1 The extracts from adipose tissue samples are treated with silica gel impregnated with sulfuric acid before chromatography on acidic silica gel, neutral alumina, and AX-21 on Celite 545® (or equivalent).

2.4.2 Fish tissue and paper pulp extracts are subjected to an acid wash treatment only, prior to chromatography on alumina and AX-21/Celite 545® (or equivalent).

2.5 The preparation of the final extract for HRGC/HRMS analysis is accomplished by adding, to the concentrated AX-21/Celite 545® (or equivalent) column eluate, 10 to 50 µL (depending on the matrix type) of a nonane solution containing 50 pg/µL of each of the two recovery standards $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD (Table 2). The former is used to determine the percent recoveries of tetra- and pentachlorinated PCDD/PCDF congeners, while the latter is used to determine the percent recoveries of the hexa-, hepta- and octachlorinated PCDD/PCDF congeners.

2.6 One to two µL of the concentrated extract are injected into an HRGC/HRMS system capable of performing selected ion monitoring at resolving powers of at least 10,000 (10 percent valley definition).

2.7 The identification of OCDD and nine of the fifteen 2,3,7,8-substituted congeners (Table 3), for which a ^{13}C-labeled standard is available in the sample fortification and recovery standard solutions (Table 2), is based on their elution at their exact retention time (within 0.005 retention time units measured in the routine calibration) and the simultaneous detection of the two most abundant ions in the molecular ion region. The remaining six 2,3,7,8-substituted congeners (i.e., 2,3,4,7,8-PeCDF; 1,2,3,4,7,8-HxCDD; 1,2,3,6,7,8-HxCDF; 1,2,3,7,8,9-HxCDF; 2,3,4,6,7,8-HxCDF, and 1,2,3,4,7,8,9-HpCDF), for which no carbon-labeled internal standards are available in the sample fortification solution, and all other identified PCDD/PCDF congeners are identified by their relative retention times falling within their respective PCDD/PCDF retention time windows, as established from the routine calibration data, and the simultaneous detection of the two most abundant ions in the molecular ion region. The identification of OCDF is based on its retention time relative to $^{13}C_{12}$-OCDD and the simultaneous detection of the two most abundant ions in the molecular ion region. Confirmation is based on a comparison of the ratios of the integrated ion abundance of the molecular ion species to their theoretical abundance ratios.

2.8 Quantitation of the individual congeners, total PCDDs and total PCDFs is achieved in conjunction with the establishment of a multipoint (five points) calibration curve for each homologue, during which each calibration solution is analyzed once.

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts or elevated baselines that may cause misinterpretation of the chromatographic data (see references 1 and 2.) All of these materials must be demonstrated to be free from interferants under the conditions of analysis by performing laboratory method blanks. Analysts should avoid using PVC gloves.

3.2 The use of high purity reagents and solvents helps minimize interference problems. Purification of solvents by distillation in all-glass systems may be necessary.

3.3 Interferants coextracted from the sample will vary considerably from matrix to matrix. PCDDs and PCDFs are often associated with other interfering chlorinated substances such as polychlorinated biphenyls (PCBs), polychlorinated diphenyl ethers (PCDPEs), polychlorinated naphthalenes, and polychlorinated alkyldibenzofurans that may be found at concentrations several orders of magnitude higher than the analytes of interest. Retention times of target analytes must be verified using reference standards. These values must correspond to the retention time windows established in Section 8.1.1.3. While certain cleanup techniques are provided as part of this method, unique samples may require additional cleanup steps to achieve lower detection limits.

3.4 A high-resolution capillary column (60 m DB-5, J&W Scientific, or equivalent) is used in this method. However, no single column is known to resolve all isomers. The 60 m DB-5 GC column is capable of 2,3,7,8-TCDD isomer specificity (Section 8.1.1). In order to determine the concentration of the 2,3,7,8-TCDF (if detected on the DB-5 column), the sample extract must be reanalyzed on a column capable of 2,3,7,8-TCDF isomer specificity (e.g., DB-225, SP-2330, SP-2331, or equivalent). When a column becomes available that resolves all isomers, then a single analysis on this column can be used instead of analyses on more than one column.

4.0 APPARATUS AND MATERIALS

4.1 High-Resolution Gas Chromatograph/High-Resolution Mass Spectrometer/Data System (HRGC/HRMS/DS) - The GC must be equipped for temperature programming, and all required accessories must be available, such as syringes, gases, and capillary columns.

4.1.1 GC Injection Port - The GC injection port must be designed for capillary columns. The use of splitless injection techniques is recommended. On column 1 µL injections can be used on the 60 m DB-5 column. The use of a moving needle injection port is also acceptable. When using the method described in this protocol, a 2 µL injection volume is used consistently (i.e., the injection volumes for all extracts, blanks, calibration solutions and the performance check samples are 2 µL). One µL injections are allowed; however, laboratories must remain consistent throughout the analyses by using the same injection volume at all times.

4.1.2 Gas Chromatograph/Mass Spectrometer (GC/MS) Interface - The GC/MS interface components should withstand 350°C. The interface must be designed so that the separation of 2,3,7,8-TCDD from the other TCDD isomers achieved in the gas chromatographic column is not appreciably degraded. Cold spots or active surfaces (adsorption sites) in the GC/MS interface can cause peak tailing and peak broadening. It is recommended that the GC column be fitted directly into the mass spectrometer ion source without being exposed to the ionizing electron beam. Graphite ferrules should be avoided in the injection port because they may adsorb the PCDDs and PCDFs. Vespel™, or equivalent, ferrules are recommended.

4.1.3 Mass Spectrometer - The static resolving power of the instrument must be maintained at a minimum of 10,000 (10 percent valley).

4.1.4 Data System - A dedicated data system is employed to control the rapid multiple-ion monitoring process and to acquire the data. Quantitation data (peak areas or peak heights) and SIM traces (displays of intensities of each ion signal being monitored including the lock-mass ion as a function of time) must be acquired during the analyses and stored. Quantitations may be reported based upon computer generated peak areas or upon measured peak heights (chart recording). The data system must be capable of acquiring data at a minimum of 10 ions in a single scan. It is also recommended to have a data system capable of switching to different sets of ions (descriptors) at specified times during an HRGC/HRMS acquisition. The data system should be able to provide hard copies of individual ion chromatograms for selected gas chromatographic time intervals. It should also be able to acquire mass spectral peak profiles (Section 8.1.2.3) and provide hard copies of peak profiles to demonstrate the required resolving power. The data system should permit the measurement of noise on the base line.

NOTE: The detector ADC zero setting must allow peak-to-peak measurement of the noise on the base line of every monitored channel and allow for good estimation of the instrument resolving power. In Figure 2, the effect of different zero settings on the measured resolving power is shown.

4.2 GC Columns

4.2.1 In order to have an isomer specific determination for 2,3,7,8-TCDD and to allow the detection of OCDD/OCDF within a reasonable time interval in one HRGC/HRMS analysis, use of the 60 m DB-5 fused silica capillary column is recommended. Minimum acceptance criteria must be demonstrated and documented (Section 8.1.1). At the beginning of each 12 hour period (after mass resolution and GC resolution is demonstrated) during which sample extracts or concentration calibration solutions will be analyzed, column operating conditions must be attained for the required separation on the column to be used for samples. Operating conditions known to produce acceptable results with the recommended column are shown in Section 7.6.

4.2.2 Isomer specificity for all 2,3,7,8-substituted PCDDs/PCDFs cannot be achieved on the 60 m DB-5 GC column alone. In order to determine the proper concentrations of the individual 2,3,7,8-substituted

congeners, the sample extract must be reanalyzed on another GC column that resolves the isomers. When such a column becomes available, and the isomer specificity can be documented, the performing laboratory will be required to use it.

4.2.3 30 m DB-225 fused silica capillary column, (J&W Scientific) or equivalent.

4.3 Miscellaneous Equipment and Materials - The following list of items does not necessarily constitute an exhaustive compendium of the equipment needed for this analytical method.

4.3.1 Nitrogen evaporation apparatus with variable flow rate.

4.3.2 Balances capable of accurately weighing to 0.01 g and 0.0001 g.

4.3.3 Centrifuge.

4.3.4 Water bath, equipped with concentric ring covers and capable of being temperature controlled within $\pm$ 2°C.

4.3.5 Stainless steel or glass container large enough to hold contents of one pint sample containers.

4.3.6 Glove box.

4.3.7 Drying oven.

4.3.8 Stainless steel spoons and spatulas.

4.3.9 Laboratory hoods.

4.3.10 Pipets, disposable, Pasteur, 150 mm long x 5 mm ID.

4.3.11 Pipets, disposable, serological, 10 mL, for the preparation of the carbon columns specified in Section 7.5.3.

4.3.12 Reaction vial, 2 mL, silanized amber glass (Reacti-vial, or equivalent).

4.3.13 Stainless steel meat grinder with a 3 to 5 mm hole size inner plate.

4.3.14 Separatory funnels, 125 mL and 2000 mL.

4.3.15 Kuderna-Danish concentrator, 500 mL, fitted with 10 mL concentrator tube and three ball Snyder column.

4.3.16 Teflon™ or carborundum (silicon carbide) boiling chips (or equivalent), washed with hexane before use.

NOTE: Teflon™ boiling chips may float in methylene chloride, may not work in the presence of any water phase, and may be penetrated by nonpolar organic compounds.

4.3.17 Chromatographic columns, glass, 300 mm x 10.5 mm, fitted with Teflon™ stopcock.

4.3.18 Adapters for concentrator tubes.

4.3.19 Glass fiber filters.

4.3.20 Dean-Stark trap, 5 or 10 mL, with T-joints, condenser and 125 mL flask.

4.3.21 Continuous liquid-liquid extractor.

4.3.22 All glass Soxhlet apparatus, 500 mL flask.

4.3.23 Soxhlet/Dean Stark extractor (optional), all glass, 500 mL flask.

4.3.24 Glass funnels, sized to hold 170 mL of liquid.

4.3.25 Desiccator.

4.3.26 Solvent reservoir (125 mL), Kontes; 12.35 cm diameter (special order item), compatible with gravity carbon column.

4.3.27 Rotary evaporator with a temperature controlled water bath.

4.3.28 High speed tissue homogenizer, equipped with an EN-8 probe, or equivalent.

4.3.29 Glass wool, extracted with methylene chloride, dried and stored in a clean glass jar.

4.3.30 Extraction jars, glass, 250 mL, with teflon lined screw cap.

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

4.3.32 Glass vials, 1 dram (or metric equivalent).

NOTE: Reuse of glassware should be minimized to avoid the risk of contamination. All glassware that is reused must be scrupulously cleaned as soon as possible after use, according to the following procedure: Rinse glassware with the last solvent used in it. Wash with hot detergent water, then rinse with copious amounts of tap water and several portions of organic-free reagent water. Rinse with high purity acetone and hexane and store it inverted or capped with solvent rinsed aluminum foil in a clean environment.

5.0 REAGENTS AND STANDARD SOLUTIONS

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 Column Chromatography Reagents

5.2.1 Alumina, neutral, 80/200 mesh (Super 1, Woelm®, or equivalent). Store in a sealed container at room temperature, in a desiccator, over self-indicating silica gel.

5.2.2 Alumina, acidic AG4, (Bio Rad Laboratories catalog #132-1240, or equivalent). Soxhlet extract with methylene chloride for 24 hours if blanks show contamination, and activate by heating in a foil covered glass container for 24 hours at 190°C. Store in a glass bottle sealed with a Teflon™ lined screw cap.

5.2.3 Silica gel, high purity grade, type 60, 70-230 mesh; Soxhlet extract with methylene chloride for 24 hours if blanks show contamination, and activate by heating in a foil covered glass container for 24 hours at 190°C. Store in a glass bottle sealed with a Teflon™ lined screw cap.

5.2.4 Silica gel impregnated with sodium hydroxide. Add one part (by weight) of 1 M NaOH solution to two parts (by weight) silica gel (extracted and activated) in a screw cap bottle and mix with a glass rod until free of lumps. Store in a glass bottle sealed with a Teflon™ lined screw cap.

5.2.5 Silica gel impregnated with 40 percent (by weight) sulfuric acid. Add two parts (by weight) concentrated sulfuric acid to three parts (by weight) silica gel (extracted and activated), mix with a glass rod until free of lumps, and store in a screw capped glass bottle. Store in a glass bottle sealed with a Teflon™ lined screw cap.

5.2.6 Celite 545® (Supelco), or equivalent.

5.2.7 Active carbon AX-21 (Anderson Development Co., Adrian, MI), or equivalent, prewashed with methanol and dried in vacuo at 110°C. Store in a glass bottle sealed with a Teflon™ lined screw cap.

5.3 Reagents

5.3.1 Sulfuric acid, H_2SO_4, concentrated, ACS grade, specific gravity 1.84.

5.3.2 Potassium hydroxide, KOH, ACS grade, 20 percent (w/v) in organic-free reagent water.

5.3.3 Sodium chloride, NaCl, analytical reagent, 5 percent (w/v) in organic-free reagent water.

5.3.4 Potassium carbonate, K_2CO_3, anhydrous, analytical reagent.

5.4 Desiccating agent

5.4.1 Sodium sulfate (powder, 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 Solvents

5.5.1 Methylene chloride, CH_2Cl_2. High purity, distilled in glass or highest available purity.

5.5.2 Hexane, C_6H_{14}. High purity, distilled in glass or highest available purity.

5.5.3 Methanol, CH_3OH. High purity, distilled in glass or highest available purity.

5.5.4 Nonane, C_9H_{20}. High purity, distilled in glass or highest available purity.

5.5.5 Toluene, $C_6H_5CH_3$. High purity, distilled in glass or highest available purity.

5.5.6 Cyclohexane, C_6H_{12}. High purity, distilled in glass or highest available purity.

5.5.7 Acetone, CH_3COCH_3. High purity, distilled in glass or highest available purity.

5.6 High-Resolution Concentration Calibration Solutions (Table 5) - Five nonane solutions containing unlabeled (totaling 17) and carbon-labeled (totaling 11) PCDDs and PCDFs at known concentrations are used to calibrate the instrument. The concentration ranges are homologue dependent, with the lowest values for the tetrachlorinated dioxin and furan (1.0 pg/μL) and the highest values for the octachlorinated congeners (1000 pg/μL).

5.6.1 Depending on the availability of materials, these high-resolution concentration calibration solutions may be obtained from the Environmental Monitoring Systems Laboratory, U.S. EPA, Cincinnati, Ohio. However, additional secondary standards must be obtained from commercial sources, and solutions must be prepared in the analyst's laboratory. Traceability of standards must be verified against EPA-supplied standard solutions. It is the responsibility of the laboratory to ascertain that the calibration solutions received (or prepared) are indeed at the appropriate concentrations before they are used to analyze samples.

5.6.2 Store the concentration calibration solutions in 1 mL minivials at room temperature in the dark.

5.7 GC Column Performance Check Solution - This solution contains the first and last eluting isomers for each homologous series from tetra- through heptachlorinated congeners. The solution also contains a series of other TCDD

isomers for the purpose of documenting the chromatographic resolution. The $^{13}C_{12}$-2,3,7,8-TCDD is also present. The laboratory is required to use nonane as the solvent and adjust the volume so that the final concentration does not exceed 100 pg/μL per congener. Table 7 summarizes the qualitative composition (minimum requirement) of this performance evaluation solution.

5.8 Sample Fortification Solution - This nonane solution contains the nine internal standards at the nominal concentrations that are listed in Table 2. The solution contains at least one carbon-labeled standard for each homologous series, and it is used to measure the concentrations of the native substances. (Note that $^{13}C_{12}$-OCDF is not present in the solution.)

5.9 Recovery Standard Solution - This nonane solution contains two recovery standards, $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD, at a nominal concentration of 50 pg/μL per compound. 10 to 50 μL of this solution will be spiked into each sample extract before the final concentration step and HRGC/HRMS analysis.

5.10 Matrix Spike Fortification Solution - Solution used to prepare the MS and MSD samples. It contains all unlabeled analytes listed in Table 5 at concentrations corresponding to the HRCC 3.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

6.2 Sample Collection

6.2.1 Sample collection personnel should, to the extent possible, homogenize samples in the field before filling the sample containers. This should minimize or eliminate the necessity for sample homogenization in the laboratory. The analyst should make a judgment, based on the appearance of the sample, regarding the necessity for additional mixing. If the sample is clearly not homogeneous, the entire contents should be transferred to a glass or stainless steel pan for mixing with a stainless steel spoon or spatula before removal of a sample portion for analysis.

6.2.2 Grab and composite samples must be collected in glass containers. Conventional sampling practices must be followed. The bottle must not be prewashed with sample before collection. Sampling equipment must be free of potential sources of contamination.

6.3 Grinding or Blending of Fish Samples - If not otherwise specified by the U.S. EPA, the whole fish (frozen) should be blended or ground to provide a homogeneous sample. The use of a stainless steel meat grinder with a 3 to 5 mm hole size inner plate is recommended. In some circumstances, analysis of fillet or specific organs of fish may be requested by the U.S. EPA. If so requested, the above whole fish requirement is superseded.

6.4 Storage and Holding Times - All samples, except fish and adipose tissue samples, must be stored at 4°C in the dark, extracted within 30 days and completely analyzed within 45 days of extraction. Fish and adipose tissue

samples must be stored at -20°C in the dark, extracted within 30 days and completely analyzed within 45 days of collection. Whenever samples are analyzed after the holding time expiration date, the results should be considered to be minimum concentrations and must be identified as such.

NOTE: The holding times listed in Section 6.4 are recommendations. PCDDs and PCDFs are very stable in a variety of matrices, and holding times under the conditions listed in Section 6.4 may be as high as a year for certain matrices. Sample extracts, however, should always be analyzed within 45 days of extraction.

6.5 Phase Separation - This is a guideline for phase separation for very wet (>25 percent water) soil, sediment and paper pulp samples. Place a 50 g portion in a suitable centrifuge bottle and centrifuge for 30 minutes at 2,000 rpm. Remove the bottle and mark the interface level on the bottle. Estimate the relative volume of each phase. With a disposable pipet, transfer the liquid layer into a clean bottle. Mix the solid with a stainless steel spatula and remove a portion to be weighed and analyzed (percent dry weight determination, extraction). Return the remaining solid portion to the original sample bottle (empty) or to a clean sample bottle that is properly labeled, and store it as appropriate. Analyze the solid phase by using only the soil, sediment and paper pulp method. Take note of, and report, the estimated volume of liquid before disposing of the liquid as a liquid waste.

6.6 Soil, Sediment, or Paper Sludge (Pulp) Percent Dry Weight Determination - The percent dry weight of soil, sediment or paper pulp samples showing detectable levels (see note below) of at least one 2,3,7,8-substituted PCDD/PCDF congener is determined according to the following procedure. Weigh a 10 g portion of the soil or sediment sample (± 0.5 g) to three significant figures. Dry it to constant weight at 110°C in an adequately ventilated oven. Allow the sample to cool in a desiccator. Weigh the dried solid to three significant figures. Calculate and report the percent dry weight. Do not use this solid portion of the sample for extraction, but instead dispose of it as hazardous waste.

NOTE: Until detection limits have been established (Section 1.3), the lower MCLs (Table 1) may be used to estimate the minimum detectable levels.

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

CAUTION: Finely divided soils and sediments contaminated with PCDDs/PCDFs are hazardous because of the potential for inhalation or ingestion of particles containing PCDDs/PCDFs (including 2,3,7,8-TCDD). Such samples should be handled in a confined environment (i.e., a closed hood or a glove box).

6.7 Lipid Content Determination

6.7.1 Fish Tissue - To determine the lipid content of fish tissue, concentrate 125 mL of the fish tissue extract (Section 7.2.2), in a tared 200 mL round bottom flask, on a rotary evaporator until a constant weight (W) is achieved.

$$\text{Percent lipid} = \frac{100\ (W)}{10}$$

Dispose of the lipid residue as a hazardous waste if the results of the analysis indicate the presence of PCDDs or PCDFs.

6.7.2 Adipose Tissue - Details for the determination of the adipose tissue lipid content are provided in Section 7.3.3.

7.0 PROCEDURE

7.1 Internal standard addition

7.1.1 Use a portion of 1 g to 1000 g (± 5 percent) of the sample to be analyzed. Typical sample size requirements for different matrices are given in Section 7.4 and in Table 1. Transfer the sample portion to a tared flask and determine its weight.

7.1.2 Except for adipose tissue, add an appropriate quantity of the sample fortification mixture (Section 5.8) to the sample. All samples should be spiked with 100 µL of the sample fortification mixture to give internal standard concentrations as indicated in Table 1. As an example, for $^{13}C_{12}$-2,3,7,8-TCDD, a 10 g soil sample requires the addition of 1000 pg of $^{13}C_{12}$-2,3,7,8-TCDD to give the required 100 ppt fortification level. The fish tissue sample (20 g) must be spiked with 200 µL of the internal standard solution, because half of the extract will be used to determine the lipid content (Section 6.7.1).

7.1.2.1 For the fortification of soil, sediment, fly ash, water, fish tissue, paper pulp and wet sludge samples, mix the sample fortification solution with 1.0 mL acetone.

7.1.2.2 Do not dilute the nonane solution for the other matrices.

7.1.2.3 The fortification of adipose tissue is carried out at the time of homogenization (Section 7.3.2.3).

7.2 Extraction and Purification of Fish and Paper Pulp Samples

7.2.1 Add 60 g anhydrous sodium sulfate to a 20 g portion of a homogeneous fish sample (Section 6.3) and mix thoroughly with a stainless steel spatula. After breaking up any lumps, place the fish/sodium sulfate mixture in the Soxhlet apparatus on top of a glasswool plug. Add 250 mL methylene chloride or hexane/methylene chloride (1:1) to the Soxhlet apparatus and reflux for 16 hours. The solvent must cycle completely through the system five times per hour. Follow the same procedure for the partially dewatered paper pulp sample (using a 10 g sample, 30 g of anhydrous sodium sulfate and 200 mL of toluene).

NOTE: As an option, a Soxhlet/Dean Stark extractor system may be used, with toluene as the solvent. No sodium sulfate is added when using this option.

7.2.2 Transfer the fish extract from Section 7.2.1 to a 250 mL volumetric flask and fill to the mark with methylene chloride. Mix well, then remove 125 mL for the determination of the lipid content (Section 6.7.1). Transfer the remaining 125 mL of the extract, plus two 15 mL hexane/methylene chloride rinses of the volumetric flask, to a KD apparatus equipped with a Snyder column. Quantitatively transfer all of the paper pulp extract to a KD apparatus equipped with a Snyder column.

NOTE: As an option, a rotary evaporator may be used in place of the KD apparatus for the concentration of the extracts.

7.2.3 Add a Teflon™, or equivalent, boiling chip. Concentrate the extract in a water bath to an apparent volume of 10 mL. Remove the apparatus from the water bath and allow to cool for 5 minutes.

7.2.4 Add 50 mL hexane and a new boiling chip to the KD flask. Concentrate in a water bath to an apparent volume of 5 mL. Remove the apparatus from the water bath and allow to cool for 5 minutes.

NOTE: The methylene chloride must have been completely removed before proceeding with the next step.

7.2.5 Remove and invert the Snyder column and rinse it into the KD apparatus with two 1 mL portions of hexane. Decant the contents of the KD apparatus and concentrator tube into a 125 mL separatory funnel. Rinse the KD apparatus with two additional 5 mL portions of hexane and add the rinses to the funnel. Proceed with the cleanup according to the instructions starting in Section 7.5.1.1, but omit the procedures described in Sections 7.5.1.2 and 7.5.1.3.

7.3 Extraction and Purification of Human Adipose Tissue

7.3.1 Human adipose tissue samples must be stored at a temperature of -20°C or lower from the time of collection until the time of analysis. The use of chlorinated materials during the collection of the samples must be avoided. Samples are handled with stainless steel forceps, spatulas, or scissors. All sample bottles (glass) are cleaned as specified in the note at the end of Section 4.3. Teflon™ lined caps should be used.

NOTE: The specified storage temperature of -20°C is the maximum storage temperature permissible for adipose tissue samples. Lower storage temperatures are recommended.

7.3.2 Adipose Tissue Extraction

7.3.2.1 Weigh, to the nearest 0.01 g, a 10 g portion of a frozen adipose tissue sample into a culture tube (2.2 x 15 cm).

NOTE: The sample size may be smaller, depending on availability. In such a situation, the analyst is

required to adjust the volume of the internal standard solution added to the sample to meet the fortification level stipulated in Table 1.

7.3.2.2 Allow the adipose tissue specimen to reach room temperature (up to 2 hours).

7.3.2.3 Add 10 mL methylene chloride and 100 µL of the sample fortification solution. Homogenize the mixture for approximately 1 minute with a tissue homogenizer.

7.3.2.4 Allow the mixture to separate, then remove the methylene chloride extract from the residual solid material with a disposable pipet. Percolate the methylene chloride through a filter funnel containing a clean glass wool plug and 10 g anhydrous sodium sulfate. Collect the dried extract in a graduated 100 mL volumetric flask.

7.3.2.5 Add a second 10 mL portion of methylene chloride to the sample and homogenize for 1 minute. Decant the solvent, dry it, and transfer it to the 100 mL volumetric flask (Section 7.3.2.4).

7.3.2.6 Rinse the culture tube with at least two additional portions of methylene chloride (10 mL each), and transfer the entire contents to the filter funnel containing the anhydrous sodium sulfate. Rinse the filter funnel and the anhydrous sodium sulfate contents with additional methylene chloride (20 to 40 mL) into the 100 mL flask. Discard the sodium sulfate.

7.3.2.7 Adjust the volume to the 100 mL mark with methylene chloride.

7.3.3 Adipose Tissue Lipid Content Determination

7.3.3.1 Preweigh a clean 1 dram (or metric equivalent) glass vial to the nearest 0.0001 g on an analytical balance tared to zero.

7.3.3.2 Accurately transfer 1.0 mL of the final extract (100 mL) from Section 7.3.2.6 to the vial. Reduce the volume of the extract on a water bath (50-60°C) by a gentle stream of purified nitrogen until an oily residue remains. Nitrogen blowdown is continued until a constant weight is achieved.

NOTE: When the sample size of the adipose tissue is smaller than 10 g, then the analyst may use a larger portion (up to 10 percent) of the extract defined in Section 7.3.2.7 for the lipid determination.

7.3.3.3 Accurately weigh the vial with the residue to the nearest 0.0001 g and calculate the weight of the lipid present in the vial based on the difference of the weights.

7.3.3.4 Calculate the percent lipid content of the original sample to the nearest 0.1 percent as shown below:

$$\text{Lipid content, LC (\%)} = \frac{W_{lr} \times V_{ext}}{W_{at} \times V_{al}} \times 100$$

where:

W_{lr} = weight of the lipid residue to the nearest 0.0001 g calculated from Section 7.3.3.3,

V_{ext} = total volume (100 mL) of the extract in mL from Section 7.3.2.6,

W_{at} = weight of the original adipose tissue sample to the nearest 0.01 g from Section 7.3.2.1, and

V_{al} = volume of the aliquot of the final extract in mL used for the quantitative measure of the lipid residue (1.0 mL).

7.3.3.5 Record the lipid residue measured in Section 7.3.3.3 and the percent lipid content from Section 7.3.3.4.

7.3.4 Adipose Tissue Extract Concentration

7.3.4.1 Quantitatively transfer the remaining extract (99.0 mL) to a 500 mL Erlenmeyer flask. Rinse the volumetric flask with 20 to 30 mL of additional methylene chloride to ensure quantitative transfer.

7.3.4.2 Concentrate the extract on a rotary evaporator and a water bath at 40°C until an oily residue remains.

7.3.5 Adipose Tissue Extract Cleanup

7.3.5.1 Add 200 mL hexane to the lipid residue in the 500 mL Erlenmeyer flask and swirl the flask to dissolve the residue.

7.3.5.2 Slowly add, with stirring, 100 g of 40 percent (w/w) sulfuric acid-impregnated silica gel. Stir with a magnetic stirrer for two hours at room temperature.

7.3.5.3 Allow the solid phase to settle, and decant the liquid through a filter funnel containing 10 g anhydrous sodium sulfate on a glass wool plug, into another 500 mL Erlenmeyer flask.

7.3.5.4 Rinse the solid phase with two 50 mL portions of hexane. Stir each rinse for 15 minutes, decant, and dry as described under Section 7.3.5.3. Combine the hexane extracts from Section 7.3.5.3 with the rinses.

7.3.5.5 Rinse the sodium sulfate in the filter funnel with an additional 25 mL hexane and combine this rinse with the hexane extracts from Section 7.3.5.4.

7.3.5.6 Prepare an acidic silica column as follows: Pack a 2 cm x 10 cm chromatographic column with a glass wool plug, add approximately 20 mL hexane, add 1 g silica gel and allow to settle, then add 4 g of 40 percent (w/w) sulfuric acid-impregnated silica gel and allow to settle. Elute the excess hexane from the column until the solvent level reaches the top of the chromatographic packing. Verify that the column does not have any air bubbles and channels.

7.3.5.7 Quantitatively transfer the hexane extract from the Erlenmeyer flask (Sections 7.3.5.3 through 7.3.5.5) to the silica gel column reservoir. Allow the hexane extract to percolate through the column and collect the eluate in a 500 mL KD apparatus.

7.3.5.8 Complete the elution by percolating 50 mL hexane through the column into the KD apparatus. Concentrate the eluate on a steam bath to approximately 5 mL. Use nitrogen blowdown to bring the final volume to about 100 µL.

NOTE: If the silica gel impregnated with 40 percent sulfuric acid is highly discolored throughout the length of the adsorbent bed, the cleaning procedure must be repeated beginning with Section 7.3.5.1.

7.3.5.9 The extract is ready for the column cleanups described in Sections 7.5.2 through 7.5.3.6.

7.4 *Extraction and Purification of Environmental and Waste Samples*

7.4.1 Sludge/Wet Fuel Oil

7.4.1.1 Extract aqueous sludge or wet fuel oil samples by refluxing a sample (e.g., 2 g) with 50 mL toluene in a 125 mL flask fitted with a Dean-Stark water separator. Continue refluxing the sample until all the water is removed.

7.4.1.2 Cool the sample, filter the toluene extract through a glass fiber filter, or equivalent, into a 100 mL round bottom flask.

7.4.1.3 Rinse the filter with 10 mL toluene and combine the extract with the rinse.

7.4.1.4 Concentrate the combined solutions to near dryness on a rotary evaporator at 50°C. Use of an inert gas to concentrate the extract is also permitted. Proceed with Section 7.4.4.

NOTE: If the sludge or fuel oil sample dissolves in toluene, treat it according to the instructions in Section 7.4.2 below. If the labeled sludge sample originates from

pulp (paper mills), treat it according to the instructions starting in Section 7.2, but without the addition of sodium sulfate.

7.4.2 Still Bottom/Oil

7.4.2.1 Extract still bottom or oil samples by mixing a sample portion (e.g., 1.0 g) with 10 mL toluene in a small beaker and filtering the solution through a glass fiber filter (or equivalent) into a 50 mL round bottom flask. Rinse the beaker and filter with 10 mL toluene.

7.4.2.2 Concentrate the combined toluene solutions to near dryness on a rotary evaporator at 50°C. Proceed with Section 7.4.4.

7.4.3 Fly Ash

NOTE: Because of the tendency of fly ash to "fly", all handling steps should be performed in a hood in order to minimize contamination.

7.4.3.1 Weigh about 10 g fly ash to two decimal places and transfer to an extraction jar. Add 100 µL sample fortification solution (Section 5.8), diluted to 1 mL with acetone, to the sample. Add 150 mL of 1 M HCl to the fly ash sample. Seal the jar with the Teflon™ lined screw cap and shake for 3 hours at room temperature.

7.4.3.2 Rinse a glass fiber filter with toluene, and filter the sample through the filter paper, placed in a Buchner funnel, into a 1 L flask. Wash the fly ash cake with approximately 500 mL organic-free reagent water and dry the filter cake overnight at room temperature in a desiccator.

7.4.3.3 Add 10 g anhydrous powdered sodium sulfate, mix thoroughly, let sit in a closed container for one hour, mix again, let sit for another hour, and mix again.

7.4.3.4 Place the sample and the filter paper into an extraction thimble, and extract in a Soxhlet extraction apparatus charged with 200 mL toluene for 16 hours using a five cycle/hour schedule.

NOTE: As an option, a Soxhlet/Dean Stark extractor system may be used, with toluene as the solvent. No sodium sulfate is added when using this option.

7.4.3.5 Cool and filter the toluene extract through a glass fiber filter into a 500 mL round bottom flask. Rinse the filter with 10 mL toluene. Add the rinse to the extract and concentrate the combined toluene solutions to near dryness on a rotary evaporator at 50°C. Proceed with Section 7.4.4.

7.4.4 Transfer the concentrate to a 125 mL separatory funnel using 15 mL hexane. Rinse the flask with two 5 mL portions of hexane and add

the rinses to the funnel. Shake the combined solutions in the separatory funnel for two minutes with 50 mL of 5 percent sodium chloride solution, discard the aqueous layer, and proceed with Section 7.5.

7.4.5 Aqueous samples

7.4.5.1 Allow the sample to come to ambient temperature, then mark the water meniscus on the side of the 1 L sample bottle for later determination of the exact sample volume. Add the required acetone diluted sample fortification solution (Section 5.8).

7.4.5.2 When the sample is judged to contain 1 percent or more solids, the sample must be filtered through a 0.45 μm glass fiber filter that has been rinsed with toluene. If the suspended solids content is too great to filter through the 0.45 μm filter, centrifuge the sample, decant, and then filter the aqueous phase.

7.4.5.3 Combine the solids from the centrifuge bottle(s) with the particulates on the filter and with the filter itself and proceed with the Soxhlet extraction as specified in Sections 7.4.6.1 through 7.4.6.4. Remove and invert the Snyder column and rinse it down into the KD apparatus with two 1 mL portions of hexane.

7.4.5.4 Pour the aqueous filtrate into a 2 L separatory funnel. Add 60 mL methylene chloride to the sample bottle, seal and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for two minutes with periodic venting.

7.4.5.5 Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation (e.g., glass stirring rod).

7.4.5.6 Collect the methylene chloride into a KD apparatus (mounted with a 10 mL concentrator tube) by passing the sample extracts through a filter funnel packed with a glass wool plug and 5 g anhydrous sodium sulfate.

NOTE: As an option, a rotary evaporator may be used in place of the KD apparatus for the concentration of the extracts.

7.4.5.7 Repeat the extraction twice with fresh 60 mL portions of methylene chloride. After the third extraction, rinse the sodium sulfate with an additional 30 mL methylene chloride to ensure quantitative transfer. Combine all extracts and the rinse in the KD apparatus.

NOTE: A continuous liquid-liquid extractor may be used in place of a separatory funnel when experience with a sample from a given source indicates that a serious

emulsion problem will result or an emulsion is encountered when using a separatory funnel. Add 60 mL methylene chloride to the sample bottle, seal, and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the extractor. Repeat the rinse of the sample bottle with an additional 50 to 100 mL portion of methylene chloride and add the rinse to the extractor. Add 200 to 500 mL methylene chloride to the distilling flask, add sufficient organic-free reagent water (Section 5.1) to ensure proper operation, and extract for 24 hours. Allow to cool, then detach the distilling flask. Dry and concentrate the extract as described in Sections 7.4.5.6 and 7.4.5.8 through 7.4.5.10. Proceed with Section 7.4.5.11.

7.4.5.8 Attach a Snyder column and concentrate the extract on a water bath until the apparent volume of the liquid is 5 mL. Remove the KD apparatus and allow it to drain and cool for at least 10 minutes.

7.4.5.9 Remove the Snyder column, add 50 mL hexane, add the concentrate obtained from the Soxhlet extraction of the suspended solids (Section 7.4.5.3), if applicable, re-attach the Snyder column, and concentrate to approximately 5 mL. Add a new boiling chip to the KD apparatus before proceeding with the second concentration step.

7.4.5.10 Rinse the flask and the lower joint with two 5 mL portions of hexane and combine the rinses with the extract to give a final volume of about 15 mL.

7.4.5.11 Determine the original sample volume by filling the sample bottle to the mark with water and transferring the water to a 1000 mL graduated cylinder. Record the sample volume to the nearest 5 mL. Proceed with Section 7.5.

7.4.6 Soil/Sediment

7.4.6.1 Add 10 g anhydrous powdered sodium sulfate to the sample portion (e.g., 10 g) and mix thoroughly with a stainless steel spatula. After breaking up any lumps, place the soil/sodium sulfate mixture in the Soxhlet apparatus on top of a glass wool plug (the use of an extraction thimble is optional).

NOTE: As an option, a Soxhlet/Dean Stark extractor system may be used, with toluene as the solvent. No sodium sulfate is added when using this option.

7.4.6.2 Add 200 to 250 mL toluene to the Soxhlet apparatus and reflux for 16 hours. The solvent must cycle completely through the system five times per hour.

NOTE: If the dried sample is not of free flowing consistency, more sodium sulfate must be added.

7.4.6.3 Cool and filter the extract through a glass fiber filter into a 500 mL round bottom flask for evaporation of the toluene. Rinse the filter with 10 mL of toluene, and concentrate the combined fractions to near dryness on a rotary evaporator at 50°C. Remove the flask from the water bath and allow to cool for 5 minutes.

7.4.6.4 Transfer the residue to a 125 mL separatory funnel, using 15 mL of hexane. Rinse the flask with two additional portions of hexane, and add the rinses to the funnel. Proceed with Section 7.5.

7.5 Cleanup

7.5.1 Partition

7.5.1.1 Partition the hexane extract against 40 mL of concentrated sulfuric acid. Shake for two minutes. Remove and discard the sulfuric acid layer (bottom). Repeat the acid washing until no color is visible in the acid layer (perform a maximum of four acid washings).

7.5.1.2 Omit this step for the fish sample extract. Partition the extract against 40 mL of 5 percent (w/v) aqueous sodium chloride. Shake for two minutes. Remove and discard the aqueous layer (bottom).

7.5.1.3 Omit this step for the fish sample extract. Partition the extract against 40 mL of 20 percent (w/v) aqueous potassium hydroxide (KOH). Shake for two minutes. Remove and discard the aqueous layer (bottom). Repeat the base washing until no color is visible in the bottom layer (perform a maximum of four base washings). Strong base (KOH) is known to degrade certain PCDDs/PCDFs, so contact time must be minimized.

7.5.1.4 Partition the extract against 40 mL of 5 percent (w/v) aqueous sodium chloride. Shake for two minutes. Remove and discard the aqueous layer (bottom). Dry the extract by pouring it through a filter funnel containing anhydrous sodium sulfate on a glass wool plug, and collect it in a 50 mL round bottom flask. Rinse the funnel with the sodium sulfate with two 15 mL portions of hexane, add the rinses to the 50 mL flask, and concentrate the hexane solution to near dryness on a rotary evaporator (35°C water bath), making sure all traces of toluene (when applicable) are removed. (Use of blowdown with an inert gas to concentrate the extract is also permitted.)

7.5.2 Silica/Alumina Column Cleanup

7.5.2.1 Pack a gravity column (glass, 30 cm x 10.5 mm), fitted with a Teflon™ stopcock, with silica gel as follows: Insert a glass wool plug into the bottom of the column. Place 1 g silica gel in the column and tap the column gently to settle the silica gel. Add 2 g sodium hydroxide-impregnated silica gel, 4 g sulfuric

acid-impregnated silica gel, and 2 g silica gel. Tap the column gently after each addition. A small positive pressure (5 psi) of clean nitrogen may be used if needed. Elute with 10 mL hexane and close the stopcock just before exposure of the top layer of silica gel to air. Discard the eluate. Check the column for channeling. If channeling is observed, discard the column. Do not tap the wetted column.

7.5.2.2 Pack a gravity column (glass, 300 mm x 10.5 mm), fitted with a Teflon™ stopcock, with alumina as follows: Insert a glass wool plug into the bottom of the column. Add a 4 g layer of sodium sulfate. Add a 4 g layer of Woelm® Super 1 neutral alumina. Tap the top of the column gently. Woelm® Super 1 neutral alumina need not be activated or cleaned before use, but it should be stored in a sealed desiccator. Add a 4 g layer of anhydrous sodium sulfate to cover the alumina. Elute with 10 mL hexane and close the stopcock just before exposure of the sodium sulfate layer to air. Discard the eluate. Check the column for channeling. If channeling is observed, discard the column. Do not tap a wetted column.

NOTE: Optionally, acidic alumina (Section 5.2.2) can be used in place of neutral alumina.

7.5.2.3 Dissolve the residue from Section 7.5.1.4 in 2 mL hexane and apply the hexane solution to the top of the silica gel column. Rinse the flask with enough hexane (3-4 mL) to complete the quantitative transfer of the sample to the surface of the silica gel.

7.5.2.4 Elute the silica gel column with 90 mL of hexane, concentrate the eluate on a rotary evaporator (35°C water bath) to approximately 1 mL, and apply the concentrate to the top of the alumina column (Section 7.5.2.2). Rinse the rotary evaporator flask twice with 2 mL of hexane, and add the rinses to the top of the alumina column.

7.5.2.5 Add 20 mL hexane to the alumina column and elute until the hexane level is just below the top of the sodium sulfate. Do not discard the eluted hexane, but collect it in a separate flask and store it for later use, as it may be useful in determining where the labeled analytes are being lost if recoveries are not satisfactory.

7.5.2.6 Add 15 mL of 60 percent methylene chloride in hexane (v/v) to the alumina column and collect the eluate in a conical shaped (15 mL) concentration tube. With a carefully regulated stream of nitrogen, concentrate the 60 percent methylene chloride/hexane fraction to about 2 mL.

7.5.3 Carbon Column Cleanup

7.5.3.1 Prepare an AX-21/Celite 545® column as follows: Thoroughly mix 5.40 g active carbon AX-21 and 62.0 g Celite 545® to

produce an 8 percent (w/w) mixture. Activate the mixture at 130°C for 6 hours and store it in a desiccator.

7.5.3.2 Cut off both ends of a 10 mL disposable serological pipet to give a 10 cm long column. Fire polish both ends and flare, if desired. Insert a glass wool plug at one end, then pack the column with enough Celite 545® to form a 1 cm plug, add 1 g of the AX-21/Celite 545® mixture, top with additional Celite 545® (enough for a 1 cm plug), and cap the packing with another glass wool plug.

NOTE: Each new batch of AX-21/Celite 545® must be checked as follows: Add 50 µL of the continuing calibration solution to 950 µL hexane. Take this solution through the carbon column cleanup step, concentrate to 50 µL and analyze. If the recovery of any of the analytes is <80 percent, discard this batch of AX-21/Celite 545®.

7.5.3.3 Rinse the AX-21/Celite 545® column with 5 mL of toluene, followed by 2 mL of 75:20:5 (v/v) methylene chloride/methanol/toluene, 1 mL of 1:1 (v/v) cyclohexane/methylene chloride, and 5 mL hexane. The flow rate should be less than 0.5 mL/min. Discard the rinses. While the column is still wet with hexane, add the sample concentrate (Section 7.5.2.6) to the top of the column. Rinse the concentrator tube (which contained the sample concentrate) twice with 1 mL hexane, and add the rinses to the top of the column.

7.5.3.4 Elute the column sequentially with two 2 mL portions of hexane, 2 mL cyclohexane/methylene chloride (50:50, v/v), and 2 mL methylene chloride/methanol/toluene (75:20:5, v/v). Combine these eluates; this combined fraction may be used as a check on column efficiency.

7.5.3.5 Turn the column upside down and elute the PCDD/PCDF fraction with 20 mL toluene. Verify that no carbon fines are present in the eluate. If carbon fines are present in the eluate, filter the eluate through a glass fiber filter (0.45 µm) and rinse the filter with 2 mL toluene. Add the rinse to the eluate.

7.5.3.6 Concentrate the toluene fraction to about 1 mL on a rotary evaporator by using a water bath at 50°C. Carefully transfer the concentrate into a 1 mL minivial and, again at elevated temperature (50°C), reduce the volume to about 100 µL using a stream of nitrogen and a sand bath. Rinse the rotary evaporator flask three times with 300 µL of a solution of 1 percent toluene in methylene chloride, and add the rinses to the concentrate. Add 10 µL of the nonane recovery standard solution for soil, sediment, water, fish, paper pulp and adipose tissue samples, or 50 µL of the recovery standard solution for sludge, still bottom and fly ash samples. Store the sample at room temperature in the dark.

7.6 Chromatographic/Mass Spectrometric Conditions and Data Acquisition Parameters

7.6.1 Gas Chromatograph

Column coating: DB-5
Film thickness: 0.25 μm
Column dimension: 60 m x 0.32 mm
Injector temperature: 270°C
Splitless valve time: 45 s
Interface temperature: Function of the final temperature
Temperature program:

Stage	Init. Temp. (°C)	Init. Hold Time (min)	Temp. Ramp (°C/min)	Final Temp. (°C)	Final Hold Time (min)
1	200	2	5	220	16
2			5	235	7
3			5	330	5

Total time: 60 min

7.6.2 Mass Spectrometer

7.6.2.1 The mass spectrometer must be operated in a selected ion monitoring (SIM) mode with a total cycle time (including the voltage reset time) of one second or less (Section 7.6.3.1). At a minimum, the ions listed in Table 6 for each of the five SIM descriptors must be monitored. Note that with the exception of the last descriptor (OCDD/OCDF), all descriptors contain 10 ions. The selection (Table 6) of the molecular ions M and M+2 for ^{13}C-HxCDF and ^{13}C-HpCDF rather than M+2 and M+4 (for consistency) was made to eliminate, even under high-resolution mass spectrometric conditions, interferences occurring in these two ion channels for samples containing high levels of native HxCDDs and HpCDDs. It is important to maintain the same set of ions for both calibration and sample extract analyses. The selection of the lock-mass ion is left to the performing laboratory.

NOTE: At the option of the analyst, the tetra- and pentachlorinated dioxins and furans can be combined into a single descriptor.

7.6.2.2 The recommended mass spectrometer tuning conditions are based on the groups of monitored ions shown in Table 6. By using a PFK molecular leak, tune the instrument to meet the minimum required resolving power of 10,000 (10 percent valley) at m/z 304.9824 (PFK) or any other reference signal close to m/z 303.9016 (from TCDF). By using peak matching conditions and the aforementioned PFK reference peak, verify that the exact mass of m/z 380.9760 (PFK) is within 5 ppm of the required value. Note that the

selection of the low- and high-mass ions must be such that they provide the largest voltage jump performed in any of the five mass descriptors (Table 6).

7.6.3 Data Acquisition

7.6.3.1 The total cycle time for data acquisition must be $\leq$ 1 second. The total cycle time includes the sum of all the dwell times and voltage reset times.

7.6.3.2 Acquire SIM data for all the ions listed in the five descriptors of Table 6.

7.7 Calibration

7.7.1 Initial Calibration - Initial calibration is required before any samples are analyzed for PCDDs and PCDFs. Initial calibration is also required if any routine calibration (Section 7.7.3) does not meet the required criteria listed in Section 9.4.

7.7.1.1 All five high-resolution concentration calibration solutions listed in Table 5 must be used for the initial calibration.

7.7.1.2 Tune the instrument with PFK as described in Section 7.6.2.2.

7.7.1.3 Inject 2 µL of the GC column performance check solution (Section 5.7) and acquire SIM mass spectral data as described earlier in Section 8.1. The total cycle time must be $\leq$ 1 second. The laboratory must not perform any further analysis until it is demonstrated and documented that the criterion listed in Section 8.1.2 was met.

7.7.1.4 By using the same GC (Section 7.6.1) and MS (Section 7.6.2) conditions that produced acceptable results with the column performance check solution, analyze a 2 µL portion of each of the five concentration calibration solutions once with the following mass spectrometer operating parameters.

7.7.1.4.1 The ratio of integrated ion current for the ions appearing in Table 8 (homologous series quantitation ions) must be within the indicated control limits (set for each homologous series).

7.7.1.4.2 The ratio of integrated ion current for the ions belonging to the carbon-labeled internal and recovery standards must be within the control limits stipulated in Table 8.

NOTE: Sections 7.7.1.4.1 and 7.7.1.4.2 require that 17 ion ratios from Section 7.7.1.4.1 and 11 ion ratios from Section 7.7.1.4.2 be within the specified control limits simultaneously in one

run. It is the laboratory's responsibility to take corrective action if the ion abundance ratios are outside the limits.

7.7.1.4.3 For each SICP and for each GC signal corresponding to the elution of a target analyte and of its labeled standards, the signal-to-noise ratio (S/N) must be better than or equal to 2.5. Measurement of S/N is required for any GC peak that has an apparent S/N of less than 5:1. The result of the calculation must appear on the SICP above the GC peak in question.

7.7.1.4.4 Referring to Table 9, calculate the 17 relative response factors (RRF) for unlabeled target analytes [RRF(n); n = 1 to 17] relative to their appropriate internal standards (Table 5) and the nine RRFs for the labeled $^{13}C_{12}$ internal standards [RRF(m); m = 18 to 26)] relative to the two recovery standards according to the following formulae:

$$RRF(n) = \frac{A_x \times Q_{is}}{Q_x \times A_{is}}$$

$$RRF(m) = \frac{A_{is} \times Q_{rs}}{Q_{is} \times A_{rs}}$$

where:

A_x = sum of the integrated ion abundances of the quantitation ions (Tables 6 and 9) for unlabeled PCDDs/PCDFs,

A_{is} = sum of the integrated ion abundances of the quantitation ions (Tables 6 and 9) for the labeled internal standards,

A_{rs} = sum of the integrated ion abundances of the quantitation ions (Tables 6 and 9) for the labeled recovery standards,

Q_{is} = quantity of the internal standard injected (pg),

Q_{rs} = quantity of the recovery standard injected (pg), and

Q_x = quantity of the unlabeled PCDD/PCDF analyte injected (pg).

The RRF(n) and RRF(m) are dimensionless quantities; the units used to express Q_{is}, Q_{rs} and Q_x must be the same.

7.7.1.4.5 Calculate the $\overline{RRF}$ and their respective percent relative standard deviations (%RSD) for the five calibration solutions:

$$\overline{RRF}(n) = 1/5 \sum_{j=1}^{5} RRFj(n)$$

Where n represents a particular PCDD/PCDF (2,3,7,8-substituted) congener (n = 1 to 17; Table 9), and j is the injection number (or calibration solution number; j = 1 to 5).

7.7.1.4.6 The relative response factors to be used for the determination of the concentration of total isomers in a homologous series (Table 9) are calculated as follows:

7.7.1.4.6.1 For congeners that belong to a homologous series containing only one isomer (e.g., OCDD and OCDF) or only one 2,3,7,8-substituted isomer (Table 4; TCDD, PeCDD, HpCDD, and TCDF), the mean $\overline{RRF}$ used will be the same as the mean $\overline{RRF}$ determined in Section 7.7.1.4.5.

NOTE: The calibration solutions do not contain $^{13}C_{12}$-OCDF as an internal standard. This is because a minimum resolving power of 12,000 is required to resolve the $[M+6]^+$ ion of $^{13}C_{12}$-OCDF from the $[M+2]^+$ ion of OCDD (and $[M+4]^+$ from $^{13}C_{12}$-OCDF with $[M]^+$ of OCDD). Therefore, the $\overline{RRF}$ for OCDF is calculated relative to $^{13}C_{12}$-OCDD.

7.7.1.4.6.2 For congeners that belong to a homologous series containing more than one 2,3,7,8-substituted isomer (Table 4), the mean $\overline{RRF}$ used for those homologous series will be the mean of the RRFs calculated for all individual 2,3,7,8-substituted congeners using the equation below:

$$\overline{RRF}(k) = \frac{1}{t} \sum_{n=1}^{t} RRF_n$$

where:

k = 27 to 30 (Table 9), with 27 = PeCDF; 28 = HxCDF; 29 = HxCDD; and 30 = HpCDF,

t = total number of 2,3,7,8-substituted isomers present in the calibration solutions (Table 5) for each homologous series (e.g., two

for PeCDF, four for HxCDF, three for HxCDD, two for HpCDF).

NOTE: Presumably, the HRGC/HRMS response factors of different isomers within a homologous series are different. However, this analytical protocol will make the assumption that the HRGC/HRMS responses of all isomers in a homologous series that do not have the 2,3,7,8-substitution pattern are the same as the responses of one or more of the 2,3,7,8-substituted isomer(s) in that homologous series.

7.7.1.4.7 Relative response factors [$\overline{RRF}(m)$] to be used for the determination of the percent recoveries for the nine internal standards are calculated as follows:

$$RRF(m) = \frac{A_{is}^{m} \times Q_{rs}}{Q_{is}^{m} \times A_{rs}}$$

$$\overline{RRF}(m) = \frac{1}{5} \sum_{j=1}^{5} RRFj(m),$$

where:

m = 18 to 26 (congener type) and j = 1 to 5 (injection number),

A_{is}^{m} = sum of the integrated ion abundances of the quantitation ions (Tables 6 and 9) for a given internal standard (m = 18 to 26),

A_{rs} = sum of the integrated ion abundances of the quantitation ions (Tables 6 and 9) for the appropriate recovery standard (see Table 5, footnotes),

Q_{rs}, Q_{is}^{m} = quantities of, respectively, the recovery standard (rs) and a particular internal standard (is = m) injected (pg),

$RRF(m)$ = relative response factor of a particular internal standard (m) relative to an appropriate recovery standard, as determined from one injection, and

$\overline{RRF}(m)$ = calculated mean relative response factor of a particular internal standard (m) relative to an appropriate recovery standard, as

determined from the five initial calibration injections (j).

7.7.2 Criteria for Acceptable Calibration - The criteria listed below for acceptable calibration must be met before the analysis is performed.

7.7.2.1 The percent relative standard deviations for the mean response factors [RRF(n) and RRF(m)] from the 17 unlabeled standards must not exceed ± 20 percent, and those for the nine labeled reference compounds must not exceed ± 30 percent.

7.7.2.2 The S/N for the GC signals present in every SICP (including the ones for the labeled standards) must be ≥ 10.

7.7.2.3 The isotopic ratios (Table 8) must be within the specified control limits.

NOTE: If the criterion for acceptable calibration listed in Section 7.7.2.1 is met, the analyte specific RRF can then be considered independent of the analyte quantity for the calibration concentration range. The mean RRFs will be used for all calculations until the routine calibration criteria (Section 7.7.4) are no longer met. At such time, new mean RRFs will be calculated from a new set of injections of the calibration solutions.

7.7.3 Routine Calibration (Continuing Calibration Check) - Routine calibrations must be performed at the beginning of a 12 hour period after successful mass resolution and GC resolution performance checks. A routine calibration is also required at the end of a 12 hour shift.

7.7.3.1 Inject 2 μL of the concentration calibration solution HRCC-3 standard (Table 5). By using the same HRGC/HRMS conditions as used in Sections 7.6.1 and 7.6.2, determine and document an acceptable calibration as provided in Section 7.7.4.

7.7.4 Criteria for Acceptable Routine Calibration - The following criteria must be met before further analysis is performed.

7.7.4.1 The measured RRFs [RRF(n) for the unlabeled standards] obtained during the routine calibration runs must be within ± 20 percent of the mean values established during the initial calibration (Section 7.7.1.4.5).

7.7.4.2 The measured RRFs [RRF(m) for the labeled standards] obtained during the routine calibration runs must be within ± 30 percent of the mean values established during the initial calibration (Section 7.7.1.4.7).

7.7.4.3 The ion-abundance ratios (Table 8) must be within the allowed control limits.

7.7.4.4 If either one of the criteria in Sections 7.7.4.1 and 7.7.4.2 is not satisfied, repeat one more time. If these criteria are still not satisfied, the entire routine calibration process (Section 7.7.1) must be reviewed. It is realized that it may not always be possible to achieve all RRF criteria. For example, it has occurred that the RRF criteria for $^{13}C_{12}$-HpCDD and $^{13}C_{12}$-OCDD were not met, however, the RRF values for the corresponding unlabeled compounds were routinely within the criteria established in the method. In these cases, 24 of the 26 RRF parameters have met the QC criteria, and the data quality for the unlabeled HpCDD and OCDD values were not compromised as a result of the calibration event. In these situations, the analyst must assess the effect on overall data quality as required for the data quality objectives and decide on appropriate action. Corrective action would be in order, for example, if the compounds for which the RRF criteria were not met included both the unlabeled and the corresponding internal standard compounds. If the ion-abundance ratio criterion (Section 7.7.4.3) is not satisfied, refer to the note in Section 7.7.1.4.2 for resolution.

NOTE: An initial calibration must be carried out whenever the HRCC-3, the sample fortification or the recovery standard solution is replaced by a new solution from a different lot.

7.8 Analysis

7.8.1 Remove the sample extract (from Section 7.5.3.6) or blank from storage. With a stream of dry, purified nitrogen, reduce the extract volume to 10 μL to 50 μL.

NOTE: A final volume of 20 μL or more should be used whenever possible. A 10 μL final volume is difficult to handle, and injection of 2 μL out of 10 μL leaves little sample for confirmations and repeat injections, and for archiving.

7.8.2 Inject a 2 μL aliquot of the extract into the GC, operated under the conditions that have been established to produce acceptable results with the performance check solution (Sections 7.6.1 and 7.6.2).

7.8.3 Acquire SIM data according to Sections 7.6.2 and 7.6.3. Use the same acquisition and mass spectrometer operating conditions previously used to determine the relative response factors (Sections 7.7.1.4.4 through 7.7.1.4.7). Ions characteristic for polychlorinated diphenyl ethers are included in the descriptors listed in Table 6.

NOTE: The acquisition period must at least encompass the PCDD/PCDF overall retention time window previously determined (Section 8.1). Selected ion current profiles (SICP) for the lock-mass ions (one per mass descriptor) must also be recorded and included in the data package. These SICPs must be true representations of the evolution of the lock-mass ions amplitudes during the HRGC/HRMS run (see Section 8.2.2 for the proper level of reference compound to be metered into the

ion chamber.) The analyst may be required to monitor a PFK ion, not as a lock mass, but as a regular ion, in order to meet this requirement. It is recommended to examine the lock-mass ion SICP for obvious basic sensitivity and stability changes of the instrument during the GC/MS run that could affect the measurements [Tondeur et al., 1984, 1987]. Report any discrepancies in the case narrative.

7.8.4 Identification Criteria - For a gas chromatographic peak to be identified as a PCDD or PCDF, it must meet all of the following criteria:

7.8.4.1 Retention Times

7.8.4.1.1 For 2,3,7,8-substituted congeners, which have an isotopically labeled internal or recovery standard present in the sample extract (this represents a total of 10 congeners including OCDD; Tables 2 and 3), the retention time (RRT; at maximum peak height) of the sample components (i.e., the two ions used for quantitation purposes listed in Table 6) must be within -1 to +3 seconds of the isotopically labelled standard.

7.8.4.1.2 For 2,3,7,8-substituted compounds that do not have an isotopically labeled internal standard present in the sample extract (this represents a total of six congeners; Table 3), the retention time must fall within 0.005 retention time units of the relative retention times measured in the routine calibration. Identification of OCDF is based on its retention time relative to $^{13}C_{12}$-OCDD as determined from the daily routine calibration results.

7.8.4.1.3 For non-2,3,7,8-substituted compounds (tetra through octa; totaling 119 congeners), the retention time must be within the corresponding homologous retention time windows established by analyzing the column performance check solution (Section 8.1.3).

7.8.4.1.4 The ion current responses for both ions used for quantitative purposes (e.g., for TCDDs: m/z 319.8965 and 321.8936) must reach maximum simultaneously ($\pm$ 2 seconds).

7.8.4.1.5 The ion current responses for both ions used for the labeled standards (e.g., for $^{13}C_{12}$-TCDD: m/z 331.9368 and m/z 333.9339) must reach maximum simultaneously ($\pm$ 2 seconds).

NOTE: The analyst is required to verify the presence of 1,2,8,9-TCDD and 1,3,4,6,8-PeCDF (Section 8.1.3) in the SICPs of the daily performance checks. Should either one compound be missing, the analyst is required to take corrective action as it may indicate a potential problem with the ability to detect all the PCDDs/PCDFs.

7.8.4.2 Ion Abundance Ratios

7.8.4.2.1 The integrated ion current for the two ions used for quantitation purposes must have a ratio between the lower and upper limits established for the homologous series to which the peak is assigned. See Sections 7.7.1.4.1 and 7.7.1.4.2 and Table 8 for details.

7.8.4.3 Signal-to-Noise Ratio

7.8.4.3.1 All ion current intensities must be $\geq$ 2.5 times noise level for positive identification of a PCDD/PCDF compound or a group of coeluting isomers. Figure 6 describes the procedure to be followed for the determination of the S/N.

7.8.4.4 Polychlorinated Diphenyl Ether Interferences

7.8.4.4.1 In addition to the above criteria, the identification of a GC peak as a PCDF can only be made if no signal having a S/N $\geq$ 2.5 is detected, at the same retention time ($\pm$ 2 seconds), in the corresponding polychlorinated diphenyl ether (PCDPE, Table 6) channel.

7.9 Calculations

7.9.1 For gas chromatographic peaks that have met the criteria outlined in Sections 7.8.4.1.1 through 7.8.4.3.1, calculate the concentration of the PCDD or PCDF compounds using the formula:

$$Cx = \frac{A_x \times Q_{is}}{A_{is} \times W \times \overline{RRF}(n)}$$

where:

C_x = concentration of unlabeled PCDD/PCDF congeners (or group of coeluting isomers within an homologous series) in pg/g,

A_x = sum of the integrated ion abundances of the quantitation ions (Table 6) for unlabeled PCDDs/PCDFs,

A_{is} = sum of the integrated ion abundances of the quantitation ions (Table 6) for the labeled internal standards,

Q_{is} = quantity, in pg, of the internal standard added to the sample before extraction,

W = weight, in g, of the sample (solid or liquid), and

$\overline{RRF}$ = calculated mean relative response factor for the analyte [$\overline{RRF}(n)$ with n = 1 to 17; Section 7.7.1.4.5].

If the analyte is identified as one of the 2,3,7,8-substituted PCDDs or PCDFs, $\overline{RRF}(n)$ is the value calculated using the equation in Section 7.7.1.4.5. However, if it is a non-2,3,7,8-substituted congener, the $\overline{RRF}(k)$ value is the one calculated using the equation in Section 7.7.1.4.6.2. [RRF(k) with k = 27 to 30].

7.9.2 Calculate the percent recovery of the nine internal standards measured in the sample extract, using the formula:

$$\text{Internal standard percent recovery} = \frac{A_{is} \times Q_{rs}}{Q_{is} \times A_{rs} \times \overline{RRF}(m)} \times 100$$

where:

A_{is} = sum of the integrated ion abundances of the quantitation ions (Table 6) for the labeled internal standard,

A_{rs} = sum of the integrated ion abundances of the quantitation ions (Table 6) for the labeled recovery standard; the selection of the recovery standard depends on the type of congeners (see Table 5, footnotes),

Q_{is} = quantity, in pg, of the internal standard added to the sample before extraction,

Q_{rs} = quantity, in pg, of the recovery standard added to the cleaned-up sample residue before HRGC/HRMS analysis, and

$\overline{RRF}(m)$ = calculated mean relative response factor for the labeled internal standard relative to the appropriate (see Table 5, footnotes) recovery standard. This represents the mean obtained in Section 7.7.1.4.7 [$\overline{RRF}(m)$ with m = 18 to 26].

NOTE: For human adipose tissue, adjust the percent recoveries by adding 1 percent to the calculated value to compensate for the 1 percent of the extract diverted for the lipid determination.

7.9.3 If the concentration in the final extract of any of the fifteen 2,3,7,8-substituted PCDD/PCDF compounds (Table 3) exceeds the upper method calibration limits (MCL) listed in Table 1 (e.g., 200 pg/μL for TCDD in soil), the linear range of response versus concentration may have been exceeded, and a second analysis of the sample (using a one tenth aliquot) should be undertaken. The volumes of the internal and recovery standard solutions should remain the same as described for the sample preparation (Sections 11.1 to 11.9.3). For the other congeners (including OCDD), however, report the measured concentration and indicate that the value exceeds the MCL.

7.9.4 The total concentration for each homologous series of PCDD and PCDF is calculated by summing up the concentrations of all positively

identified isomers of each homologous series. Therefore, the total should also include the 2,3,7,8-substituted congeners. The total number of GC signals included in the homologous total concentration value must be specified in the report.

7.9.5 Sample Specific Estimated Detection Limit - The sample specific estimated detection limit (EDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. An EDL is calculated for each 2,3,7,8-substituted congener that is not identified, regardless of whether or not other non-2,3,7,8-substituted isomers are present. Two methods of calculation can be used, as follows, depending on the type of response produced during the analysis of a particular sample.

7.9.5.1 Samples giving a response for both quantitation ions (Tables 6 and 9) that is less than 2.5 times the background level.

7.9.5.1.1 Use the expression for EDL (specific 2,3,7,8-substituted PCDD/PCDF) below to calculate an EDL for each absent 2,3,7,8-substituted PCDD/PCDF (i.e., S/N < 2.5). The background level is determined by measuring the range of the noise (peak to peak) for the two quantitation ions (Table 6) of a particular 2,3,7,8-substituted isomer within an homologous series, in the region of the SICP trace corresponding to the elution of the internal standard (if the congener possesses an internal standard) or in the region of the SICP where the congener is expected to elute by comparison with the routine calibration data (for those congeners that do not have a ^{13}C-labeled standard), multiplying that noise height by 2.5, and relating the product to an estimated concentration that would produce that peak height.

Use the formula:

$$\text{EDL (specific 2,3,7,8-subst. PCDD/PCDF)} = \frac{2.5 \times A_x \times Q_{is}}{A_{is} \times W \times \overline{RRF}(n)}$$

where:

EDL = estimated detection limit for homologous 2,3,7,8-substituted PCDDs/PCDFs.

A_x, A_{is}, W, $\overline{RRF}(n)$, and Q_{is} retain the same meanings as defined in Section 7.9.1.

7.9.5.2 Samples characterized by a response above the background level with a S/N of at least 2.5 for both quantitation ions (Tables 6 and 9).

7.9.5.2.1 When the response of a signal having the same retention time as a 2,3,7,8-substituted congener has a

S/N in excess of 2.5 and does not meet any of the other qualitative identification criteria listed in Section 7.8.4, calculate the "Estimated Maximum Possible Concentration" (EMPC) according to the expression shown in Section 7.9.1, except that A^x in Section 7.9.1 should represent the sum of the area under the smaller peak and of the other peak area calculated using the theoretical chlorine isotope ratio.

7.9.6 The relative percent difference (RPD) is calculated as follows:

$$RPD = \frac{| S_1 - S_2 |}{(S_1 + S_2) / 2} \times 100$$

S_1 and S_2 represent sample and duplicate sample results.

7.9.7 The 2,3,7,8-TCDD toxicity equivalents (TE) of PCDDs and PCDFs present in the sample are calculated, if requested by the data user, according to the method recommended by the Chlorinated Dioxins Workgroup (CDWG) of the EPA and the Center for Disease Control (CDC). This method assigns a 2,3,7,8-TCDD toxicity equivalency factor (TEF) to each of the fifteen 2,3,7,8-substituted PCDDs and PCDFs (Table 3) and to OCDD and OCDF, as shown in Table 10. The 2,3,7,8-TCDD equivalent of the PCDDs and PCDFs present in the sample is calculated by summing the TEF times their concentration for each of the compounds or groups of compounds listed in Table 10. The exclusion of other homologous series such as mono-, di-, and tri- chlorinated dibenzodioxins and dibenzofurans does not mean that they are non-toxic. However, their toxicity, as known at this time, is much lower than the toxicity of the compounds listed in Table 10. The above procedure for calculating the 2,3,7,8-TCDD toxicity equivalents is not claimed by the CDWG to be based on a thoroughly established scientific foundation. The procedure, rather, represents a "consensus recommendation on science policy". Since the procedure may be changed in the future, reporting requirements for PCDD and PCDF data would still include the reporting of the analyte concentrations of the PCDD/PCDF congener as calculated in Sections 7.9.1 and 7.9.4.

7.9.7.1 Two GC Column TEF Determination

7.9.7.1.1 The concentration of 2,3,7,8-TCDD (see note below), is calculated from the analysis of the sample extract on the 60 m DB-5 fused silica capillary column. The experimental conditions remain the same as the conditions described previously in Section 7.8, and the calculations are performed as outlined in Section 7.9. The chromatographic separation between the 2,3,7,8-TCDD and its close eluters (1,2,3,7/1,2,3,8-TCDD and 1,2,3,9-TCDD) must be equal or less than 25 percent valley.

7.9.7.1.2 The concentration of the 2,3,7,8-TCDF is obtained from the analysis of the sample extract on the 30 m DB-225 fused silica capillary column. However, the GC/MS

conditions must be altered so that: (1) only the first three descriptors (i.e., tetra-, penta-, and hexachlorinated congeners) of Table 6 are used; and (2) the switching time between descriptor 2 (pentachlorinated congeners) and descriptor 3 (hexachlorinated congeners) takes place following the elution of $^{13}C_{12}$-1,2,3,7,8-PeCDD. The concentration calculations are performed as outlined in Section 7.9. The chromatographic separation between the 2,3,7,8-TCDF and its close eluters (2,3,4,7-TCDF and 1,2,3,9-TCDF) must be equal or less than 25 percent valley.

NOTE: The confirmation and quantitation of 2,3,7,8-TCDD (Section 7.9.7.1.1) may be accomplished on the SP-2330 GC column instead of the DB-5 column, provided the criteria listed in Section 8.1.2 are met and the requirements described in Section 17.2.2 are followed.

7.9.7.1.3 For a gas chromatographic peak to be identified as a 2,3,7,8-substituted PCDD/PCDF congener, it must meet the ion abundance and signal-to-noise ratio criteria listed in Sections 7.8.4.2 and 7.8.4.3, respectively. In addition, the retention time identification criterion described in Section 7.8.4.1.1 applies here for congeners for which a carbon-labeled analogue is available in the sample extract. However, the relative retention time (RRT) of the 2,3,7,8-substituted congeners for which no carbon-labeled analogues are available must fall within 0.006 units of the carbon-labeled standard RRT. Experimentally, this is accomplished by using the attributions described in Table 11 and the results from the routine calibration run on the SP-2330 column.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control (QC) procedures. Quality control to validate sample extraction is covered in Method 3500. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 System Performance Criteria - System performance criteria are presented below. The laboratory may use the recommended GC column described in Section 4.2. It must be documented that all applicable system performance criteria (specified in Sections 8.2.1 and 8.2.2) were met before analysis of any sample is performed. Section 7.6 provides recommended GC conditions that can be used to satisfy the required criteria. Figure 3 provides a typical 12 hour analysis sequence, whereby the response factors and mass spectrometer resolving power checks must be performed at the beginning and the end of each 12 hour period of operation. A GC column performance check is only required at the beginning of each 12 hour period during which samples are analyzed. An HRGC/HRMS method blank run is required between a calibration run and the first sample run. The same method blank extract may thus be analyzed more than once if the number of samples within a batch requires more than 12 hours of analyses.

8.2.1 GC Column Performance

8.2.1.1 Inject 2 μL (Section 4.1.1) of the column performance check solution (Section 5.7) and acquire selected ion monitoring (SIM) data as described in Section 7.6.2 within a total cycle time of ≤ 1 second (Section 7.6.3.1).

8.2.1.2 The chromatographic separation between 2,3,7,8-TCDD and the peaks representing any other unlabeled TCDD isomers must be resolved with a valley of ≤ 25 percent (Figure 4), where:

Valley percent = (x/y) (100)

x = measured as in Figure 4 from the 2,3,7,8-closest TCDD eluting isomer, and
y = the peak height of 2,3,7,8-TCDD.

It is the responsibility of the laboratory to verify the conditions suitable for the appropriate resolution of 2,3,7,8-TCDD from all other TCDD isomers. The GC column performance check solution also contains the known first and last PCDD/PCDF eluters under the conditions specified in this protocol. Their retention times are used to determine the eight homologue retention time windows that are used for qualitative (Section 7.8.4.1) and quantitative purposes. All peaks (that includes $^{13}C_{12}$-2,3,7,8-TCDD) should be labeled and identified on the chromatograms. Furthermore, all first eluters of a homologous series should be labeled with the letter F, and all last eluters of a homologous series should be labeled with the letter L (Figure 4 shows an example of peak labeling for TCDD isomers). Any individual selected ion current profile (SICP) (for the tetras, this would be the SICP for m/z 322 and m/z 304) or the reconstructed homologue ion current (for the tetras, this would correspond to m/z 320 + m/z 322 + m/z 304 + m/z 306) constitutes an acceptable form of data presentation. An SICP for the labeled compounds (e.g., m/z 334 for labeled TCDD) is also required.

8.2.1.3 The retention times for the switching of SIM ions characteristic of one homologous series to the next higher homologous series must be indicated in the SICP. Accurate switching at the appropriate times is absolutely necessary for accurate monitoring of these compounds. Allowable tolerance on the daily verification with the GC performance check solution should be better than 10 seconds for the absolute retention times of all the components of the mixture. Particular caution should be exercised for the switching time between the last tetrachlorinated congener (i.e., 1,2,8,9-TCDD) and the first pentachlorinated congener (i.e., 1,3,4,6,8-PeCDF), as these two compounds elute within 15 seconds of each other on the 60 m DB-5 column. A laboratory with a GC/MS system that is not capable of detecting both congeners (1,2,8,9-TCDD and 1,3,4,6,8-PeCDF) within one analysis must take corrective action. If the recommended column is not used, then the first and

last eluting isomer of each homologue must be determined experimentally on the column which is used, and the appropriate isomers must then be used for window definition and switching times.

8.2.2 Mass Spectrometer Performance

8.2.2.1 The mass spectrometer must be operated in the electron ionization mode. A static resolving power of at least 10,000 (10 percent valley definition) must be demonstrated at appropriate masses before any analysis is performed (Section 7.8). Static resolving power checks must be performed at the beginning and at the end of each 12 hour period of operation. However, it is recommended that a check of the static resolution be made and documented before and after each analysis. Corrective action must be implemented whenever the resolving power does not meet the requirement.

8.2.2.2 Chromatography time for PCDDs and PCDFs exceeds the long term mass stability of the mass spectrometer. Because the instrument is operated in the high-resolution mode, mass drifts of a few ppm (e.g., 5 ppm in mass) can have serious adverse effects on instrument performance. Therefore, a mass drift correction is mandatory. To that effect, it is recommended to select a lock-mass ion from the reference compound (PFK is recommended) used for tuning the mass spectrometer. The selection of the lock-mass ion is dependent on the masses of the ions monitored within each descriptor. Table 6 offers some suggestions for the lock-mass ions. However, an acceptable lock-mass ion at any mass between the lightest and heaviest ion in each descriptor can be used to monitor and correct mass drifts. The level of the reference compound (PFK) metered into the ion chamber during HRGC/HRMS analyses should be adjusted so that the amplitude of the most intense selected lock-mass ion signal (regardless of the descriptor number) does not exceed 10 percent of the full scale deflection for a given set of detector parameters. Under those conditions, sensitivity changes that might occur during the analysis can be more effectively monitored.

NOTE: Excessive PFK (or any other reference substance) may cause noise problems and contamination of the ion source resulting in an increase in downtime for source cleaning.

8.2.2.3 Documentation of the instrument resolving power must then be accomplished by recording the peak profile of the high-mass reference signal (m/z 380.9760) obtained during the above peak matching experiment by using the low-mass PFK ion at m/z 304.9824 as a reference. The minimum resolving power of 10,000 must be demonstrated on the high-mass ion while it is transmitted at a lower accelerating voltage than the low-mass reference ion, which is transmitted at full sensitivity. The format of the peak profile representation (Figure 5) must allow manual determination of the resolution, i.e., the horizontal axis must be a calibrated mass scale (amu or ppm per division). The result of the peak width

measurement (performed at 5 percent of the maximum, which corresponds to the 10 percent valley definition) must appear on the hard copy and cannot exceed 100 ppm at m/z 380.9760 (or 0.038 amu at that particular mass).

8.3 Quality Control Samples

8.3.1 Performance Evaluation Samples - Included among the samples in all batches may be samples (blind or double blind) containing known amounts of unlabeled 2,3,7,8-substituted PCDDs/PCDFs or other PCDD/PCDF congeners.

8.3.2 Performance Check Solutions

8.3.2.1 At the beginning of each 12 hour period during which samples are to be analyzed, an aliquot of the 1) GC column performance check solution and 2) high-resolution concentration calibration solution No. 3 (HRCC-3; see Table 5) shall be analyzed to demonstrate adequate GC resolution and sensitivity, response factor reproducibility, and mass range calibration, and to establish the PCDD/PCDF retention time windows. A mass resolution check shall also be performed to demonstrate adequate mass resolution using an appropriate reference compound (PFK is recommended). If the required criteria are not met, remedial action must be taken before any samples are analyzed.

8.3.2.2 To validate positive sample data, the routine or continuing calibration (HRCC-3; Table 5) and the mass resolution check must be performed also at the end of each 12 hour period during which samples are analyzed. Furthermore, an HRGC/HRMS method blank run must be recorded following a calibration run and the first sample run.

8.3.2.2.1 If the laboratory operates only during one period (shift) each day of 12 hours or less, the GC performance check solution must be analyzed only once (at the beginning of the period) to validate the data acquired during the period. However, the mass resolution and continuing calibration checks must be performed at the beginning as well as at the end of the period.

8.3.2.2.2 If the laboratory operates during consecutive 12 hour periods (shifts), analysis of the GC performance check solution must be performed at the beginning of each 12 hour period. The mass resolution and continuing calibration checks from the previous period can be used for the beginning of the next period.

8.3.2.3 Results of at least one analysis of the GC column performance check solution and of two mass resolution and continuing calibration checks must be reported with the sample data collected during a 12 hour period.

8.3.2.4 Deviations from criteria specified for the GC performance check or for the mass resolution check invalidate all positive sample data collected between analyses of the performance check solution, and the extracts from those positive samples shall be reanalyzed.

If the routine calibration run fails at the beginning of a 12 hour shift, the instructions in Section 7.7.4.4 must be followed. If the continuing calibration check performed at the end of a 12 hour period fails by no more than 25 percent RPD for the 17 unlabelled compounds and 35 percent RPD for the 9 labelled reference compounds, use the mean $\overline{RRF}$s from the two daily routine calibration runs to compute the analyte concentrations, instead of the $\overline{RRF}$s obtained from the initial calibration. A new initial calibration (new $\overline{RRF}$s) is required immediately (within two hours) following the analysis of the samples, whenever the RPD from the end-of-shift routine calibration exceeds 25 percent or 35 percent, respectively. Failure to perform a new initial calibration immediately following the analysis of the samples will automatically require reanalysis of all positive sample extracts analyzed before the failed end-of-shift continuing calibration check.

8.3.3 The GC column performance check mixture, high-resolution concentration calibration solutions, and the sample fortification solutions may be obtained from the EMSL-CIN. However, if not available from the EMSL-CIN, standards can be obtained from other sources, and solutions can be prepared in the laboratory. Concentrations of all solutions containing 2,3,7,8-substituted PCDDs/PCDFs, which are not obtained from the EMSL-CIN, must be verified by comparison with the EPA standard solutions that are available from the EMSL-CIN.

8.3.4 Field Blanks - Each batch of samples usually contains a field blank sample of uncontaminated soil, sediment or water that is to be fortified before analysis according to Section 8.3.4.1. In addition to this field blank, a batch of samples may include a rinsate, which is a portion of the solvent (usually trichloroethylene) that was used to rinse sampling equipment. The rinsate is analyzed to assure that the samples were not contaminated by the sampling equipment.

8.3.4.1 Fortified Field Blank

8.3.4.1.1 Weigh a 10 g portion or use 1 L (for aqueous samples) of the specified field blank sample and add 100 µL of the solution containing the nine internal standards (Table 2) diluted with 1.0 mL acetone (Section 7.1).

8.3.4.1.2 Extract by using the procedures beginning in Sections 7.4.5 or 7.4.6, as applicable, add 10 µL of the recovery standard solution (Section 7.5.3.6) and analyze a 2 µL aliquot of the concentrated extract.

8.3.4.1.3 Calculate the concentration (Section 7.9.1) of 2,3,7,8-substituted PCDDs/PCDFs and the percent recovery of the internal standards (Section 7.9.2).

8.3.4.1.4 Extract and analyze a new simulated fortified field blank whenever new lots of solvents or reagents are used for sample extraction or for column chromatographic procedures.

8.3.4.2 Rinsate Sample

8.3.4.2.1 The rinsate sample must be fortified like a regular sample.

8.3.4.2.2 Take a 100 mL (± 0.5 mL) portion of the sampling equipment rinse solvent (rinsate sample), filter, if necessary, and add 100 µL of the solution containing the nine internal standards (Table 2).

8.3.4.2.3 Using a KD apparatus, concentrate to approximately 5 mL.

NOTE: As an option, a rotary evaporator may be used in place of the KD apparatus for the concentration of the rinsate.

8.3.4.2.4 Transfer the 5 mL concentrate from the KD concentrator tube in 1 mL portions to a 1 mL minivial, reducing the volume in the minivial as necessary with a gentle stream of dry nitrogen.

8.3.4.2.5 Rinse the KD concentrator tube with two 0.5 mL portions of hexane and transfer the rinses to the 1 mL minivial. Blow down with dry nitrogen as necessary.

8.3.4.2.6 Just before analysis, add 10 µL recovery standard solution (Table 2) and reduce the volume to its final volume, as necessary (Section 7.8.1). No column chromatography is required.

8.3.4.2.7 Analyze an aliquot following the same procedures used to analyze samples.

8.3.4.2.8 Report percent recovery of the internal standard and the presence of any PCDD/PCDF compounds in µg/L of rinsate solvent.

8.3.5 Duplicate Analyses

8.3.5.1 In each batch of samples, locate the sample specified for duplicate analysis, and analyze a second 10 g soil or sediment sample portion or 1 L water sample, or an appropriate amount of the type of matrix under consideration.

8.3.5.1.1 The results of the laboratory duplicates (percent recovery and concentrations of 2,3,7,8-substituted PCDD/PCDF compounds) should agree within 25 percent relative

difference (difference expressed as percentage of the mean). Report all results.

8.3.5.1.2 Recommended actions to help locate problems:

8.3.5.1.2.1 Verify satisfactory instrument performance (Sections 8.2 and 8.3).

8.3.5.1.2.2 If possible, verify that no error was made while weighing the sample portions.

8.3.5.1.2.3 Review the analytical procedures with the performing laboratory personnel.

8.3.6 Matrix Spike and Matrix Spike Duplicate

8.3.6.1 Locate the sample for the MS and MSD analyses (the sample may be labeled "double volume").

8.3.6.2 Add an appropriate volume of the matrix spike fortification solution (Section 5.10) and of the sample fortification solution (Section 5.8), adjusting the fortification level as specified in Table 1 under IS Spiking Levels.

8.3.6.3 Analyze the MS and MSD samples as described in Section 7.

8.3.6.4 The results obtained from the MS and MSD samples (concentrations of 2,3,7,8-substituted PCDDs/PCDFs) should agree within 20 percent relative difference.

8.4 Percent Recovery of the Internal Standards - For each sample, method blank and rinsate, calculate the percent recovery (Section 7.9.2). The percent recovery should be between 40 percent and 135 percent for all 2,3,7,8-substituted internal standards.

NOTE: A low or high percent recovery for a blank does not require discarding the analytical data but it may indicate a potential problem with future analytical data.

8.5 Identification Criteria

8.5.1 If either one of the identification criteria appearing in Sections 7.8.4.1.1 through 7.8.4.1.4 is not met for an homologous series, it is reported that the sample does not contain unlabeled 2,3,7,8-substituted PCDD/PCDF isomers for that homologous series at the calculated detection limit (Section 7.9.5)

8.5.2 If the first initial identification criteria (Sections 7.8.4.1.1 through 7.8.4.1.4) are met, but the criteria appearing in Sections 7.8.4.1.5 and 7.8.4.2.1 are not met, that sample is presumed to contain interfering contaminants. This must be noted on the analytical report form, and the sample should be rerun or the extract reanalyzed.

8.6 Unused portions of samples and sample extracts must be preserved for six months after sample receipt to allow further analyses.

8.7 Reuse of glassware is to be minimized to avoid the risk of contamination.

9.0 METHOD PERFORMANCE

9.1 Data are currently not available.

10.0 REFERENCES

1. "Control of Interferences in the Analysis of Human Adipose Tissue for 2,3,7,8-Tetrachlorodibenzo-p-dioxin". D. G. Patterson, J.S. Holler, D.F. Grote, L.R. Alexander, C.R. Lapeza, R.C. O'Connor and J.A. Liddle. Environ. Toxicol. Chem. 5, 355-360 (1986).

2. "Method 8290: Analytical Procedures and Quality Assurance for Multimedia Analysis of Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry". Y. Tondeur and W.F. Beckert. U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, NV.

3. "Carcinogens - Working with Carcinogens", Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control. National Institute for Occupational Safety and Health. Publication No. 77-206, August 1977.

4. "OSHA Safety and Health Standards, General Industry", (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206 (revised January 1976).

5. "Safety in Academic Chemistry Laboratories", American Chemical Society Publication, Committee on Chemical Safety (3rd Edition, 1979.)

6. "Hybrid HRGC/MS/MS Method for the Characterization of Tetrachlorinated Dibenzo-p-dioxins in Environmental Samples." Y. Tondeur, W.J. Niederhut, S.R. Missler, and J.E. Campana, Mass Spectrom. 14, 449-456 (1987).

11.0 SAFETY

11.1 The following safety practices are excerpts from EPA Method 613, Section 4 (July 1982 version) and amended for use in conjunction with this method. The 2,3,7,8-TCDD isomer has been found to be acnegenic, carcinogenic, and teratogenic in laboratory animal studies. Other PCDDs and PCDFs containing chlorine atoms in positions 2,3,7,8 are known to have toxicities comparable to that of 2,3,7,8-TCDD. The analyst should note that finely divided dry soils contaminated with PCDDs and PCDFs are particularly hazardous because of the potential for inhalation and ingestion. It is recommended that such samples be

processed in a confined environment, such as a hood or a glove box. Laboratory personnel handling these types of samples should wear masks fitted with charcoal filters to prevent inhalation of dust.

11.2 The toxicity or carcinogenicity of each reagent used in this method is not precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be kept to a minimum. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should be made available to all personnel involved in the chemical analysis of samples suspected to contain PCDDs and/or PCDFs. Additional references to laboratory safety are given in references 3, 4 and 5.

11.3 Each laboratory must develop a strict safety program for the handling of PCDDs and PCDFs. The laboratory practices listed below are recommended.

11.3.1 Contamination of the laboratory will be minimized by conducting most of the manipulations in a hood.

11.3.2 The effluents of sample splitters for the gas chromatograph and roughing pumps on the HRGC/HRMS system should pass through either a column of activated charcoal or be bubbled through a trap containing oil or high boiling alcohols.

11.3.3 Liquid waste should be dissolved in methanol or ethanol and irradiated with ultraviolet light at a wavelength less than 290 nm for several days (use F 40 BL lamps, or equivalent). Using this analytical method, analyze the irradiated liquid wastes and dispose of the solutions when 2,3,7,8-TCDD and -TCDF congeners can no longer be detected.

11.4 The following precautions were issued by Dow Chemical U.S.A. (revised 11/78) for safe handling of 2,3,7,8-TCDD in the laboratory and amended for use in conjunction with this method.

11.4.1 The following statements on safe handling are as complete as possible on the basis of available toxicological information. The precautions for safe handling and use are necessarily general in nature since detailed, specific recommendations can be made only for the particular exposure and circumstances of each individual use. Assistance in evaluating the health hazards of particular plant conditions may be obtained from certain consulting laboratories and from State Departments of Health or of Labor, many of which have an industrial health service. The 2,3,7,8-TCDD isomer is extremely toxic to certain kinds of laboratory animals. However, it has been handled for years without injury in analytical and biological laboratories. Many techniques used in handling radioactive and infectious materials are applicable to 2,3,7,8-TCDD.

11.4.1.1 Protective Equipment: Throw away plastic gloves, apron or lab coat, safety glasses and laboratory hood adequate for radioactive work. However, PVC gloves should not be used.

11.4.1.2 Training: Workers must be trained in the proper method of removing contaminated gloves and clothing without contacting the exterior surfaces.

11.4.1.3 Personal Hygiene: Thorough washing of hands and forearms after each manipulation and before breaks (coffee, lunch, and shift).

11.4.1.4 Confinement: Isolated work area, posted with signs, segregated glassware and tools, plastic backed absorbent paper on benchtops.

11.4.1.5 Waste: Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans.

11.4.1.6 Disposal of Hazardous Wastes: Refer to the November 7, 1986 issue of the Federal Register on Land Ban Rulings for details concerning the handling of dioxin containing wastes.

11.4.1.7 Decontamination: Personnel - apply a mild soap with plenty of scrubbing action. Glassware, tools and surfaces - Chlorothene NU Solvent (Trademark of the Dow Chemical Company) is the least toxic solvent shown to be effective. Satisfactory cleaning may be accomplished by rinsing with Chlorothene, then washing with a detergent and water. Dish water may be disposed to the sewer after percolation through a charcoal bed filter. It is prudent to minimize solvent wastes because they require special disposal through commercial services that are expensive.

11.4.1.8 Laundry: Clothing known to be contaminated should be disposed with the precautions described under "Disposal of Hazardous Wastes". Laboratory coats or other clothing worn in 2,3,7,8-TCDD work area may be laundered. Clothing should be collected in plastic bags. Persons who convey the bags and launder the clothing should be advised of the hazard and trained in proper handling. The clothing may be put into a washer without contact if the launderer knows the problem. The washer should be run through one full cycle before being used again for other clothing.

11.4.1.9 Wipe Tests: A useful method for determining cleanliness of work surfaces and tools is to wipe the surface with a piece of filter paper, extract the filter paper and analyze the extract.

NOTE: A procedure for the collection, handling, analysis, and reporting requirements of wipe tests performed within the laboratory is described in Attachment A. The results and decision making processes are based on the presence of 2,3,7,8-substituted PCDDs/PCDFs.

11.4.1.10 Inhalation: Any procedure that may generate airborne contamination must be carried out with good ventilation.

Gross losses to a ventilation system must not be allowed. Handling of the dilute solutions normally used in analytical and animal work presents no significant inhalation hazards except in case of an accident.

11.4.1.11 Accidents: Remove contaminated clothing immediately, taking precautions not to contaminate skin or other articles. Wash exposed skin vigorously and repeatedly until medical attention is obtained.

Attachment A

PROCEDURES FOR THE COLLECTION, HANDLING, ANALYSIS, AND REPORTING OF WIPE TESTS PERFORMED WITHIN THE LABORATORY

This procedure is designed for the periodic evaluation of potential contamination by 2,3,7,8-substituted PCDD/PCDF congeners of the working areas inside the laboratory.

A.1 Perform the wipe tests on surface areas of two inches by one foot with glass fiber paper saturated with distilled in glass acetone using a pair of clean stainless steel forceps. Use one wiper for each of the designated areas. Combine the wipers to one composite sample in an extraction jar containing 200 mL distilled in glass acetone. Place an equal number of unused wipers in 200 mL acetone and use this as a control. Add 100 µL of the sample fortification solution to each jar containing used or unused wipers (Section 5.8).

A.1.1 Close the jar containing the wipers and the acetone and extract for 20 minutes using a wrist action shaker. Transfer the extract into a KD apparatus fitted with a concentration tube and a three ball Snyder column. Add two Teflon™ or Carborundum™ boiling chips and concentrate the extract to an apparent volume of 1.0 mL on a steam bath. Rinse the Snyder column and the KD assembly with two 1 mL portions of hexane into the concentrator tube, and concentrate its contents to near dryness with a gentle stream of nitrogen. Add 1.0 mL hexane to the concentrator tube and swirl the solvent on the walls.

A.1.2 Prepare a neutral alumina column as described in Section 7.5.2.2 and follow the steps outlined in Sections 7.5.2.3 through 7.5.2.5.

A.1.3 Add 10 µL of the recovery standard solution as described in Section 7.5.3.6.

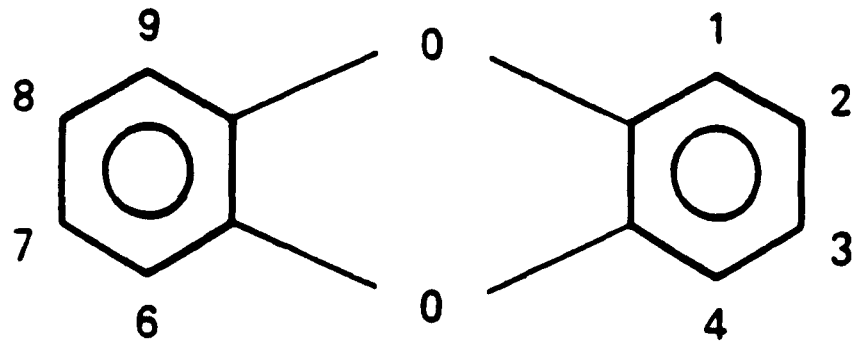
A.2 Concentrate the contents of the vial to a final volume of 10 µL (either in a minivial or in a capillary tube). Inject 2 µL of each extract (wipe and control) onto a capillary column and analyze for 2,3,7,8-substituted PCDDs/PCDFs as specified in the analytical method in Section 7.8. Perform calculations according to Section 7.9.

A.3 Report the presence of 2,3,7,8-substituted PCDDs and PCDFs as a quantity (pg or ng) per wipe test experiment (WTE). Under the conditions outlined in this analytical protocol, a lower limit of calibration of 10 pg/WTE is expected for 2,3,7,8-TCDD. A positive response for the blank (control) is defined as a signal in the TCDD retention time window at any of the masses monitored which is equivalent to or above 3 pg of 2,3,7,8-TCDD per WTE. For other congeners, use the multiplication factors listed in Table 1, footnote (a) (e.g., for OCDD, the lower MCL is 10 x 5 = 50 pg/WTE and the positive response for the blank would be 3 x 5 = 15 pg). Also, report the recoveries of the internal standards during the simplified cleanup procedure.

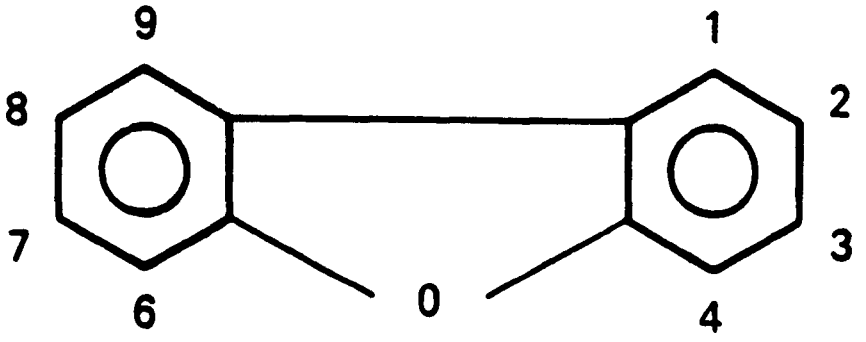
A.4 At a minimum, wipe tests should be performed when there is evidence of contamination in the method blanks.

A.5 An upper limit of 25 pg per TCDD isomer and per wipe test experiment is allowed (use multiplication factors listed in footnote (a) from Table 1 for other congeners). This value corresponds to 2½ times the lower calibration limit of the analytical method. Steps to correct the contamination must be taken whenever these levels are exceeded. To that effect, first vacuum the working places (hoods, benches, sink) using a vacuum cleaner equipped with a high efficiency particulate absorbent (HEPA) filter and then wash with a detergent. A new set of wipes should be analyzed before anyone is allowed to work in the dioxin area of the laboratory after corrective action has been taken.

Figure 1.



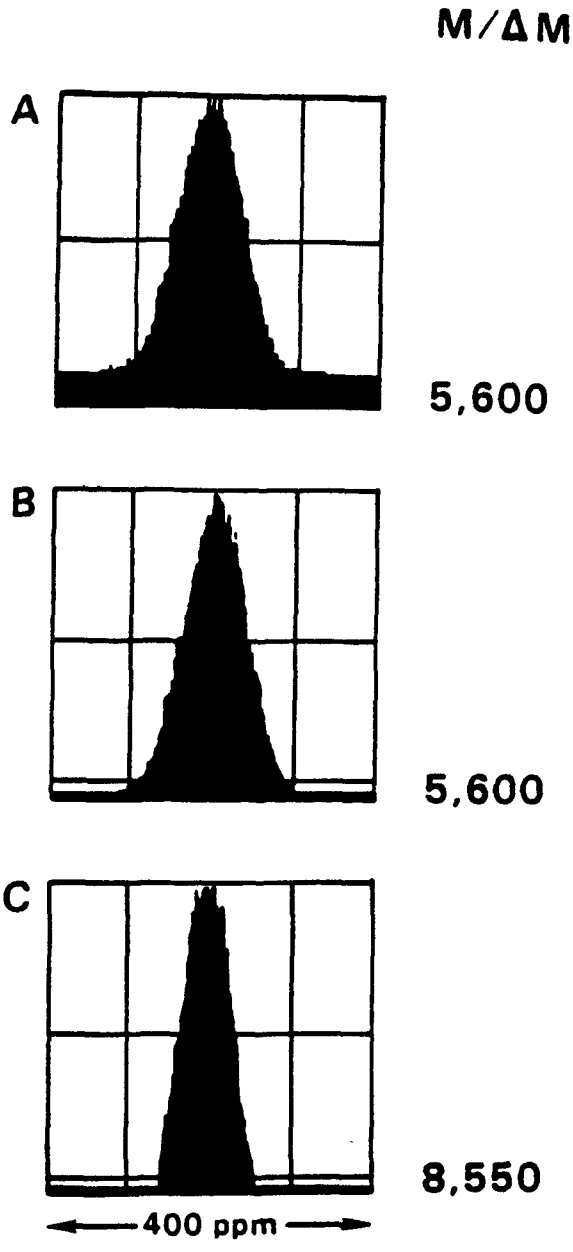
Dibenzodioxin



Dibenzofuran

General structures of dibenzo-p-dioxin and dibenzofuran.

Figure 2.



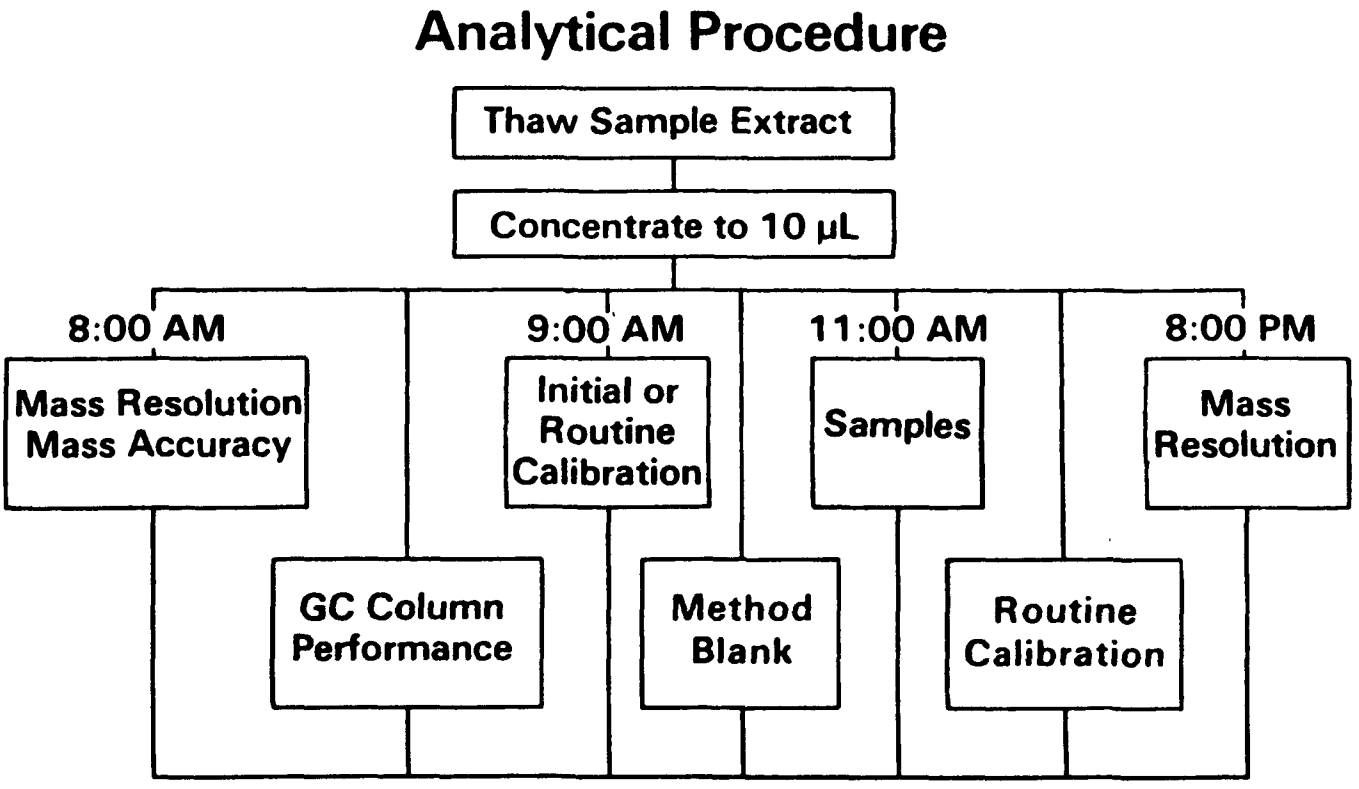
Peak profile displays demonstrating the effect of the detector zero on the measured resolving power. In this example, the true resolving power is 5,600.

A) The zero was set too high; no effect is observed upon the measurement of the resolving power.

B) The zero was adjusted properly.

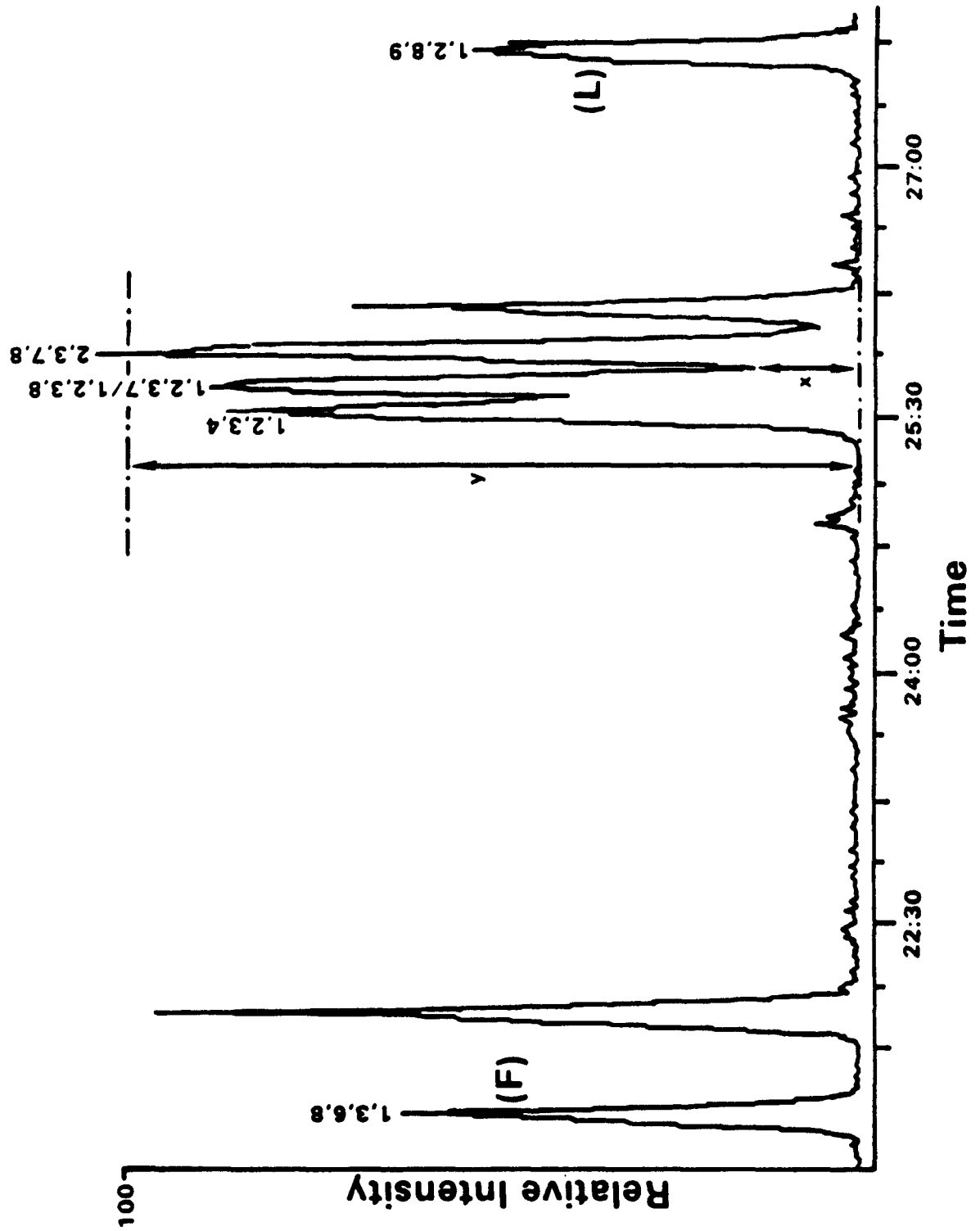
C) The zero was set too low; this results in overestimating the actual resolving power because the peak-to-peak noise cannot be measured accurately.

Figure 3.



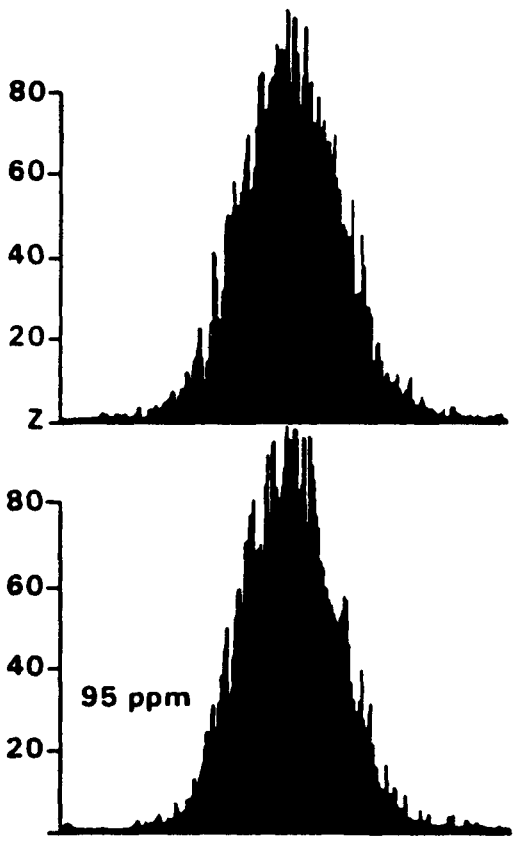
Typical 12 hour analysis sequence of events.

Figure 4.



Selected ion current profile for m/z 322 (TCDDs) produced by MS analysis of the GC performance check solution on a 60 m DB-5 fused silica capillary column under the conditions listed in Section 7.6.

Figure 5.



Ref. mass 304.9824 Peak top
Span. 200 ppm

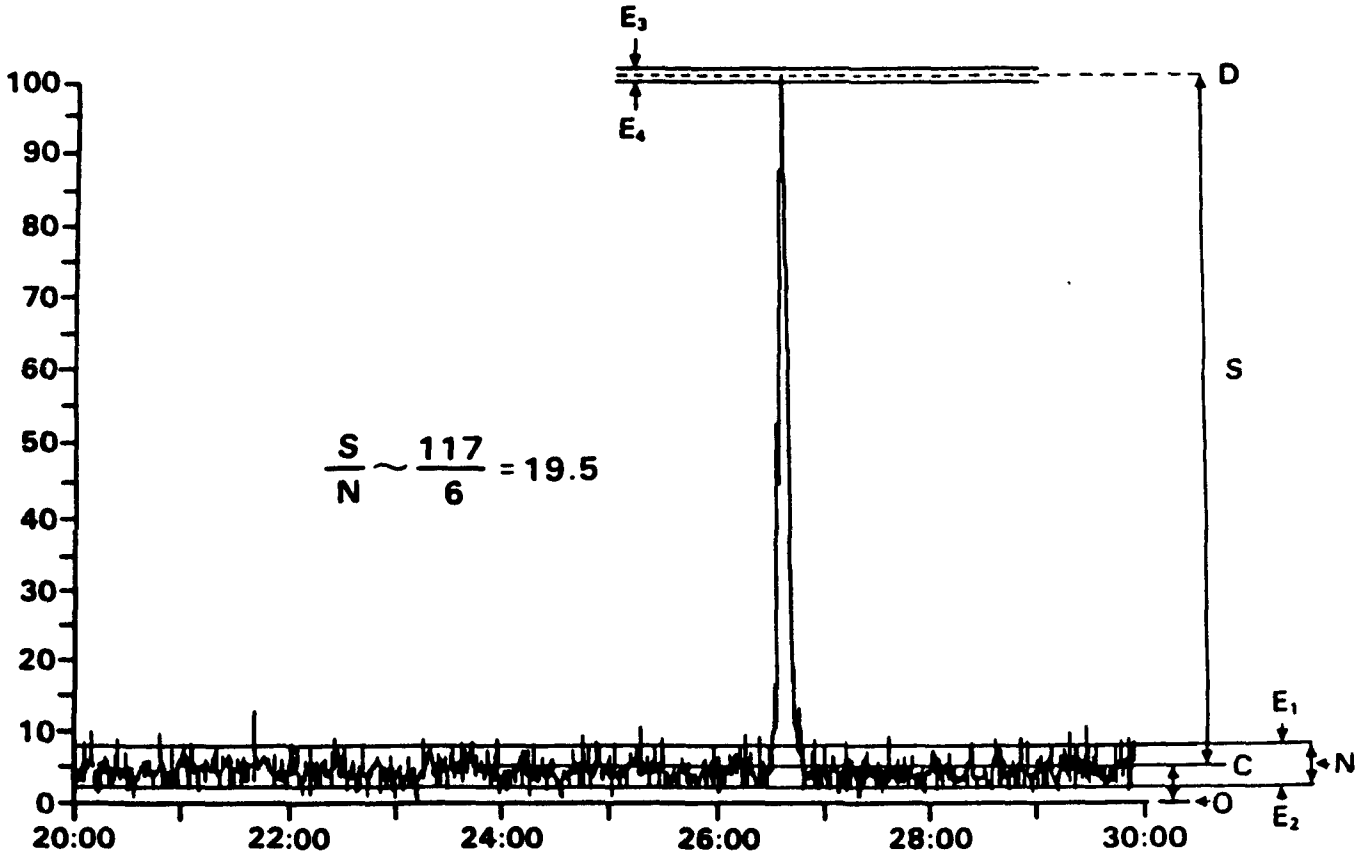
System file name	YVES150
Data file name	A:85Z567
Resolution	10000
Group number	1
Ionization mode	EI+
Switching	VOLTAGE
Ref. masses	304.9824
	380.9260

M/ΔM~10,500

Channel B 380.9260 Lock mass
Span 200 ppm

Peak profiles representing two PFK reference ions at m/z 305 and 381. The resolution of the high-mass signal is 95 ppm at 5 percent of the peak height; this corresponds to a resolving power M/ΔM of 10,500 (10 percent valley definition).

Figure 6.



Manual determination of S/N.

The peak height (S) is measured between the mean noise (lines C and D). These mean signal values are obtained by tracing the line between the baseline average noise extremes, E1 and E2, and between the apex average noise extremes, E3 and E4, at the apex of the signal.

NOTE: It is imperative that the instrument interface amplifier electronic zero offset be set high enough so that negative going baseline noise is recorded.

Table 1.

Types of Matrices, Sample Sizes and 2,3,7,8-TCDD-Based Method Calibration Limits (Parts per Trillion)

	Water	Soil Sediment Paper Pulp[b]	Fly Ash	Fish Tissue[c]	Human Adipose Tissue	Sludges, Fuel Oil	Still-Bottom
Lower MCL[(a)]	0.01	1.0	1.0	1.0	1.0	5.0	10
Upper MCL[(a)]	2	200	200	200	200	1000	2000
Weight (g)	1000	10	10	20	10	2	1
IS Spiking Levels (ppt)	1	100	100	100	100	500	1000
Final Extr. Vol. (μL)[(d)]	10-50	10-50	50	10-50	10-50	50	50

(a) For other congeners multiply the values by 1 for TCDF/PeCDD/PeCDF, by 2.5 for HxCDD/HxCDF/HpCDD/HpCDF, and by 5 for OCDD/OCDF.

(b) Sample dewatered according to Section 6.5.

(c) One half of the extract from the 20 g sample is used for determination of lipid content (Section 7.2.2).

(d) See Section 7.8.1, Note.

NOTE: Chemical reactor residues are treated as still bottoms if their appearances so suggest.

Table 2.

Composition of the Sample Fortification and Recovery Standard Solutions[a]

Analyte	Sample Fortification Solution Concentration (pg/μL; Solvent: Nonane)	Recovery Standard Solution Concentration (pg/μL; Solvent: Nonane)
$^{13}C_{12}$-2,3,7,8-TCDD	10	--
$^{13}C_{12}$-2,3,7,8-TCDF	10	--
$^{13}C_{12}$-1,2,3,4-TCDD	--	50
$^{13}C_{12}$-1,2,3,7,8-PeCDD	10	--
$^{13}C_{12}$-1,2,3,7,8-PeCDF	10	--
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	25	--
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25	--
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	--	50
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	25	--
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	25	--
$^{13}C_{12}$-OCDD	50	--

(a) These solutions should be made freshly every day because of the possibility of adsorptive losses to glassware. If these solutions are to be kept for more than one day, then the sample fortification solution concentrations should be increased ten fold, and the recovery standard solution concentrations should be doubled. Corresponding adjustments of the spiking volumes must then be made.

Table 3.

The Fifteen 2,3,7,8-Substituted PCDD and PCDF Congeners

PCDD	PCDF
2,3,7,8-TCDD(*)	2,3,7,8-TCDF(*)
1,2,3,7,8-PeCDD(*)	1,2,3,7,8-PeCDF(*)
1,2,3,6,7,8-HxCDD(*)	2,3,4,7,8-PeCDF
1,2,3,4,7,8-HxCDD	1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDD(+)	1,2,3,7,8,9-HxCDF
1,2,3,4,6,7,8-HpCDD(*)	1,2,3,4,7,8-HxCDF(*)
	2,3,4,6,7,8-HxCDF
	1,2,3,4,6,7,8-HpCDF(*)
	1,2,3,4,7,8,9-HpCDF

(*) The 13C-labeled analogue is used as an internal standard.

(+) The 13C-labeled analogue is used as a recovery standard.

Table 4.

Isomers of Chlorinated Dioxins and Furans as a Function of the Number of Chlorine Atoms

Number of Chlorine Atoms	Number of Dioxin Isomers	Number of 2,3,7,8 Isomers	Number of Furan Isomers	Number of 2,3,7,8 Isomers
1	2	---	4	---
2	10	---	16	---
3	14	---	28	---
4	22	1	38	1
5	14	1	28	2
6	10	3	16	4
7	2	1	4	2
8	1	1	1	1
Total	75	7	135	10

Table 5.

High-Resolution Concentration Calibration Solutions

Compound	HRCC	Concentration (pg/μL, in Nonane) 5	4	3	2	1
Unlabeled Analytes						
2,3,7,8-TCDD		200	50	10	2.5	1
2,3,7,8-TCDF		200	50	10	2.5	1
1,2,3,7,8-PeCDD		500	125	25	6.25	2.5
1,2,3,7,8-PeCDF		500	125	25	6.25	2.5
2,3,4,7,8-PeCDF		500	125	25	6.25	2.5
1,2,3,4,7,8-HxCDD		500	125	25	6.25	2.5
1,2,3,6,7,8-HxCDD		500	125	25	6.25	2.5
1,2,3,7,8,9-HxCDD		500	125	25	6.25	2.5
1,2,3,4,7,8-HxCDF		500	125	25	6.25	2.5
1,2,3,6,7,8-HxCDF		500	125	25	6.25	2.5
1,2,3,7,8,9-HxCDF		500	125	25	6.25	2.5
2,3,4,6,7,8-HxCDF		500	125	25	6.25	2.5
1,2,3,4,6,7,8-HpCDD		500	125	25	6.25	2.5
1,2,3,4,6,7,8-HpCDF		500	125	25	6.25	2.5
1,2,3,4,7,8,9-HpCDF		500	125	25	6.25	2.5
OCDD		1,000	250	50	12.5	5
OCDF		1,000	250	50	12.5	5
Internal Standards						
$^{13}C_{12}$-2,3,7,8-TCDD		50	50	50	50	50
$^{13}C_{12}$-2,3,7,8-TCDF		50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8-PeCDD		50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8-PeCDF		50	50	50	50	50
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD		125	125	125	125	125
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF		125	125	125	125	125
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD		125	125	125	125	125
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF		125	125	125	125	125
$^{13}C_{12}$-OCDD		250	250	250	250	250
Recovery Standards						
$^{13}C_{12}$-1,2,3,4-TCDD[a]		50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD[b]		125	125	125	125	125

[a] Used for recovery determinations of TCDD, TCDF, PeCDD and PeCDF internal standards.

[b] Used for recovery determinations of HxCDD, HxCDF, HpCDD, HpCDF and OCDD internal standards.

Table 6.

Ions Monitored for HRGC/HRMS Analysis of PCDDs/PCDFs

Descriptor	Accurate[(a)] Mass	Ion ID	Elemental Composition	Analyte
1	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}Cl_4O_2$	TCDD
	321.8936	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD (S)
	333.9338	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD (S)
	375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
	[354.9792]	LOCK	C_9F_{13}	PFK
2	339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF
	341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF (S)
	355.8546	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD (S)
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCDPE
	[354.9792]	LOCK	C_9F_{13}	PFK
3	373.8208	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF
	375.8178	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)
	385.8610	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8156	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M+4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD (S)
	445.7555	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
	[430.9728]	LOCK	C_9F_{17}	PFK

Table 6.
Continued

Descriptor	Accurate[a] Mass	Ion ID	Elemental Composition	Analyte
4	407.7818	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7788	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8250	M	$^{13}C_{12}H^{35}Cl_7O$	HpCDF (S)
	419.8220	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	423.7767	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	435.8169	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD (S)
	437.8140	M+4	$^{13}C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD (S)
	479.7165	M+4	$C_{12}H^{35}Cl_7{}^{37}Cl_2O$	NCDPE
	[430.9728]	LOCK	C_9F_{17}	PFK
5	441.7428	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	443.7399	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7780	M+2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD (S)
	471.7750	M+4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD (S)
	513.6775	M+4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O$	DCDPE
	[442.9278]	LOCK	$C_{10}F_{17}$	PFK

[a] The following nuclidic masses were used:

H	=	1.007825	O	=	15.994915
C	=	12.000000	^{35}Cl	=	34.968853
^{13}C	=	13.003355	^{37}Cl	=	36.965903
F	=	18.9984			

S = internal/recovery standard

Table 7.

PCDD and PCDF Congeners Present in the GC Performance Evaluation Solution and Used for Defining the Homologous GC Retention Time Windows on a 60 m DB-5 Column

No. of Chlorine Atoms	PCDD Positional Isomer		PCDF Positional Isomer	
	First Eluter	Last Eluter	First Eluter	Last Eluter
4[a]	1,3,6,8	1,2,8,9	1,3,6,8	1,2,8,9
5	1,2,4,6,8/ 1,2,4,7,9	1,2,3,8,9	1,3,4,6,8	1,2,3,8,9
6	1,2,4,6,7,9/ 1,2,4,6,8,9	1,2,3,4,6,7	1,2,3,4,6,8	1,2,3,4,8,9
7	1,2,3,4,6,7,9	1,2,3,4,6,7,8	1,2,3,4,6,7,8	1,2,3,4,7,8,9
8		1,2,3,4,6,7,8,9		1,2,3,4,6,7,8,9

(a) In addition to these two TCDD isomers, the 1,2,3,4-, 1,2,3,7-, 1,2,3,8-, 2,3,7,8-, $^{13}C_{12}$-2,3,7,8-, and 1,2,3,9-TCDD isomers must also be present as a check of column resolution.

Table 8.

Theoretical Ion Abundance Ratios and Their Control Limits for PCDDs and PCDFs

Number of Chlorine Atoms	Ion Type	Theoretical Ratio	Control Limits lower	Control Limits upper
4	$\frac{M}{M+2}$	0.77	0.65	0.89
5	$\frac{M+2}{M+4}$	1.55	1.32	1.78
6	$\frac{M+2}{M+4}$	1.24	1.05	1.43
6[(a)]	$\frac{M}{M+2}$	0.51	0.43	0.59
7[(b)]	$\frac{M}{M+2}$	0.44	0.37	0.51
7	$\frac{M+2}{M+4}$	1.04	0.88	1.20
8	$\frac{M+2}{M+4}$	0.89	0.76	1.02

(a) Used only for ^{13}C-HxCDF (IS).

(b) Used only for ^{13}C-HpCDF (IS).

Table 9.

Relative Response Factor [RRF (number)] Attributions

Number	Specific Congener Name
1	2,3,7,8-TCDD (and total TCDDs)
2	2,3,7,8-TCDF (and total TCDFs)
3	1,2,3,7,8-PeCDD (and total PeCDDs)
4	1,2,3,7,8-PeCDF
5	2,3,4,7,8-PeCDF
6	1,2,3,4,7,8-HxCDD
7	1,2,3,6,7,8-HxCDD
8	1,2,3,7,8,9-HxCDD
9	1,2,3,4,7,8-HxCDF
10	1,2,3,6,7,8-HxCDF
11	1,2,3,7,8,9-HxCDF
12	2,3,4,6,7,8-HxCDF
13	1,2,3,4,6,7,8-HpCDD (and total HpCDDs)
14	1,2,3,4,6,7,8-HpCDF
15	1,2,3,4,7,8,9-HpCDF
16	OCDD
17	OCDF
18	$^{13}C_{12}$-2,3,7,8-TCDD
19	$^{13}C_{12}$-2,3,7,8-TCDF
20	$^{13}C_{12}$-1,2,3,7,8-PeCDD
21	$^{13}C_{12}$-1,2,3,7,8-PeCDF
22	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
23	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF
24	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD
25	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
26	$^{13}C_{12}$-OCDD
27	Total PeCDFs
28	Total HxCDFs
29	Total HxCDDs
30	Total HpCDFs

Table 10.

2,3,7,8-TCDD Toxicity Equivalency Factors (TEFs) for the Polychlorinated Dibenzodioxins and Dibenzofurans

Number	Compound(s)	TEF
1	2,3,7,8-TCDD	1.00
2	1,2,3,7,8-PeCDD	0.50
3	1,2,3,6,7,8-HxCDD	0.10
4	1,2,3,7,8,9-HxCDD	0.10
5	1,2,3,4,7,8-HxCDD	0.10
6	1,2,3,4,6,7,8-HpCDD	0.01
7	1,2,3,4,6,7,8,9-OCDD	0.001
8	2,3,7,8-TCDF	0.1
9	1,2,3,7,8-PeCDF	0.05
10	2,3,4,7,8-PeCDF	0.5
11	1,2,3,6,7,8-HxCDF	0.1
12	1,2,3,7,8,9-HxCDF	0.1
13	1,2,3,4,7,8-HxCDF	0.1
14	2,3,4,6,7,8-HxCDF	0.1
15	1,2,3,4,6,7,8-HpCDF	0.01
16	1,2,3,4,7,8,9-HpCDF	0.01
17	1,2,3,4,6,7,8,9-OCDF	0.001

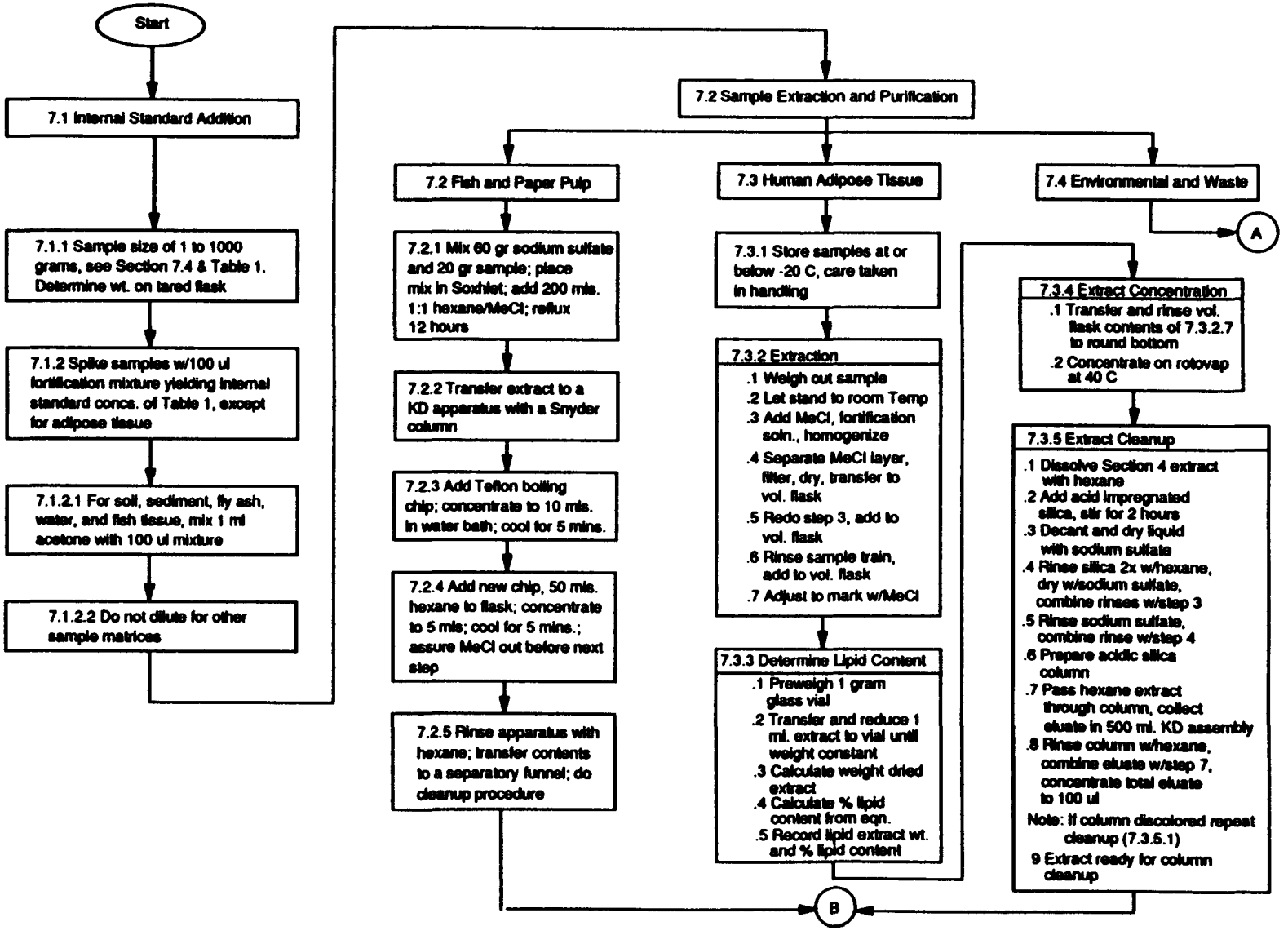
Table 11.

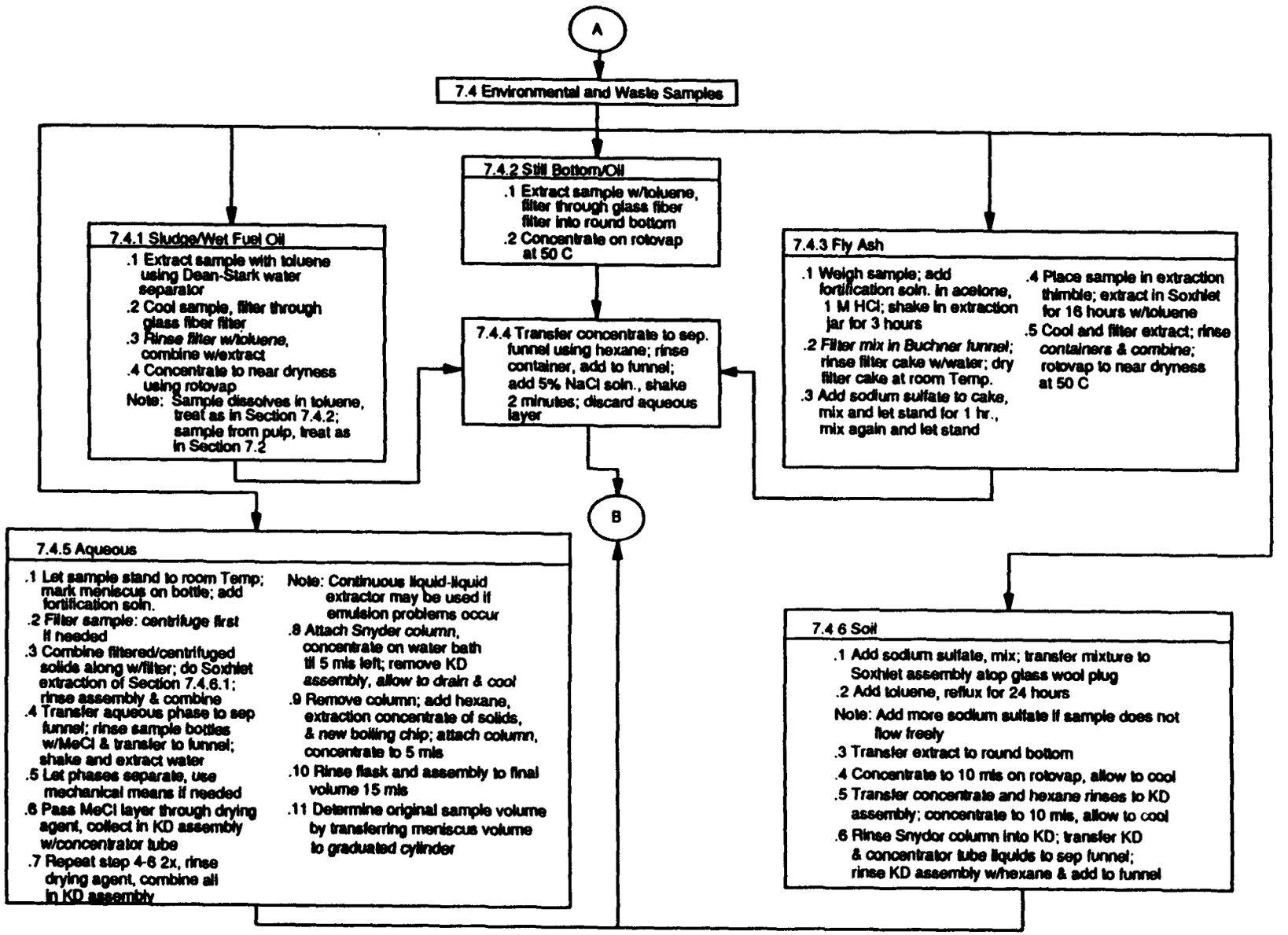
Analyte Relative Retention Time Reference Attributions

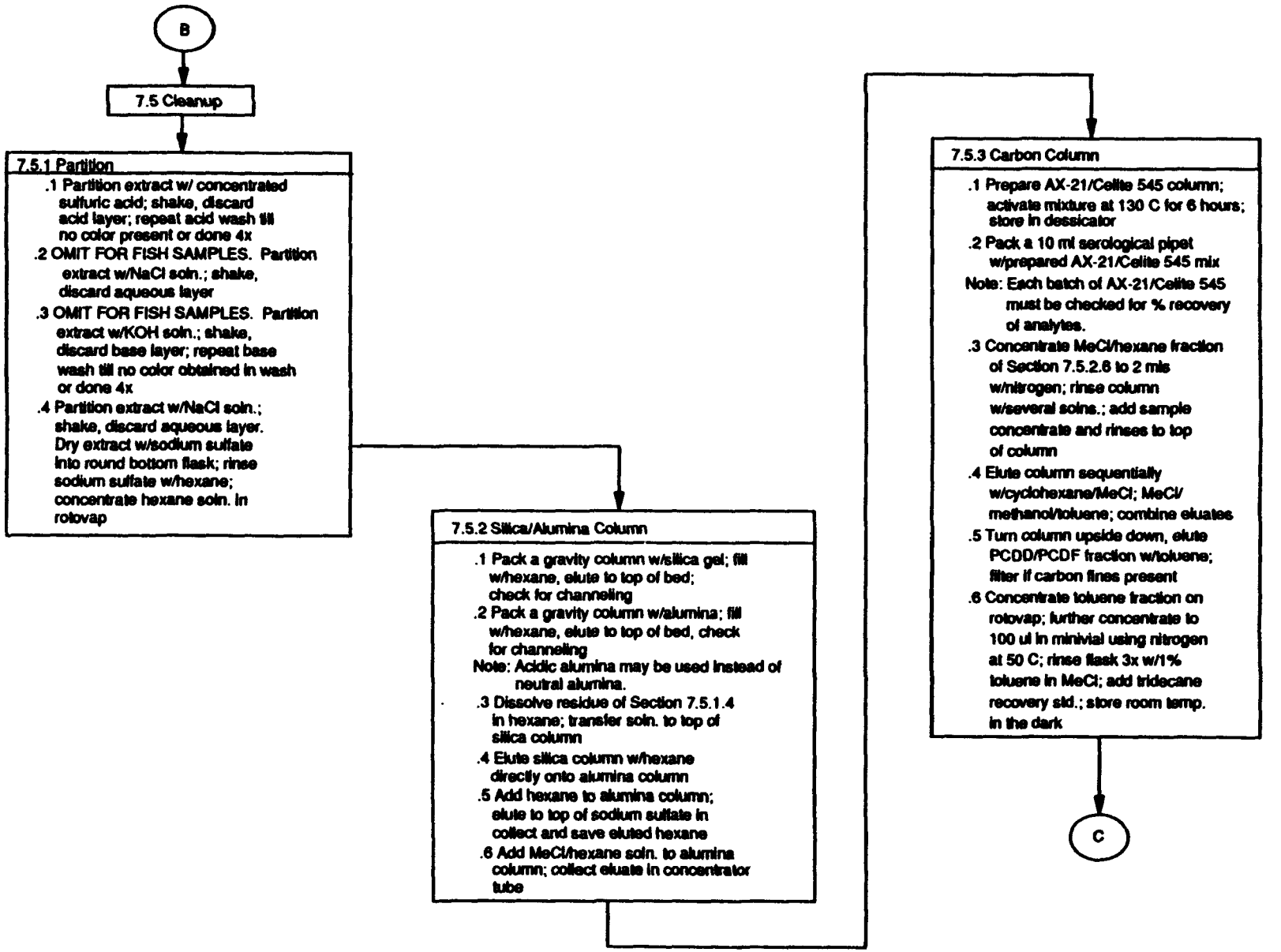
Analyte	Analyte RRT Reference[a]
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF

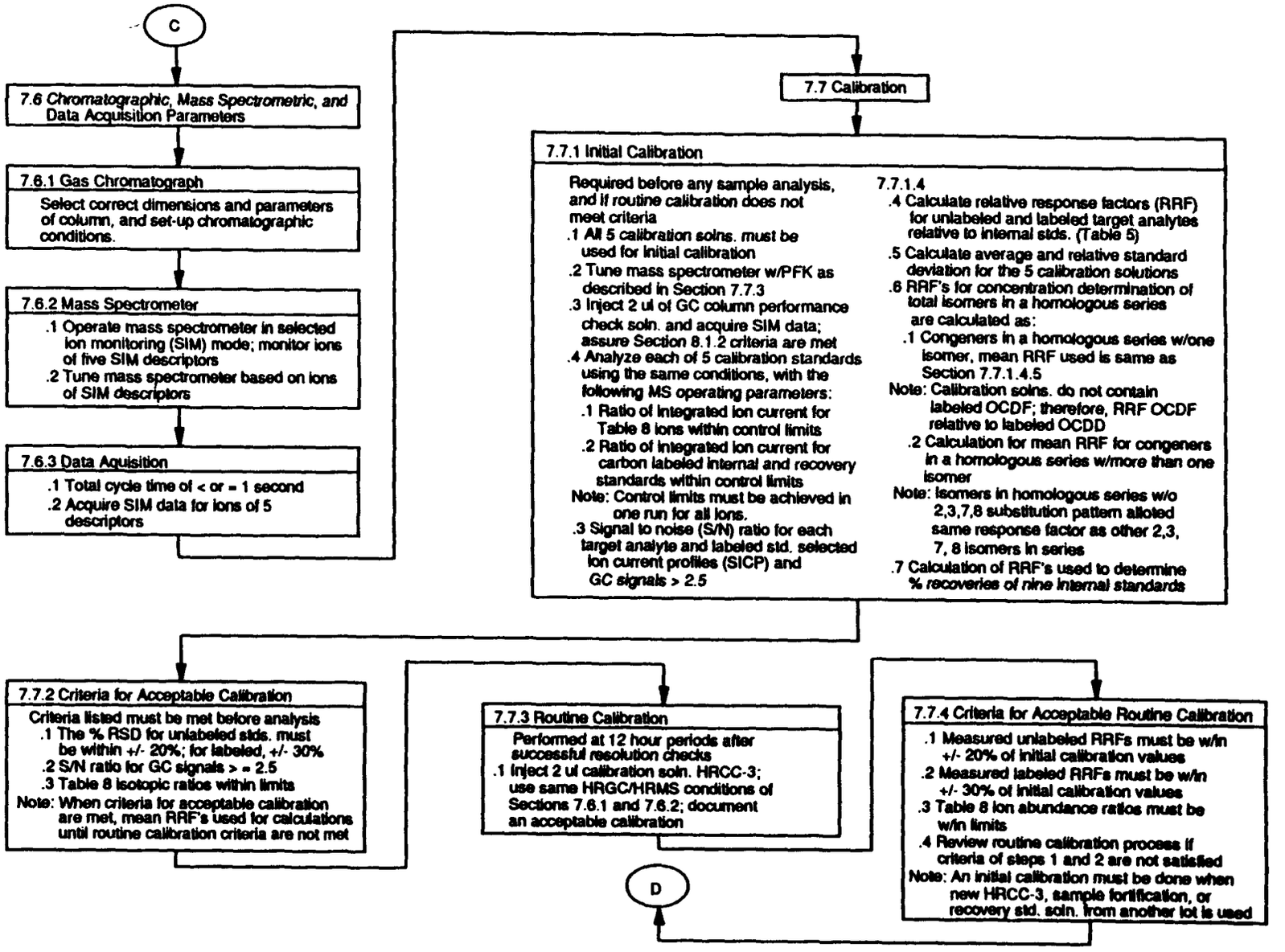
(a) The retention time of 2,3,4,7,8-PeCDF on the DB-5 column is measured relative to $^{13}C_{12}$-1,2,3,7,8-PeCDF and the retention time of 1,2,3,4,7,8,9-HpCDF relative to $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF.

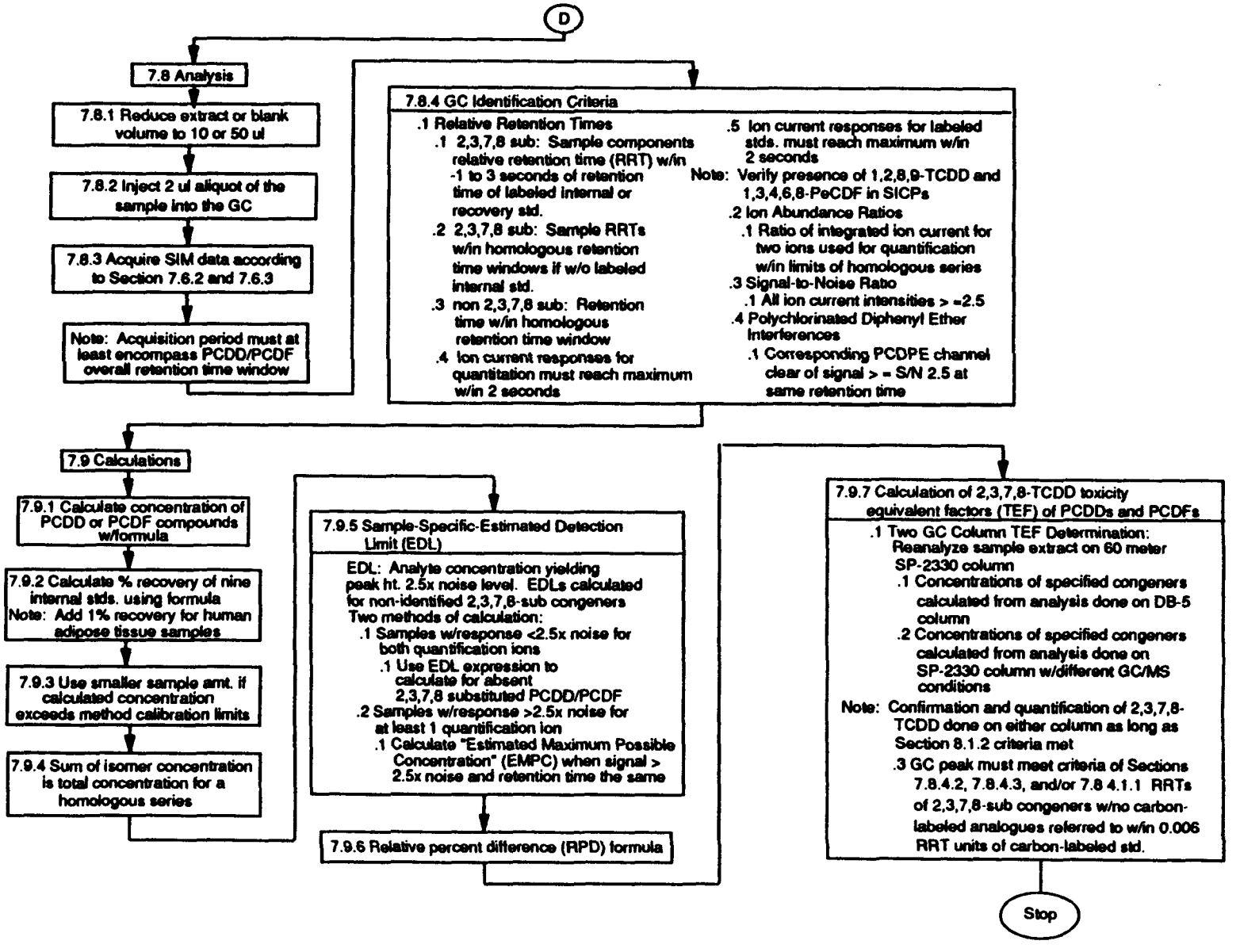
METHOD 8290
POLYCHLORINATED DIBENZODIOXINS (PCDDs) AND POLYCHLORINATED DIBENZOFURANS (PCDFs) BY HIGH-RESOLUTION GAS CHROMATOGRAPHY/HIGH-RESOLUTION MASS SPECTROMETRY (HRGC/HRMS)




A
7.4 Environmental and Waste Samples
7.4.1 Sludge/Wet Fuel Oil
.1 Extract sample with toluene using Dean-Stark water separator
.2 Cool sample, filter through glass fiber filter
.3 Rinse filter w/toluene, combine w/extract
.4 Concentrate to near dryness using rotovap
Note: Sample dissolves in toluene, treat as in Section 7.4.2; sample from pulp, treat as in Section 7.2
7.4.2 Still Bottom/Oil
.1 Extract sample w/toluene, filter through glass fiber filter into round bottom
.2 Concentrate on rotovap at 50 C
7.4.3 Fly Ash
.1 Weigh sample; add fortification soln. in acetone, 1 M HCl; shake in extraction jar for 3 hours
.2 Filter mix in Buchner funnel; rinse filter cake w/water; dry filter cake at room Temp.
.3 Add sodium sulfate to cake, mix and let stand for 1 hr., mix again and let stand
.4 Place sample in extraction thimble; extract in Soxhlet for 16 hours w/toluene
.5 Cool and filter extract; rinse containers & combine; rotovap to near dryness at 50 C
7.4.4 Transfer concentrate to sep. funnel using hexane; rinse container, add to funnel; add 5% NaCl soln., shake 2 minutes; discard aqueous layer
B
7.4.5 Aqueous
.1 Let sample stand to room Temp; mark meniscus on bottle; add fortification soln.
.2 Filter sample: centrifuge first if needed
.3 Combine filtered/centrifuged solids along w/filter; do Soxhlet extraction of Section 7.4.6.1; rinse assembly & combine
.4 Transfer aqueous phase to sep funnel; rinse sample bottles w/MeCl & transfer to funnel; shake and extract water
.5 Let phases separate, use mechanical means if needed
.6 Pass MeCl layer through drying agent, collect in KD assembly w/concentrator tube
.7 Repeat step 4-6 2x, rinse drying agent, combine all in KD assembly
Note: Continuous liquid-liquid extractor may be used if emulsion problems occur
.8 Attach Snyder column, concentrate on water bath til 5 mls left; remove KD assembly, allow to drain & cool
.9 Remove column; add hexane, extraction concentrate of solids, & new boiling chip; attach column, concentrate to 5 mls
.10 Rinse flask and assembly to final volume 15 mls
.11 Determine original sample volume by transferring meniscus volume to graduated cylinder
7.4 6 Soil
.1 Add sodium sulfate, mix; transfer mixture to Soxhlet assembly atop glass wool plug
.2 Add toluene, reflux for 24 hours
Note: Add more sodium sulfate if sample does not flow freely
.3 Transfer extract to round bottom
.4 Concentrate to 10 mls on rotovap, allow to cool
.5 Transfer concentrate and hexane rinses to KD assembly; concentrate to 10 mls, allow to cool
.6 Rinse Snydor column into KD; transfer KD & concentrator tube liquids to sep funnel; rinse KD assembly w/hexane & add to funnel


B
7.5 Cleanup
7.5.1 Partition
.1 Partition extract w/ concentrated sulfuric acid; shake, discard acid layer; repeat acid wash till no color present or done 4x
.2 OMIT FOR FISH SAMPLES. Partition extract w/NaCl soln.; shake, discard aqueous layer
.3 OMIT FOR FISH SAMPLES. Partition extract w/KOH soln.; shake, discard base layer; repeat base wash till no color obtained in wash or done 4x
.4 Partition extract w/NaCl soln.; shake, discard aqueous layer. Dry extract w/sodium sulfate into round bottom flask; rinse sodium sulfate w/hexane; concentrate hexane soln. in rotovap
7.5.2 Silica/Alumina Column
.1 Pack a gravity column w/silica gel; fill w/hexane, elute to top of bed; check for channeling
.2 Pack a gravity column w/alumina; fill w/hexane, elute to top of bed, check for channeling
Note: Acidic alumina may be used instead of neutral alumina.
.3 Dissolve residue of Section 7.5.1.4 in hexane; transfer soln. to top of silica column
.4 Elute silica column w/hexane directly onto alumina column
.5 Add hexane to alumina column; elute to top of sodium sulfate in collect and save eluted hexane
.6 Add MeCl/hexane soln. to alumina column; collect eluate in concentrator tube
7.5.3 Carbon Column
.1 Prepare AX-21/Celite 545 column; activate mixture at 130 C for 6 hours; store in dessicator
.2 Pack a 10 ml serological pipet w/prepared AX-21/Celite 545 mix
Note: Each batch of AX-21/Celite 545 must be checked for % recovery of analytes.
.3 Concentrate MeCl/hexane fraction of Section 7.5.2.6 to 2 mls w/nitrogen; rinse column w/several solns.; add sample concentrate and rinses to top of column
.4 Elute column sequentially w/cyclohexane/MeCl; MeCl/methanol/toluene; combine eluates
.5 Turn column upside down, elute PCDD/PCDF fraction w/toluene; filter if carbon fines present
.6 Concentrate toluene fraction on rotovap; further concentrate to 100 ul in minivial using nitrogen at 50 C; rinse flask 3x w/1% toluene in MeCl; add tridecane recovery std.; store room temp. in the dark
C


C
7.6 Chromatographic, Mass Spectrometric, and Data Acquisition Parameters
7.6.1 Gas Chromatograph
Select correct dimensions and parameters of column, and set-up chromatographic conditions.
7.6.2 Mass Spectrometer
.1 Operate mass spectrometer in selected ion monitoring (SIM) mode; monitor ions of five SIM descriptors
.2 Tune mass spectrometer based on ions of SIM descriptors
7.6.3 Data Aquisition
.1 Total cycle time of < or = 1 second
.2 Acquire SIM data for ions of 5 descriptors
7.7 Calibration
7.7.1 Initial Calibration
Required before any sample analysis, and if routine calibration does not meet criteria
.1 All 5 calibration solns. must be used for initial calibration
.2 Tune mass spectrometer w/PFK as described in Section 7.7.3
.3 Inject 2 ul of GC column performance check soln. and acquire SIM data; assure Section 8.1.2 criteria are met
.4 Analyze each of 5 calibration standards using the same conditions, with the following MS operating parameters:
.1 Ratio of integrated ion current for Table 8 ions within control limits
.2 Ratio of integrated ion current for carbon labeled internal and recovery standards within control limits
Note: Control limits must be achieved in one run for all ions.
.3 Signal to noise (S/N) ratio for each target analyte and labeled std. selected ion current profiles (SICP) and GC signals > 2.5
7.7.1.4
.4 Calculate relative response factors (RRF) for unlabeled and labeled target analytes relative to internal stds. (Table 5)
.5 Calculate average and relative standard deviation for the 5 calibration solutions
.6 RRF's for concentration determination of total isomers in a homologous series are calculated as:
.1 Congeners in a homologous series w/one isomer, mean RRF used is same as Section 7.7.1.4.5
Note: Calibration solns. do not contain labeled OCDF; therefore, RRF OCDF relative to labeled OCDD
.2 Calculation for mean RRF for congeners in a homologous series w/more than one isomer
Note: Isomers in homologous series w/o 2,3,7,8 substitution pattern alloted same response factor as other 2,3, 7, 8 isomers in series
.7 Calculation of RRF's used to determine % recoveries of nine internal standards
7.7.2 Criteria for Acceptable Calibration
Criteria listed must be met before analysis
.1 The % RSD for unlabeled stds. must be within +/- 20%; for labeled, +/- 30%
.2 S/N ratio for GC signals > = 2.5
.3 Table 8 isotopic ratios within limits
Note: When criteria for acceptable calibration are met, mean RRF's used for calculations until routine calibration criteria are not met
7.7.3 Routine Calibration
Performed at 12 hour periods after successful resolution checks
.1 Inject 2 ul calibration soln. HRCC-3; use same HRGC/HRMS conditions of Sections 7.6.1 and 7.6.2; document an acceptable calibration
7.7.4 Criteria for Acceptable Routine Calibration
.1 Measured unlabeled RRFs must be w/in +/- 20% of initial calibration values
.2 Measured labeled RRFs must be w/in +/- 30% of initial calibration values
.3 Table 8 ion abundance ratios must be w/in limits
.4 Review routine calibration process if criteria of steps 1 and 2 are not satisfied
Note: An initial calibration must be done when new HRCC-3, sample fortification, or recovery std. soln. from another lot is used
D


D
7.8 Analysis
7.8.1 Reduce extract or blank volume to 10 or 50 ul
7.8.2 Inject 2 ul aliquot of the sample into the GC
7.8.3 Acquire SIM data according to Section 7.6.2 and 7.6.3
Note: Acquisition period must at least encompass PCDD/PCDF overall retention time window
7.8.4 GC Identification Criteria
.1 Relative Retention Times
.1 2,3,7,8 sub: Sample components relative retention time (RRT) w/in -1 to 3 seconds of retention time of labeled internal or recovery std.
.2 2,3,7,8 sub: Sample RRTs w/in homologous retention time windows if w/o labeled internal std.
.3 non 2,3,7,8 sub: Retention time w/in homologous retention time window
.4 Ion current responses for quantitation must reach maximum w/in 2 seconds
.5 Ion current responses for labeled stds. must reach maximum w/in 2 seconds
Note: Verify presence of 1,2,8,9-TCDD and 1,3,4,6,8-PeCDF in SICPs
.2 Ion Abundance Ratios
.1 Ratio of integrated ion current for two ions used for quantification w/in limits of homologous series
.3 Signal-to-Noise Ratio
.1 All ion current intensities > =2.5
.4 Polychlorinated Diphenyl Ether Interferences
.1 Corresponding PCDPE channel clear of signal > = S/N 2.5 at same retention time
7.9 Calculations
7.9.1 Calculate concentration of PCDD or PCDF compounds w/formula
7.9.2 Calculate % recovery of nine internal stds. using formula
Note: Add 1% recovery for human adipose tissue samples
7.9.3 Use smaller sample amt. if calculated concentration exceeds method calibration limits
7.9.4 Sum of isomer concentration is total concentration for a homologous series
7.9.5 Sample-Specific-Estimated Detection Limit (EDL)
EDL: Analyte concentration yielding peak ht. 2.5x noise level. EDLs calculated for non-identified 2,3,7,8-sub congeners
Two methods of calculation:
.1 Samples w/response <2.5x noise for both quantification ions
.1 Use EDL expression to calculate for absent 2,3,7,8 substituted PCDD/PCDF
.2 Samples w/response >2.5x noise for at least 1 quantification ion
.1 Calculate "Estimated Maximum Possible Concentration" (EMPC) when signal > 2.5x noise and retention time the same
7.9.6 Relative percent difference (RPD) formula
7.9.7 Calculation of 2,3,7,8-TCDD toxicity equivalent factors (TEF) of PCDDs and PCDFs
.1 Two GC Column TEF Determination: Reanalyze sample extract on 60 meter SP-2330 column
.1 Concentrations of specified congeners calculated from analysis done on DB-5 column
.2 Concentrations of specified congeners calculated from analysis done on SP-2330 column w/different GC/MS conditions
Note: Confirmation and quantification of 2,3,7,8-TCDD done on either column as long as Section 8.1.2 criteria met
.3 GC peak must meet criteria of Sections 7.8.4.2, 7.8.4.3, and/or 7.8 4.1.1 RRTs of 2,3,7,8-sub congeners w/no carbon-labeled analogues referred to w/in 0.006 RRT units of carbon-labeled std.
Stop

METHOD 8315

DETERMINATION OF CARBONYL COMPOUNDS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

1.0 SCOPE AND APPLICATION

1.1 This method provides procedures for the determination of free carbonyl compounds in various matrices by derivatization with 2,4-dinitrophenylhydrazine (DNPH). The method utilizes high performance liquid chromatography (HPLC) with ultraviolet/visible (UV/vis) detection to identify and quantitate the target analytes using two different sets of conditions: Option 1 and Option 2. Option 1 has been shown to perform well for one set of target analytes for aqueous samples, soil or waste samples, and stack samples collected by Method 0011. Option 2 has been shown to work well for another set of target analytes in indoor air samples collected by Method 0100. The two sets of target analytes overlap for some compounds. Refer to the Analysis Option listed in the following table to determine which analytes may be analyzed by which option. The following compounds may be determined by this method:

Compound Name	CAS No.[a]	Analysis Option[b]
Acetaldehyde	75-07-0	1,2
Acetone	67-64-1	2
Acrolein	107-02-8	2
Benzaldehyde	100-52-7	2
Butanal (butyraldehyde)	123-72-8	1,2
Crotonaldehyde	123-73-9	1,2
Cyclohexanone	108-94-1	1
Decanal	112-31-2	1
2,5-Dimethylbenzaldehyde	5779-94-2	2
Formaldehyde	50-00-0	1,2
Heptanal	111-71-7	1
Hexanal (hexaldehyde)	66-25-1	1,2
Isovaleraldehyde	590-86-3	2
Nonanal	124-19-6	1
Octanal	124-13-0	1
Pentanal (valeraldehyde)	110-62-3	1,2
Propanal (propionaldehyde)	123-38-6	1,2
m-Tolualdehyde	620-23-5	2
o-Tolualdehyde	529-20-4	2
p-Tolualdehyde	104-87-0	2

[a] Chemical Abstract Services Registry Number.

[b] This list of target analytes contains an overlapping list of compounds that have been evaluated using modifications of the analysis. Refer to the respective option number when choosing the appropriate analysis technique for a particular compound.

1.2 The Option 1 method detection limits (MDL) are listed in Tables 1 and 2. The sensitivity data for sampling and analysis using Method 0100 (Option 2) are given in Table 3. The MDL for a specific sample may differ from that listed, depending upon the nature of interferences in the sample matrix and the amount of sample used in the procedure.

1.3 The extraction procedure for solid samples is similar to that specified in Method 1311[1]. Thus, a single sample may be extracted to measure the analytes included in the scope of other appropriate methods. The analyst is allowed the flexibility to select chromatographic conditions appropriate for the simultaneous measurement of combinations of these analytes.

1.4 When this method is used to analyze unfamiliar sample matrices, compound identification should be supported by at least one additional qualitative technique. A gas chromatograph/mass spectrometer (GC/MS) may be used for the qualitative confirmation of results for the target analytes, using the extract produced by this method.

1.5 This method is restricted to use by, or under the supervision of, analysts experienced in the use of chromatography and in the interpretation of chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method, using the procedure described in Section 7.0.

2.0 SUMMARY OF METHOD

2.1 Liquid and Solid Samples (Option 1)

2.1.1 For wastes comprised of solids, or for aqueous wastes containing significant amounts of solid material, the aqueous phase, if any, is separated from the solid phase and stored for later analysis. If necessary, the particle size of the solids in the waste is reduced. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A special extractor vessel is used when testing for volatiles. Following extraction, the aqueous extract is separated from the solid phase by filtration employing 0.6 to 0.8 μm glass fiber filter.

2.1.2 If compatible (i.e., multiple phases will not form on combination), the initial aqueous phase of the waste is added to the aqueous extract, and these liquids are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

2.1.3 A measured volume of aqueous sample (approx. 100 mL) or an appropriate amount of solids extract (approx. 25 g), is buffered to pH 3 and derivatized with 2,4-dinitrophenylhydrazine (DNPH), using either the liquid-solid or a liquid-liquid extraction option. If the liquid-solid option is used, the derivative is extracted using solid sorbent cartridges, followed by elution with ethanol. If the liquid-liquid option is used, the derivative is extracted from the sample with three (3) portions of methylene chloride. The methylene chloride extracts are

concentrated using the Kuderna-Danish (K-D) procedure and exchanged with acetonitrile prior to HPLC analysis. Liquid chromatographic conditions are described which permit the separation and measurement of various carbonyl compounds in the extract by absorbance detection at 360 nm.

2.1.4 If formaldehyde is the only analyte of interest, the aqueous sample or solids extract should be buffered to pH 5.0 to minimize artifact formaldehyde formation.

2.2 Stack Gas Samples Collected by Method 0011 (Option 1) - The entire sample returned to the laboratory is extracted with methylene chloride and the methylene chloride extract is brought up to a known volume. An aliquot of the methylene chloride extract is solvent exchanged and concentrated or diluted as necessary. Liquid chromatographic conditions are described that permit the separation and measurement of various carbonyl compounds in the extract by absorbance detection at 360 nm.

2.3 Indoor Air Samples by Method 0100 (Option 2) - The sample cartridges are returned to the laboratory and backflushed with acetonitrile into a 5 mL volumetric flask. The eluate is brought up to volume with more acetonitrile. Two (2) aliquots of the acetonitrile extract are pipetted into two (2) sample vials having Teflon-lined septa. Liquid chromatographic conditions are described that permit the separation and measurement of the various carbonyl compounds in the extract by absorbance detection at 360 nm.

3.0 INTERFERENCES

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by analyzing laboratory reagent blanks as described in Section 8.5.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water, and rinses with tap water and organic-free reagent water. It should then be drained, dried, and heated in a laboratory oven at 130°C for several hours before use. Solvent rinses with acetonitrile may be substituted for the oven heating. After drying and cooling, glassware should be stored in a clean environment to prevent any accumulation of dust or other contaminants.

NOTE: Do not use acetone or methanol. These solvents react with DNPH to form interfering compounds.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all glass systems may be required.

3.1.3 Polyethylene gloves must be worn when handling the silica gel cartridges to reduce the possibility of contamination.

3.2 Formaldehyde contamination of the DNPH reagent is a frequently encountered problem due to its widespread occurrence in the environment. The DNPH reagent in Option 2 must be purified by multiple recrystallizations in UV-grade acetonitrile. Recrystallization is accomplished, at 40-60°C, by slow evaporation of the solvent to maximize crystal size. The purified DNPH crystals are stored under UV-grade acetonitrile until use. Impurity levels of carbonyl compounds in the DNPH are determined prior to the analysis of the samples and should be less than 25 mg/L. Refer to Appendix A for the recrystallization procedure.

3.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the matrix being sampled. Although the HPLC conditions described allow for a resolution of the specific compounds covered by this method, other matrix components may interfere. If interferences occur in subsequent samples, some additional cleanup may be necessary.

3.4 In Option 1, acetaldehyde is generated during the derivatization step if ethanol is present in the sample. This background will impair the measurement of acetaldehyde at levels below 0.5 ppm (500 ppb).

3.5 For Option 2, at the stated two column analysis conditions, the identification and quantitation of butyraldehyde may be difficult due to coelution with isobutyraldehyde and methyl ethyl ketone. Precautions should be taken and adjustment of the analysis conditions should be done, if necessary, to avoid potential problems.

4.0 APPARATUS AND MATERIALS

4.1 High performance liquid chromatograph (modular)

4.1.1 Pumping system - Gradient, with constant flow control capable of 1.50 mL/min.

4.1.2 High pressure injection valve with 20 µL loop.

4.1.3 Column - 250 mm x 4.6 mm ID, 5 µm particle size, C18 (Zorbax or equivalent).

4.1.4 Absorbance detector - 360 nm.

4.1.5 Strip-chart recorder compatible with detector - Use of a data system for measuring peak areas and retention times is recommended.

4.1.6 Helium Gas - for degassing mobile phase solvents. (Options 1 and 2)

4.1.7 Mobile Phase Reservoirs and Suction Filtration Apparatus - For holding and filtering HPLC mobile phase. Filtering system should be all glass and Teflon and use a 0.22 µm polyester membrane filter. (Option 2)

4.1.8 Syringes - for HPLC injection loop loading, with capacity at least four times the loop volume.

4.2 Apparatus and Materials for Option 1

4.2.1 Reaction vessel - 250 mL Florence flask.

4.2.2 Separatory funnel - 250 mL, with Teflon stopcock.

4.2.3 Kuderna-Danish (K-D) apparatus.

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

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

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

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

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

4.2.4 Boiling chips - Solvent extracted with methylene chloride, approximately 10/40 mesh (silicon carbide or equivalent).

4.2.5 pH meter - Capable of measuring to the nearest 0.01 units.

4.2.6 Glass fiber filter paper - 1.2 μm pore size (Fisher Grade G4 or equivalent).

4.2.7 Solid sorbent cartridges - Packed with 2 g C18 (Baker or equivalent).

4.2.8 Vacuum manifold - Capable of simultaneous extraction of up to 12 samples (Supelco or equivalent).

4.2.9 Sample reservoirs - 60 mL capacity (Supelco or equivalent).

4.2.10 Pipet - Capable of accurately delivering 0.10 mL solution (Pipetman or equivalent).

4.2.11 Water bath - Heated, with concentric ring cover, capable of temperature control ($\pm$ 2°C). The bath should be used under a hood.

4.2.12 Sample shaker - Controlled temperature incubator ($\pm$ 2°C) with orbital shaking (Lab-Line Orbit Environ-Shaker Model 3527 or equivalent).

4.2.13 Syringes - 5 mL, 500 µL, 100 µL, (Luer-Lok or equivalent).

4.2.14 Syringe Filters - 0.45 µm filtration disks (Gelman Acrodisc 4438 or equivalent).

4.3 Apparatus and Materials for Option 2

4.3.1 Syringes - 10 mL, with Luer-Lok type adapter, used to backflush the sample cartridges by gravity feed.

4.3.2 Syringe Rack - made of an aluminum plate with adjustable legs on all four corners. Circular holes of a diameter slightly larger than the diameter of the 10 mL syringes are drilled through the plate to allow batch processing of cartridges for cleaning, coating, and sample elution. A plate (0.16 x 36 x 53 cm) with 45 holes in a 5x9 matrix is recommended. See Figure 2 in Method 0100.

4.4 Volumetric Flasks - 5 mL, 10 mL, and 250 or 500 mL.

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

4.6 Balance - Analytical, capable of accurately weighing to the nearest 0.0001 g.

4.7 Glass Funnels

4.8 Polyethylene Gloves - used to handle silica gel cartridges.

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 - Water in which an interferant is not observed at the method detection limit for the compounds of interest.

5.3 Formalin - Solution of formaldehyde (CH_2O) in organic-free reagent water, nominally 37.6 percent (w/w). Exact concentration will be determined for the stock solution in Section 5.7.1.1.

5.4 Aldehydes and ketones - analytical grade, used for preparation of DNPH derivative standards of target analytes other than formaldehyde. Refer to the target analyte list.

5.5 Option 1 Reagents

5.5.1 Methylene chloride, CH_2Cl_2 - HPLC grade or equivalent.

5.5.2 Acetonitrile, CH_3CN - HPLC grade or equivalent.

5.5.3 Sodium hydroxide solutions, NaOH, 1.0 N and 5 N.

5.5.4 Sodium chloride, NaCl, saturated solution - Prepare by dissolving an excess of the reagent grade solid in organic-free reagent water.

5.5.5 Sodium sulfite solution, Na_2SO_3, 0.1 M.

5.5.6 Sodium sulfate, Na_2SO_4 - granular, anhydrous.

5.5.7 Citric Acid, $C_8H_8O_7$, 1.0 M solution.

5.5.8 Sodium Citrate, $C_6H_5Na_3O_7.2H_2O$, 1.0 M trisodium salt dihydrate solution.

5.5.9 Acetic acid (glacial), CH_3CO_2H.

5.5.10 Sodium acetate, CH_3CO_2Na.

5.5.11 Hydrochloric Acid, HCl, 0.1 N.

5.5.12 Citrate buffer, 1 M, pH 3 - Prepare by adding 80 mL of 1 M citric acid solution to 20 mL of 1 M sodium citrate solution. Mix thoroughly. Adjust pH with NaOH or HCl as needed.

5.5.13 pH 5.0 Acetate buffer (5M) - Formaldehyde analysis only. Prepared by adding 40 mL 5M acetic acid solution to 60 mL 5M sodium acetate solution. Mix thoroughly. Adjust pH with NaOH or HCl as needed.

5.5.14 2,4-Dinitrophenylhydrazine, $2,4\text{-}(O_2N)_2C_6H_3]NHNH_2$, (DNPH), 70% in organic-free reagent water (W/W).

5.5.14.1 DNPH (3.00 mg/mL) - Dissolve 428.7 mg of 70% (w/w) DNPH solution in 100 mL acetonitrile.

5.5.15 Extraction fluid for Option 1 - Dilute 64.3 mL of 1.0 N NaOH and 5.7 mL glacial acetic acid to 900 mL with organic-free reagent water. Dilute to 1 liter with organic-free reagent water. The pH should be 4.93 ± 0.02.

5.6 Option 2 Reagents

5.6.1 Acetonitrile, CH_3CN - UV grade.

5.6.2 2,4-Dinitrophenylhydrazine, $C_6H_6N_4O_4$, (DNPH) - recrystallize at least twice with UV grade acetonitrile using the procedure in Appendix A.

5.7 Stock Standard Solutions for Option 1

5.7.1 Stock formaldehyde (approximately 1000 mg/L) - Prepare by diluting an appropriate amount of the certified or standardized formaldehyde (approximately 265 μL) to 100 mL with organic-free reagent water. If a certified formaldehyde solution is not available or there is any question regarding the quality of a certified solution, the solution may be standardized using the procedure in Section 5.7.1.1.

5.7.1.1 Standardization of formaldehyde stock solution - Transfer a 25 mL aliquot of a 0.1 M Na_2SO_3 solution to a beaker and record the pH. Add a 25.0 mL aliquot of the formaldehyde stock solution (Section 5.18.1) and record the pH. Titrate this mixture back to the original pH using 0.1 N HCl. The formaldehyde concentration is calculated using the following equation:

$$\text{Concentration (mg/L)} = \frac{(30.03)(\text{N HCl})(\text{mL HCl})}{25.0 \text{ mL}}$$

where:

N HCl = Normality of HCl solution used (in milli-equivalents/mL) (1 mmole of HCl = 1 milli-equivalent of HCl)
mL HCl= mL of standardized HCl solution used
30.03 = Molecular of weight of formaldehyde (in mg/mmole)

5.7.2 Stock aldehyde(s) and ketone(s) - Prepare by adding an appropriate amount of the pure material to 90 mL of acetonitrile and dilute to 100 mL, to give a final concentration of 1000 mg/L.

5.8 Stock Standard Solutions for Option 2

5.8.1 Preparation of the DNPH Derivatives for HPLC analysis

5.8.1.1 To a portion of the recrystallized DNPH, add sufficient 2N HCl to obtain an approximately saturated solution. Add to this solution the target analyte in molar excess of the DNPH. Filter the DNPH derivative precipitate, wash it with 2N HCl, wash it again with water, and allow it to dry in air.

5.8.1.2 Check the purity of the DNPH derivative by melting point determination or HPLC analysis. If the impurity level is not acceptable, recrystallize the derivative in acetonitrile. Repeat the purity check and recrystallization as necessary until 99% purity is achieved.

5.8.2 Preparation of DNPH Derivative Standards and Calibration Standards for HPLC analysis

5.8.2.1 Stock Standard Solutions - Prepare individual stock standard solutions for each of the target analyte DNPH derivatives by dissolving accurately weighed amounts in

acetonitrile. Individual stock solutions of approximately 100 mg/L may be prepared by dissolving 0.010 g of the solid derivative in 100 mL of acetonitrile.

5.8.2.2 Secondary Dilution Standard(s) - Using the individual stock standard solutions, prepare secondary dilution standards in acetonitrile containing the DNPH derivatives from the target analytes mixed together. Solutions of 100 µg/L may be prepared by placing 100 µL of a 100 mg/L solution in a 100 mL volumetric flask and diluting to the mark with acetonitrile.

5.8.2.3 Calibration Standards - Prepare a working calibration standard mix from the secondary dilution standard, using the mixture of DNPH derivatives at concentrations of 0.5-2.0 µg/L (which spans the concentration of interest for most indoor air work). The concentration of the DNPH derivative in the standard mix solutions may need to be adjusted to reflect relative concentration distribution in a real sample.

5.9 Standard Storage - Store all standard solutions at 4°C in a glass vial with a Teflon-lined cap, with minimum headspace, and in the dark. They should be stable for about 6 weeks. All standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.10 Calibration Standards

5.10.1 Prepare calibration solutions at a minimum of 5 concentrations for each analyte of interest in organic-free reagent water (or acetonitrile for Option 2) from the stock standard solution. The lowest concentration of each analyte should be at, or just above, the MDLs listed in Tables 1 or 2. The other concentrations of the calibration curve should correspond to the expected range of concentrations found in real samples.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

6.2 Samples must be refrigerated at 4°C. Aqueous samples must be derivatized and extracted within 3 days of sample collection. Higher molecular weight aldehydes (heptanal to decanal) evidenced losses greater than 50% in a liquid matrix over a 3 day holding time. Accordingly, liquid samples should be derivatized and extracted within 24 hours of sample collection. Likewise, the holding times of extracts of solid samples should be kept at a minimum. All derivatized sample extracts should be analyzed within 3 days after preparation.

6.3 Samples collected by Methods 0011 or 0100 must be refrigerated at 4°C. It is recommended that samples be extracted and analyzed within 30 days of collection.

7.0 PROCEDURE

7.1 Extraction of Solid Samples (Option 1)

7.1.1 All solid samples should be made as homogeneous as possible by stirring and removal of sticks, rocks, and other extraneous material. When the sample is not dry, determine the dry weight of the sample, using a representative aliquot.

7.1.1.1 Determination of dry weight - In certain cases, sample results are desired based on a dry weight basis. When such data are desired or required, a portion of sample for dry weight 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.

7.1.1.2 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:

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

7.1.2 Measure 25 g of solid into a 500 mL bottle with a Teflon lined screw cap or crimp top, and add 500 mL of extraction fluid (Section 5.5.15). Extract the solid by rotating the bottle at approximately 30 rpm for 18 hours. Filter the extract through glass fiber filter paper and store in sealed bottles at 4°C. Each mL of extract represents 0.050 g solid. Smaller quantities of solid sample may be used with correspondingly reduced volumes of extraction fluid maintaining the 1:20 mass to volume ratio.

7.2 Cleanup and Separation (Option 1)

7.2.1 Cleanup procedures may not be necessary for a relatively clean sample matrix. The cleanup procedures recommended in this method have been used for the analysis of various sample types. If particular samples demand the use of an alternative cleanup procedure, the analyst must determine the elution profile and demonstrate that the recovery of formaldehyde from a spiked sample is greater than 85%. Recovery may be lower for samples which form emulsions.

7.2.2 If the sample is not clear, or the complexity is unknown, the entire sample should be centrifuged at 2500 rpm for 10 minutes. Decant the supernatant liquid from the centrifuge bottle, and filter through glass fiber filter paper into a container which can be tightly sealed.

7.3 Derivatization (Option 1)

7.3.1 For aqueous samples, measure an aliquot of sample which is appropriate to the anticipated analyte concentration range (nominally 100 mL). Quantitatively transfer the sample aliquot to the reaction vessel (Section 4.2).

7.3.2 For solid samples, 1 to 10 mL of extract (Section 7.1) will usually be required. The amount used for a particular sample must be determined through preliminary experiments.

NOTE: In cases where the selected sample or extract volume is less than 100 mL, the total volume of the aqueous layer should be adjusted to 100 mL with organic-free reagent water. Record original sample volume prior to dilution.

7.3.3 Derivatization and extraction of the target analytes may be accomplished using the liquid-solid (Section 7.3.4) or liquid-liquid (Section 7.3.5) procedures.

7.3.4 Liquid-Solid Derivatization and Extraction

7.3.4.1 For analytes other than formaldehyde, add 4 mL of citrate buffer and adjust the pH to 3.0 $\pm$ 0.1 with 6 M HCl or 6 M NaOH. Add 6 mL of DNPH reagent, seal the container, and place in a heated (40°C), orbital shaker (Section 4.2.12) for 1 hour. Adjust the agitation to produce a gentle swirling of the reaction solution.

7.3.4.2 If formaldehyde is the only analyte of interest, add 4 mL acetate buffer and adjust pH to 5.0 $\pm$ 0.1 with 6M HCl or 6M NaOH. Add 6 mL of DNPH reagent, seal the container, and place in a heated (40°C), orbital shaker (Section 4.2.12) for 1 hour. Adjust the agitation to produce a gentle swirling of the reaction solution.

7.3.4.3 Assemble the vacuum manifold and connect to a water aspirator or vacuum pump. Attach 2 g sorbent cartridge to the vacuum manifold. Condition each cartridge by passing 10 mL dilute citrate buffer (10 mL of 1 M citrate buffer dissolved in 250 mL of organic-free reagent water) through each sorbent cartridge.

7.3.4.4 Remove the reaction vessel from the shaker immediately at the end of the one hour reaction period and add 10 mL saturated NaCl solution to the vessel.

7.3.4.5 Add the reaction solution to the sorbent cartridge and apply a vacuum so that the solution is drawn through the cartridge at a rate of 3 to 5 mL/min. Continue applying the vacuum for about 1 minute after the liquid sample has passed through the cartridge.

7.3.4.6 While maintaining vacuum conditions described in Section 7.3.4.4, elute each cartridge train with approximately 9 mL of acetonitrile directly into a 10 mL volumetric flask. Dilute the

solution to volume with acetonitrile , mix thoroughly, and place in a tightly sealed vial until analyzed.

NOTE: Because this method uses an excess of DNPH, the cartridges will remain a yellow color after completion of Section 7.3.4.5. The presence of this color is not indicative of non-recovery of the analyte derivatives.

7.3.5 Liquid-Liquid Derivatization and Extraction

7.3.5.1 For analytes other than formaldehyde, add 4 mL of citrate buffer and adjust the pH to 3.0 ± 0.1 with 6 M HCl or 6 M NaOH. Add 6 mL of DNPH reagent, seal the container, and place in a heated (40°C), orbital shaker for 1 hour. Adjust the agitation to produce a gentle swirling of the reaction solution.

7.3.5.2 If formaldehyde is the only analyte of interest, add 4 mL acetate buffer and adjust pH to 5.0 ± 0.1 with 6M HCl or 6M NaOH. Add 6 mL of DNPH reagent, seal the container, and place in a heated (40°C), orbital shaker for 1 hour. Adjust the agitation to produce a gentle swirling of the reaction solution.

7.3.5.3 Serially extract the solution with three 20 mL portions of methylene chloride using a 250 mL separatory funnel. If an emulsion forms upon extraction, remove the entire emulsion and centrifuge at 2000 rpm for 10 minutes. Separate the layers and proceed with the next extraction. Combine the methylene chloride layers in a 125 mL Erlenmeyer flask containing 5.0 grams of anhydrous sodium sulfate. Swirl contents to complete the extract drying process.

7.3.5.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporator flask. Pour the extract into the evaporator flask being careful to minimize transfer of sodium sulfate granules. Wash the Erlenmeyer flask with 30 mL of methylene chloride and add wash to the evaporator flask to complete quantitative transfer.

7.3.5.5 Add one to two clean boiling chips to the evaporative 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 5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.3.5.6 Prior to liquid chromatographic analysis, the extract solvent must be exchanged to acetonitrile . The analyst must ensure quantitative transfer of the extract concentrate. The exchange is performed as follows:

7.3.5.6.1 Remove the three-ball Snyder column and evaporator flask. Add 5 mL of acetonitrile , a new glass bead or boiling chip, and attach the micro-Snyder column to the concentrator tube. Concentrate the extract using 1 mL of acetonitrile to prewet the Snyder column. Place the K-D apparatus on the 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 concentration. 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 less than 5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

7.3.5.6.2 Remove the Snyder column and rinse the flask and its lower joint with 1-2 mL of acetonitrile and add to concentrator tube. Quantitatively transfer the sample to a 10 mL volumetric flask using a 5 mL syringe with an attached Acrodisk 0.45 μm filter cassette. Adjust the extract volume to 10 mL. Stopper the flask and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two (2) days, it should be transferred to a vial with a Teflon lined screw cap or crimp top. Proceed with HPLC chromatographic analysis if further cleanup is not required.

7.4 Extraction of Samples from Methods 0011 and 0100 (Options 1 and 2)

7.4.1 Stack gas samples collected by Method 0011 (Option 1)

7.4.1.1 Measure the volume of the aqueous phase of the sample prior to extraction (for moisture determination in case the volume was not measured in the field). Pour the sample into a separatory funnel and drain the methylene chloride into a volumetric flask.

7.4.1.2 Extract the aqueous solution with two or three aliquots of methylene chloride. Add the methylene chloride extracts to the volumetric flask.

7.4.1.3 Fill the volumetric flask to the line with methylene chloride. Mix well and remove an aliquot.

7.4.1.4 If high concentrations of formaldehyde are present, the extract can be diluted with mobile phase, otherwise the extract solvent must be exchanged as described in Section 7.3.5.5. If low concentrations of formaldehyde are present, the sample should be concentrated during the solvent exchange procedure.

7.4.1.5 Store the sample at 4°C. If the extract will be stored longer than two days, it should be transferred to a vial with a Teflon-lined screw cap, or a crimp top with a Teflon-lined septum. Proceed with HPLC chromatographic analysis if further cleanup is not required.

7.4.2 Ambient air samples collected by Method 0100 (Option 2)

7.4.2.1 The samples will be received by the laboratory in a friction-top can containing 2 to 5 cm of granular charcoal, and should be stored in this can, in a refrigerator, until analysis. Alternatively, the samples may also be stored alone in their individual glass containers. The time between sampling and analysis should not exceed 30 days.

7.4.2.2 Remove the sample cartridge from the labeled culture tube. Connect the sample cartridge (outlet or long end during sampling) to a clean syringe.

NOTE: The liquid flow during desorption should be in the opposite direction from the air flow during sample collection (i.e, backflush the cartridge).

7.4.2.3 Place the cartridge/syringe in the syringe rack.

7.4.2.4 Backflush the cartridge (gravity feed) by passing 6 mL of acetonitrile from the syringe through the cartridge to a graduated test tube, or to a 5 mL volumetric flask.

NOTE: A dry cartridge has an acetonitrile holdup volume slightly greater than 1 mL. The eluate flow may stop before the acetonitrile in the syringe is completely drained into the cartridge because of air trapped between the cartridge filter and the syringe Luer-Lok tip. If this happens, displace the trapped air with the acetonitrile in the syringe using a long-tip disposable Pasteur pipet.

7.4.2.5 Dilute to the 5 mL mark with acetonitrile. Label the flask with sample identification. Pipet two aliquots into sample vials having Teflon-lined septa.

7.4.2.6 Store the sample at 4°C. Proceed with HPLC chromatographic analysis of the first aliquot if further cleanup is not required. Store the second aliquot in the refrigerator until the results of the analysis of the first aliquot are complete and validated. The second aliquot can be used for confirmatory analysis, if necessary.

7.5 Chromatographic Conditions (Recommended):

7.5.1 Option 1 - For aqueous samples, soil or waste samples, and stack gas samples collected by Method 0011.

Column:	C18, 4.6 mm x 250 mm ID, 5 μm particle size
Mobile Phase Gradient:	70%/30% acetonitrile/water (v/v), hold for 20 min.
	70%/30% acetonitrile/water to 100% acetonitrile in 15 min.
	100% acetonitrile for 15 min.
Flow Rate:	1.2 mL/min
Detector:	Ultraviolet, operated at 360 nm
Injection Volume:	20 μL

7.5.2 Option 2 - For ambient air samples collected by Method 0100.

Column:	Two HPLC columns, 4.6 mm x 250 mm ID, (Zorbax ODS, or equivalent) in series
Mobile Phase Gradient:	60%/40% CH_3CN/H_2O, hold for 0 min.
	60%/40% to 75%/25% CH_3CN/H_2O, linearly in 30 min.
	75%/25% to 100%/0% CH_3CN/H_2O, linearly in 20 min.
	100% CH_3CN for 5 minutes.
	100%/0% to 60%/40% CH_3CN/H_2O, linearly in 1 min.
	60%/40% CH_3CN/H_2O for 15 minutes.
Detector:	Ultraviolet, operated at 360 nm
Flow Rate:	1.0 mL/min
Sample Injection volume:	25 μL (suggested)

NOTE: For Options 1 and 2, analysts are advised to adjust their HPLC systems to optimize chromatographic conditions for their particular analytical needs. The separation of acrolein, acetone, and propionaldehyde should be a minimum criterion of the optimization in Option 2.

7.5.3 Filter and degas the mobile phase to remove dissolved gasses, using the following procedure:

7.5.3.1 Filter each solvent (water and acetonitrile) through a 0.22 μm polyester membrane filter, in an all glass and Teflon suction filtration apparatus.

7.5.3.2 Degas each filtered solution by purging with helium for 10-15 minutes (100 mL/min) or by heating to 60°C for 5-10 minutes in an Erlenmeyer flask covered with a watch glass. A constant back pressure restrictor (350 kPa) or 15-30 cm of 0.25 mm ID Teflon tubing should be placed after the detector to eliminate further mobile phase outgassing.

7.5.3.3 Place the mobile phase components in their respective HPLC solvent reservoirs, and program the gradient system according to the conditions listed in Section 7.5.2. Allow the system to pump for 20-30 minutes at a flow rate of 1.0 mL/min with

the initial solvent mixture ratio (60%/40% CH_3CN/H_2O). Display the detector output on a strip chart recorder or similar output device to establish a stable baseline.

7.6 Calibration

7.6.1 Establish liquid chromatographic operating conditions to produce a retention time similar to that indicated in Table 1 for the liquid-solid derivatization and extraction or in Table 2 for liquid-liquid derivatization and extraction. Suggested chromatographic conditions are provided in Section 7.5.

7.6.2 Process each calibration standard solution through derivatization and extraction, using the same procedure employed for sample processing (Sections 7.3.4 or 7.3.5).

7.6.3 Analyze a solvent blank to ensure that the system is clean and interference free.

NOTE: The samples and standards must be allowed to come to ambient temperature before analysis.

7.6.4 Analyze each processed calibration standard using the chromatographic conditions listed in Section 7.5, and tabulate peak area against calibration solution concentration in $\mu g/L$.

7.6.5 Tabulate the peak area along with standard concentration injected to determine the response factor (RF) for the analyte at each concentration (see Section 7.8.1 for equations). The percent relative standard deviation (%RSD) of the mean RF of the calibration standards should be no greater than $\pm$ 20 percent or a system check will have to be performed. If a calibration check after the system check does not meet the criteria, a recalibration will have to be performed. If the recalibration does not meet the established criteria, new calibration standards must be made.

7.6.6 The working calibration curve must be verified each day, before and after analyses are performed, by analyzing one or more calibration standards. The response obtained should fall within $\pm$ 15 percent of the initially established response or a system check will have to be performed. If a calibration check after the system check does not meet the criteria, the system must be recalibrated.

7.6.7 After 10 sample runs, or less, one of the calibration standards must be reanalyzed to ensure that the DNPH derivative response factors remain within $\pm$15% of the original calibration response factors.

7.7 Sample Analysis

7.7.1 Analyze samples by HPLC, using conditions established in Section 7.5. For analytes to be analyzed by Option 1, Tables 1 and 2 list the retention times and MDLs that were obtained under these conditions. For Option 2 analytes, refer to Figure 3 for the sample chromatogram.

7.7.2 If the peak area exceeds the linear range of the calibration curve, a smaller sample injection volume should be used. Alternatively, the final solution may be diluted with acetonitrile and reanalyzed.

7.7.3 After elution of the target analytes, calculate the concentration of analytes found in the samples using the equations found in Section 7.8 or the specific sampling method used.

7.7.4 If the peak area measurement is prevented by the presence of observed interferences, further cleanup is required.

7.8 Calculations

7.8.1 Calculate each response factor, mean response factor, and percent relative standard deviation as follows:

$$RF_i = \frac{\text{Concentration of standard injected, } \mu g/L}{\text{Area of signal}}$$

$$\text{Mean RF} = \overline{RF} = \frac{\sum RF_i}{N}$$

$$\%RSD = \frac{\sqrt{\Sigma\ (RF_i - \overline{RF})^2\ /N-1}}{\overline{RF}} \times 100\%$$

where:

$\overline{RF}$ = Mean response factor or mean of the response factors using the 5 calibration concentrations.
RF_i = Response factor for calibration standard i (i = 1-5).
%RSD = Percent relative standard deviation of the response factors.
N = Number of calibration standards.

7.8.2 Calculate the analyte concentrations in liquid samples as follows:

$$\text{Concentration of aldehydes in } \mu g/L = (\overline{RF})(\text{Area of signal})(100/V_s)$$

where:

$\overline{RF}$ = Mean response factor for a particular analyte.
V_s = Volume of sample in mL.

7.8.3 Calculate the analyte concentration in solid samples as follows:

Concentration of aldehydes in $\mu g/g = (\overline{RF})(\text{Area of signal})(20/ V_{ex})$

where:

$\overline{RF}$ = Mean response factor for a particular analyte.
V_{ex} = Volume of extraction fluid aliquot in mL .

7.8.4 Calculate the concentration of formaldehyde in stack gas samples (Method 0011) as follows: (Option 1)

7.8.4.1 Calculation of Total Formaldehyde: To determine the total formaldehyde in mg, use the following equation:

$$\text{Total mg formaldehyde} = C_d \times V \times DF \times \frac{\text{[g/mole formaldehyde]}}{\text{[g/mole DNPH derivative]}} \times 10^{-3} \text{ mg}/\mu g$$

where:

C_d = measured concentration of DNPH-formaldehyde derivative, mg/L
V = organic extract volume, mL
DF = dilution factor

7.8.4.2 Formaldehyde concentration in stack gas: Determine the formaldehyde concentration in the stack gas using the following equation:

$$C_f = K \text{ [total formaldehyde, mg]} / V_{m(std)}$$

where:

K = 35.31 ft^3/m^3, if $V_{m(std)}$ is expressed in English units
= 1.00 m^3/m^3, if $V_{m(std)}$ is expressed in metric units
$V_{m(std)}$ = volume of gas sample as measured by dry gas meter, corrected to standard conditions, dscm (dscf)

7.8.5 Calculation of the Concentration of Formaldehyde and Other Carbonyls from Indoor Air Sampling by Method 0100. (Option 2)

7.8.5.1 The concentration of target analyte "a" in air at standard conditions (25°C and 101.3 kPa), $Conc_{astd}$ in ng/L, may be calculated using the following equation:

$$Conc_a = \frac{(Area_a)(\overline{RF})(Vol_a)(MW_a)(1000 \text{ ng}/\mu g)}{(MW_d)(V_{TotStd})(1000 \text{ mL/L})} \times DF$$

where:

$\underline{Area}_a$ = Area of the sample peak for analyte "a".
$\overline{RF}$ = Mean response factor for analyte "a" from the calibration in µg/L. (See Section 7.8.1)
Vol_a = Total volume of the sample cartridge eluate in mL.
MW_a = Molecular weight of analyte "a" in g/mole.
MW_d = Molecular weight of the DNPH derivative of analyte "a" in g/mole.
V_{TotStd} = Total volume of air sampled converted to standard conditions in liters (L). (To calculate the concentration at sampling conditions use V_{tot}.)(See Section 9.1.3 of Method 0100)
DF = Dilution Factor for the sample cartridge eluate, if any. If there is no dilution, DF = 1.

7.8.5.2 The target analyte "a" concentration at standard conditions may be converted to parts per billion by volume, $Conc_a$ in ppbv, using the following equation:

$$Conc_a \text{ in ppbv} = \frac{(Conc_a)(22.4)}{(MW_a)}$$

where:

$Conc_a$ = Concentration of analyte "a" in ng/L.
22.4 = Ideal gas law volume (22.4 nL of gas = 1 nmole at standard conditions).
MW_a = Molecular weight of analyte "a" in g/mole (or ng/nmole).

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures. Refer to Table 4 for QC acceptance limits derived from the interlaboratory method validation study on Method 8315.

9.0 METHOD PERFORMANCE

9.1 The MDLs for Option 1 listed in Table 1 were obtained using organic-free reagent water and liquid-solid extraction. The MDLs for Option 1 listed in Table 2 were obtained using organic-free reagent water and methylene chloride extraction. Results reported in Tables 1 and 2 were achieved using fortified reagent water volumes of 100 mL. Lower detection limits may be obtained using larger sample volumes.

9.1.1 Option 1 of this method has been tested for linearity of recovery from spiked organic-free reagent water and has been demonstrated to be applicable over the range 50-1000µg/L .

9.1.2 To generate the MDL and precision and accuracy data reported in this section, analytes were segregated into two spiking groups, A and B. Representative chromatograms using liquid-solid and liquid-liquid extraction are presented in Figures 1 (a and b) and 2 (a and b), respectively.

9.2 The Sensitivity of Option 2 sampling (Method 0100) and analysis is listed in Table 3.

9.3 Method 8315, Option 1, was tested by 12 laboratories using reagent water and ground waters spiked at six concentration levels over the range 30-2200 µg/L. Method accuracy and precision were found to be directly related to the concentration of the analyte and independent of the sample matrix. Mean recovery weighted linear regression equations, calculated as a function of spike concentration, as well as overall and single-analyst precision regression equations, calculated as functions of mean recovery, are presented in Table 5. These equations can be used to estimate mean recovery and precision at any concentration value within the range tested.

10.0 REFERENCES

1. Federal Register, Vol. 51, 40643-40652; November 7, 1986.

2. "OSHA Safety and Health Standards, General Industry", (29CRF1910). Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

11.0 SAFETY

11.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method[2]. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available.

11.2 Formaldehyde has been tentatively classified as a known or suspected, human or mammalian carcinogen.

TABLE 1.

OPTION 1 - METHOD DETECTION LIMITS[a] USING
LIQUID-SOLID EXTRACTION

Analyte	Retention Time (minutes)	MDL (μg/L)[a]
Formaldehyde	5.3	6.2
Acetaldehyde	7.4	43.7[b]
Propanal	11.7	11.0
Crotonaldehyde	16.1	5.9
Butanal	18.1	6.3
Cyclohexanone	27.6	5.8
Pentanal	28.4	15.3
Hexanal	34.1	10.7
Heptanal	35.0	10.0
Octanal	40.1	6.9
Nonanal	40.4	13.6
Decanal	44.1	4.4

[a] The method detection limit (MDL) is defined as the minimum concentration that can be measured with 99% confidence that the value is above background level. With the exception of acetaldehyde, all reported MDLs are based upon analyses of 6 to 8 replicate blanks spiked at 25 μg/L. The MDL was computed as follows:

$$MDL = t_{(N-1,\ 0.01)}(\text{Std. Dev.})$$

where:

$t_{(N-1,\ 0.01)}$ = The upper first percentile point of the t-distribution with n-1 degrees of freedom.

Std. Dev. = Standard deviation.

[b] The reported MDL is based upon analyses of 3 replicate, fortified blanks at 250 μg/L.

TABLE 2.

OPTION 1 - METHOD DETECTION LIMITS[a] USING
LIQUID-LIQUID EXTRACTION

Analyte	Retention Time (minutes)	MDL (μg/L)[a]
Formaldehyde	5.3	23.2
Acetaldehyde	7.4	110.2[b]
Propanal	11.7	8.4
Crotonaldehyde	16.1	5.9
Butanal	18.1	7.8
Cyclohexanone	27.6	6.9
Pentanal	28.4	13.4
Hexanal	34.1	12.4
Heptanal	35.0	6.6
Octanal	40.1	9.9
Nonanal	40.4	7.4
Decanal	44.1	13.1

[a] The method detection limit (MDL) is defined as the minimum concentration that can be measured with 99% confidence that the value is above background level. With the exception of acetaldehyde, all reported MDLs are based upon analyses of 6 to 8 replicate blanks spiked at 25 μg/L. The MDL was computed as follows:

$$MDL = t_{(N-1,\ 0.01)}(\text{Std. Dev.})$$

where:

$t_{(N-1,\ 0.01)}$ = The upper first percentile point of the t-distribution with n-1 degrees of freedom.
Std. Dev. = Standard deviation.

[b] The reported MDL is based upon analyses of 3 replicate, fortified blanks at 250 μg/L.

TABLE 3.

OPTION 2 - SENSITIVITY (ppb, v/v) OF SAMPLING AND ANALYSIS FOR CARBONYL COMPOUNDS IN AMBIENT AIR USING AN ADSORBENT CARTRIDGE FOLLOWED BY GRADIENT HPLC[a]

	Sample Volume (L)[b]									
Compound	10	20	30	40	50	100	200	300	400	500
Acetaldehyde	1.36	0.68	0.45	0.34	0.27	0.14	0.07	0.05	0.03	0.03
Acetone	1.28	0.64	0.43	0.32	0.26	0.13	0.06	0.04	0.03	0.03
Acrolein	1.29	0.65	0.43	0.32	0.26	0.13	0.06	0.04	0.03	0.03
Benzaldehyde	1.07	0.53	0.36	0.27	0.21	0.11	0.05	0.04	0.03	0.02
Butyraldehyde	1.21	0.61	0.40	0.30	0.24	0.12	0.06	0.04	0.03	0.02
Crotonaldehyde	1.22	0.61	0.41	0.31	0.24	0.12	0.06	0.04	0.03	0.02
2,5-Dimethyl-benzaldehyde	0.97	0.49	0.32	0.24	0.19	0.10	0.05	0.03	0.02	0.02
Formaldehyde	1.45	0.73	0.48	0.36	0.29	0.15	0.07	0.05	0.04	0.03
Hexanal	1.09	0.55	0.36	0.27	0.22	0.11	0.05	0.04	0.03	0.02
Isovaleraldehyde	1.15	0.57	0.38	0.29	0.23	0.11	0.06	0.04	0.03	0.02
Propionaldehyde	1.28	0.64	0.43	0.32	0.26	0.13	0.06	0.04	0.03	0.03
m-Tolualdehyde	1.02	0.51	0.34	0.25	0.20	0.10	0.05	0.03	0.03	0.02
o-Tolualdehyde	1.02	0.51	0.34	0.25	0.20	0.10	0.05	0.03	0.03	0.02
p-Tolualdehyde	1.02	0.51	0.34	0.25	0.20	0.10	0.05	0.03	0.03	0.02
Valeraldehyde	1.15	0.57	0.38	0.29	0.23	0.11	0.06	0.04	0.03	0.02

[a] The ppb values are measured at 1 atm and 25°C. The sample cartridge is eluted with 5 mL acetonitrile and 25 µL is injected into the HPLC. The maximum sampling flow through a DNPH-coated Sep-Pak is about 1.5 L/minute.

[b] A sample volume of 1000 L was also done. The results show a sensitivity of 0.01 ppb for all the target analytes.

TABLE 4.

PERFORMANCE-BASED QC ACCEPTANCE LIMITS CALCULATED USING THE COLLABORATIVE STUDY DATA

Analyte	Spike Concentration[a]	X^b	$S_R{}^c$	Acceptance Limits, %[d]
Formaldehyde	160	154	30.5	39-153
Propanal	160	148	22.4	50-134
Crotonaldehyde	160	160	34.8	35-165
Butanal	160	151	22.7	52-137
Cyclohexanone	160	169	39.2	32-179
Hexanal	160	151	34.6	30-159
Octanal	160	145	40.1	15-166
Decanal	160	153	40.0	21-171

[a] Spike concentration, µg/L.
[b] Mean recovery calculated using the reagent water, mean recovery, linear regression equation, µg/L.
[c] Overall standard deviation calculated using the reagent water, overall standard deviation linear regression equation, µg/L.
[d] Acceptance limits calculated as $(X \pm 3s_R)100$/spike concentration.

TABLE 5.

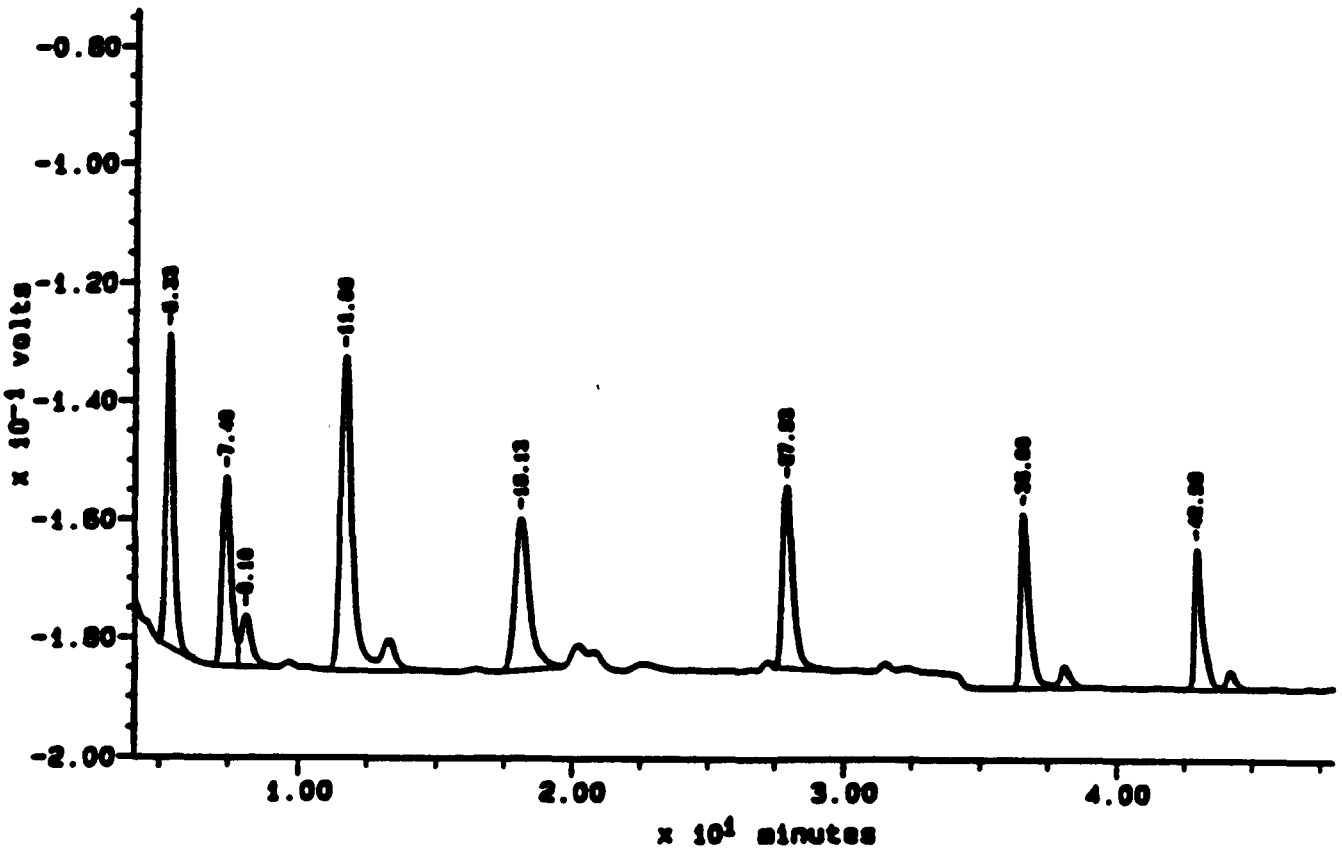
WEIGHTED LINEAR REGRESSION EQUATIONS FOR MEAN RECOVERY AND PRECISION (µg/L)

Analyte	Applicable Conc. Range		Reagent Water	Ground Water
Formaldehyde	39.2-2450	X	0.909C + 8.79	0.870C +14.84
		s_R	0.185X + 1.98[a]	0.177X + 13.85
		s_r	0.093X + 5.79	0.108X + 6.24
Propanal	31.9-2000	X	0.858C + 10.49	0.892C + 22.22
		s_R	0.140X + 1.63	0.180X + 12.37
		s_r	0.056X + 2.76	0.146X + 2.08[a]
Crotonaldehyde	32.4-2030	X	0.975C + 4.36	0.971C + 2.94
		s_R	0.185X + 5.15	0.157X + 6.09
		s_r	0.096X + 1.85	0.119X - 2.27
Butanal	35.4-2220	X	0.902C + 6.65	0.925C + 12.71
		s_R	0.149X + 0.21	0.140X + 6.89
		s_r	0.086X - 0.71	0.108X - 1.63[a]
Cyclohexanone	31.6-1970	X	0.962C + 14.97	0.946C + 28.95
		s_R	0.204X + 4.73[a]	0.345X + 5.02
		s_r	0.187X + 3.46	0.123X + 7.64
Hexanal	34.1-2130	X	0.844C + 15.81	0.926C + 9.16
		s_R	0.169X + 9.07	0.132X + 8.31
		s_r	0.098X + 0.37[a]	0.074X - 0.40[a]
Octanal	32.9-2050	X	0.856C + 7.88	0.914C + 13.09
		s_R	0.200X + 11.17	0.097X + 12.41
		s_r	0.092X + 1.71[a]	0.039X + 1.14
Decanal	33.2-2080	X	0.883C + 12.00	0.908C + 6.46
		s_R	0.225X + 5.52	0.153X + 2.23
		s_r	0.088X + 2.28[a]	0.052X + 0.37

[a] COD_w < 0.50. Variance is not constant over concentration range.
X Mean recovery, µg/L, exclusive of outliers.
s_R Overall standard deviation, µg/L, exclusive of outliers.
s_r Single-analyst standard deviation, µg/L, exclusive of outliers.

FIGURE 1a.

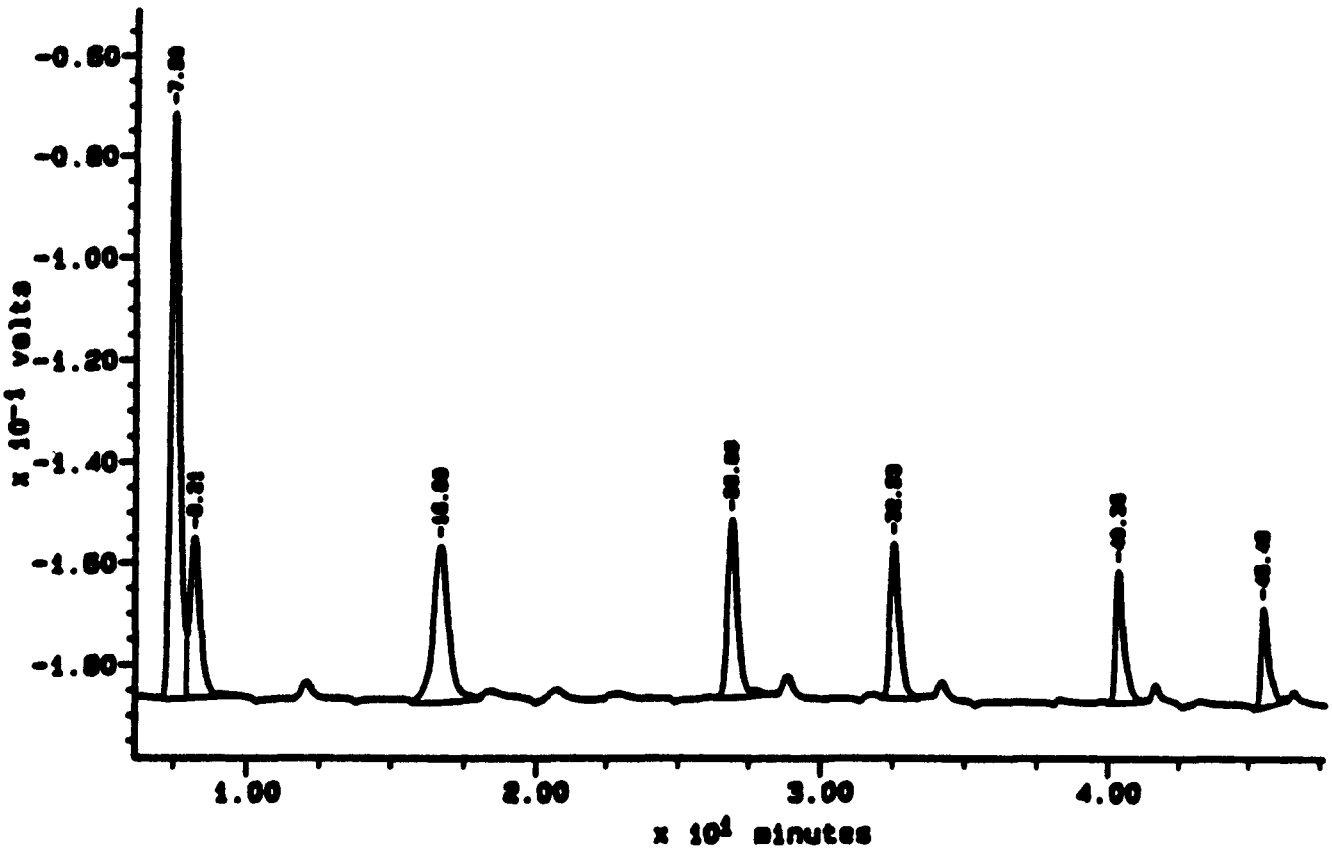
OPTION 2 - LIQUID-SOLID PROCEDURAL STANDARD OF GROUP A ANALYTES AT 625 µg/L



Retention Time (minutes)	Analyte Derivative
5.33	Formaldehyde
11.68	Propanal
18.13	Butanal
27.93	Cyclohexanone
36.60	Heptanal
42.99	Nonanal

FIGURE 1b.

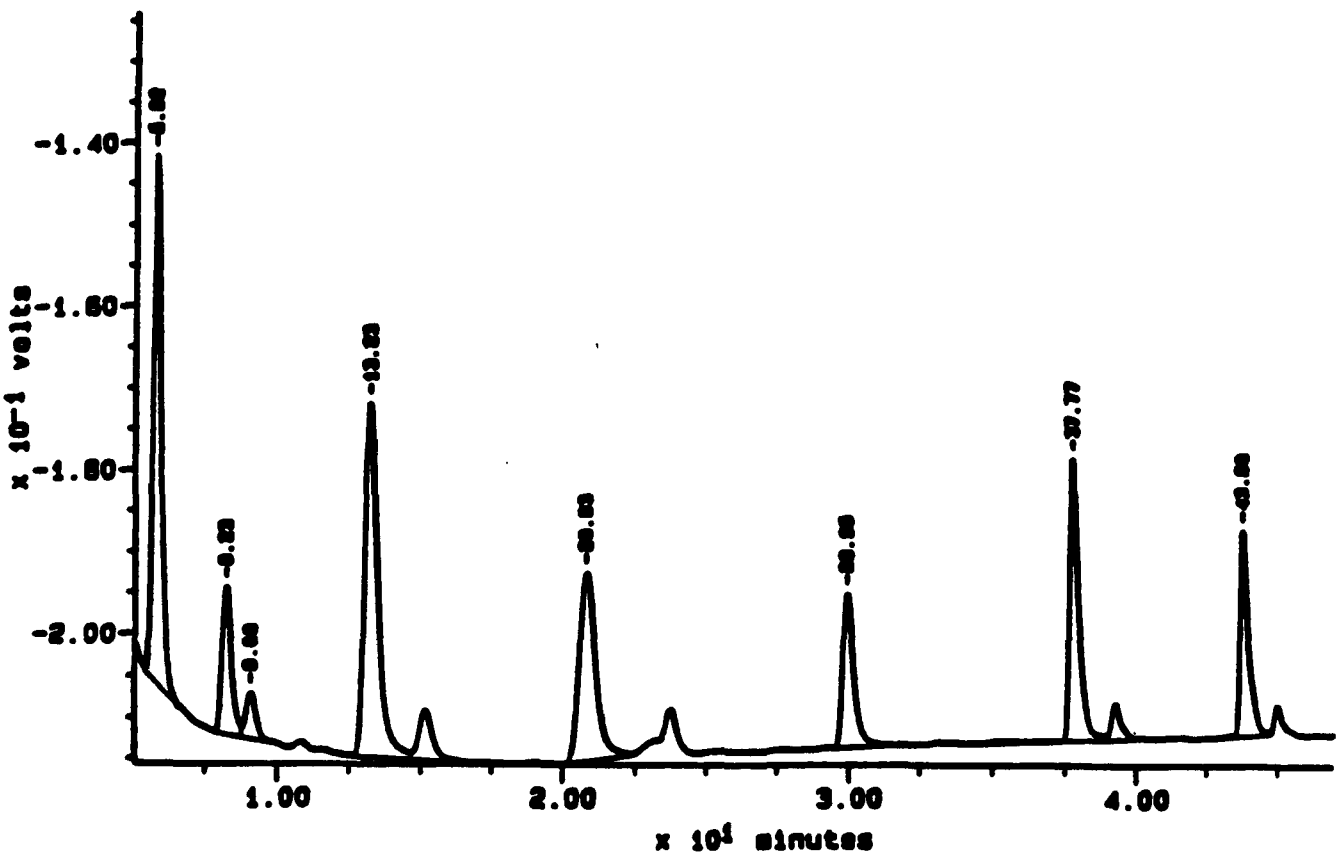
OPTION 1 - LIQUID-SOLID PROCEDURAL STANDARD OF GROUP B ANALYTES AT 625 µg/L



Retention Time (minutes)	Analyte Derivative
7.50	Acetaldehyde
16.68	Crotonaldehyde
26.88	Pentanal
32.53	Hexanal
40.36	Octanal
45.49	Decanal

FIGURE 2a.

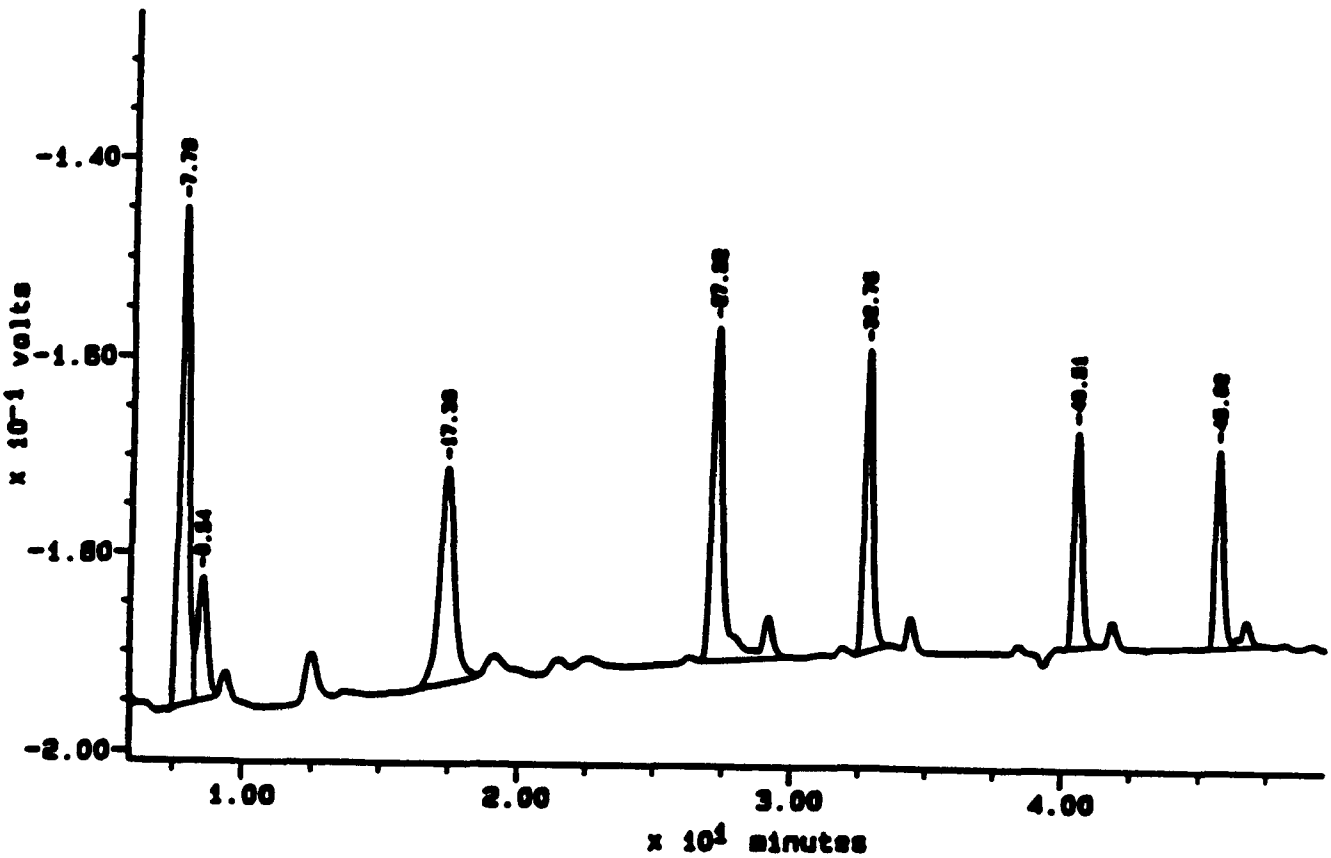
OPTION 1 - LIQUID-LIQUID PROCEDURAL STANDARD OF GROUP A ANALYTES AT 625 µg/L



Retention Time (minutes)	Analyte Derivative
5.82	Formaldehyde
13.23	Propanal
20.83	Butanal
29.95	Cyclohexanone
37.77	Heptanal
43.80	Nonanal

FIGURE 2b.

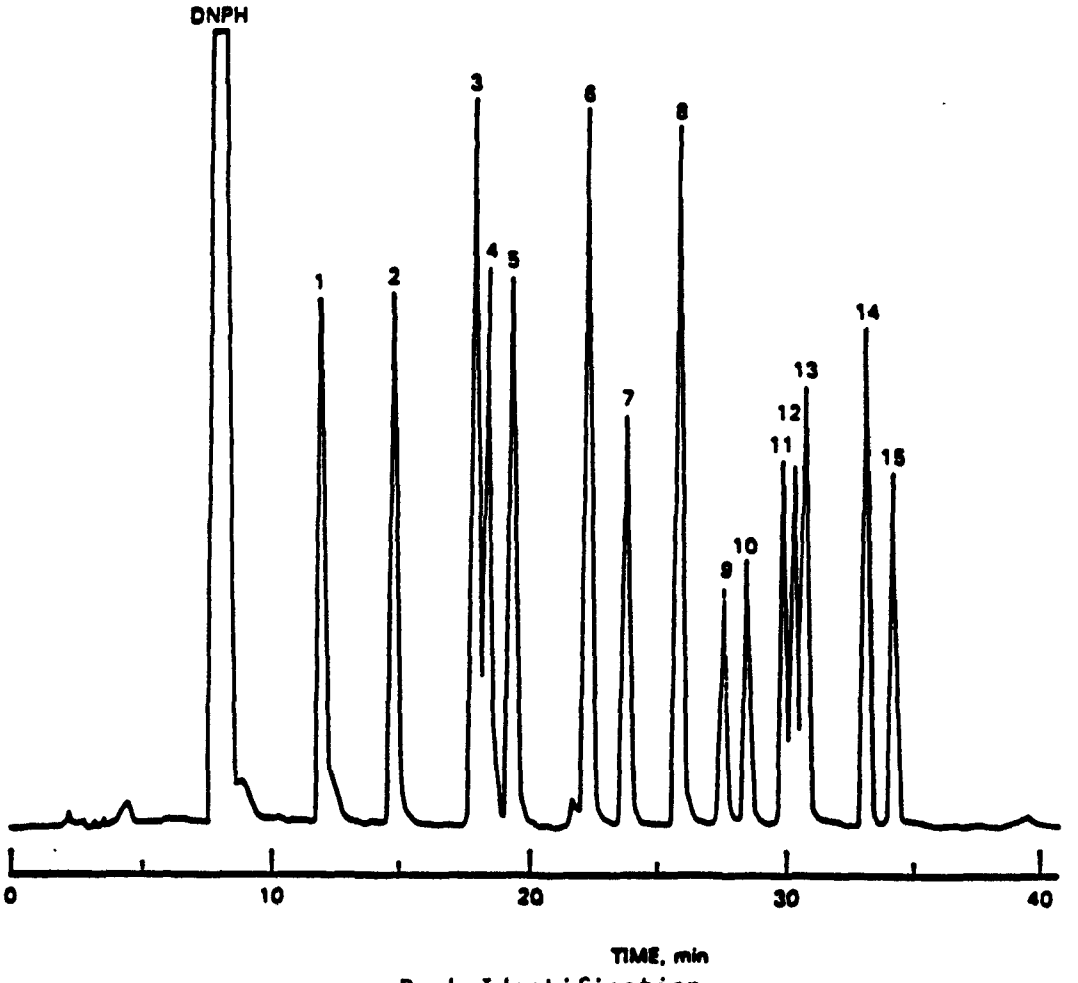
OPTION 1 - LIQUID-LIQUID PROCEDURAL STANDARD OF GROUP B ANALYTES AT 625 µg/L



Retention Time (minutes)	Analyte Derivative
7.79	Acetaldehyde
17.38	Crotonaldehyde
27.22	Pentanal
32.76	Hexanal
40.51	Octanal
45.62	Decanal

FIGURE 3.

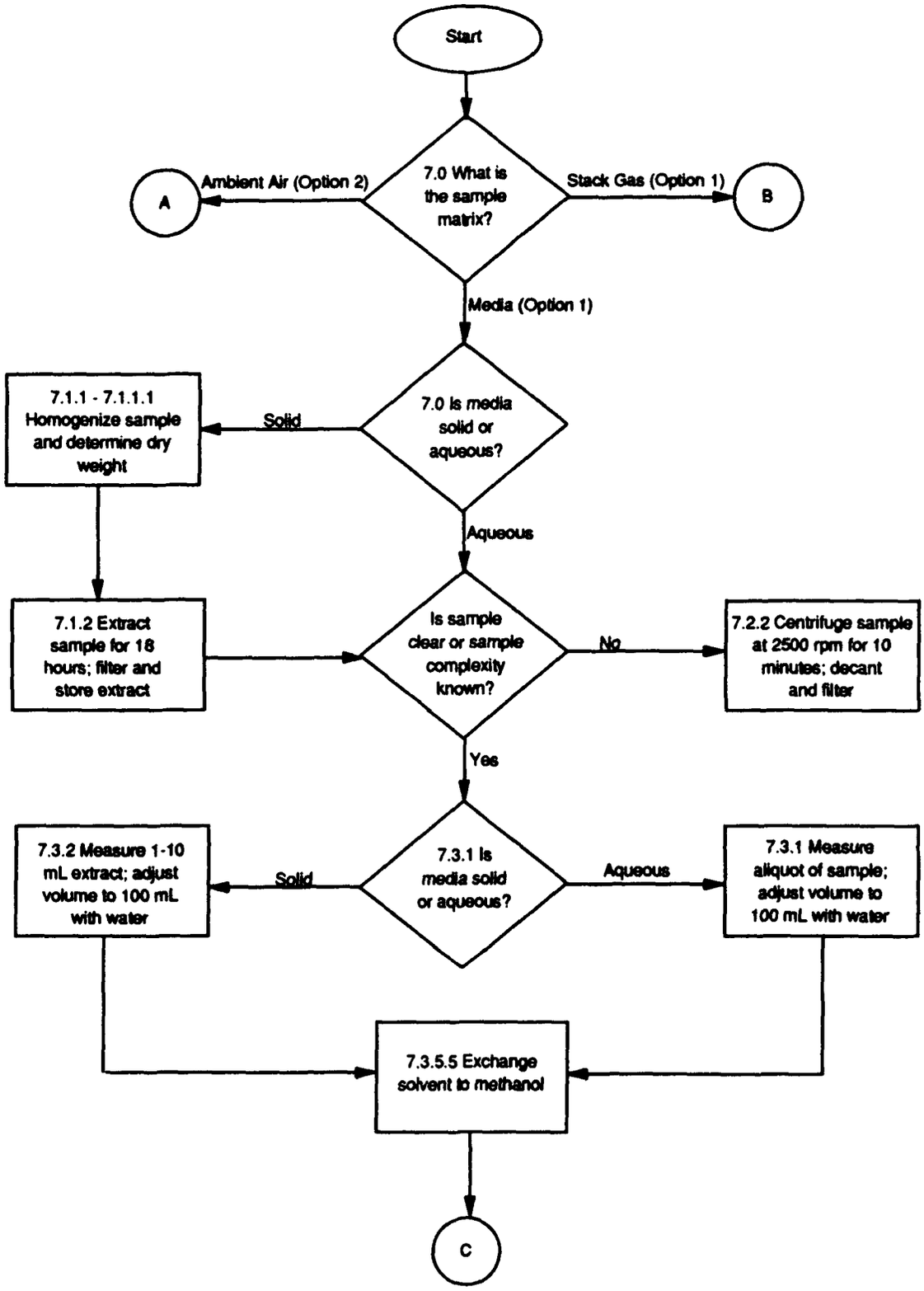
OPTION 2 - CHROMATOGRAPHIC SEPARATION OF THE DNPH DERIVATIVES OF 15 CARBONYL COMPOUNDS

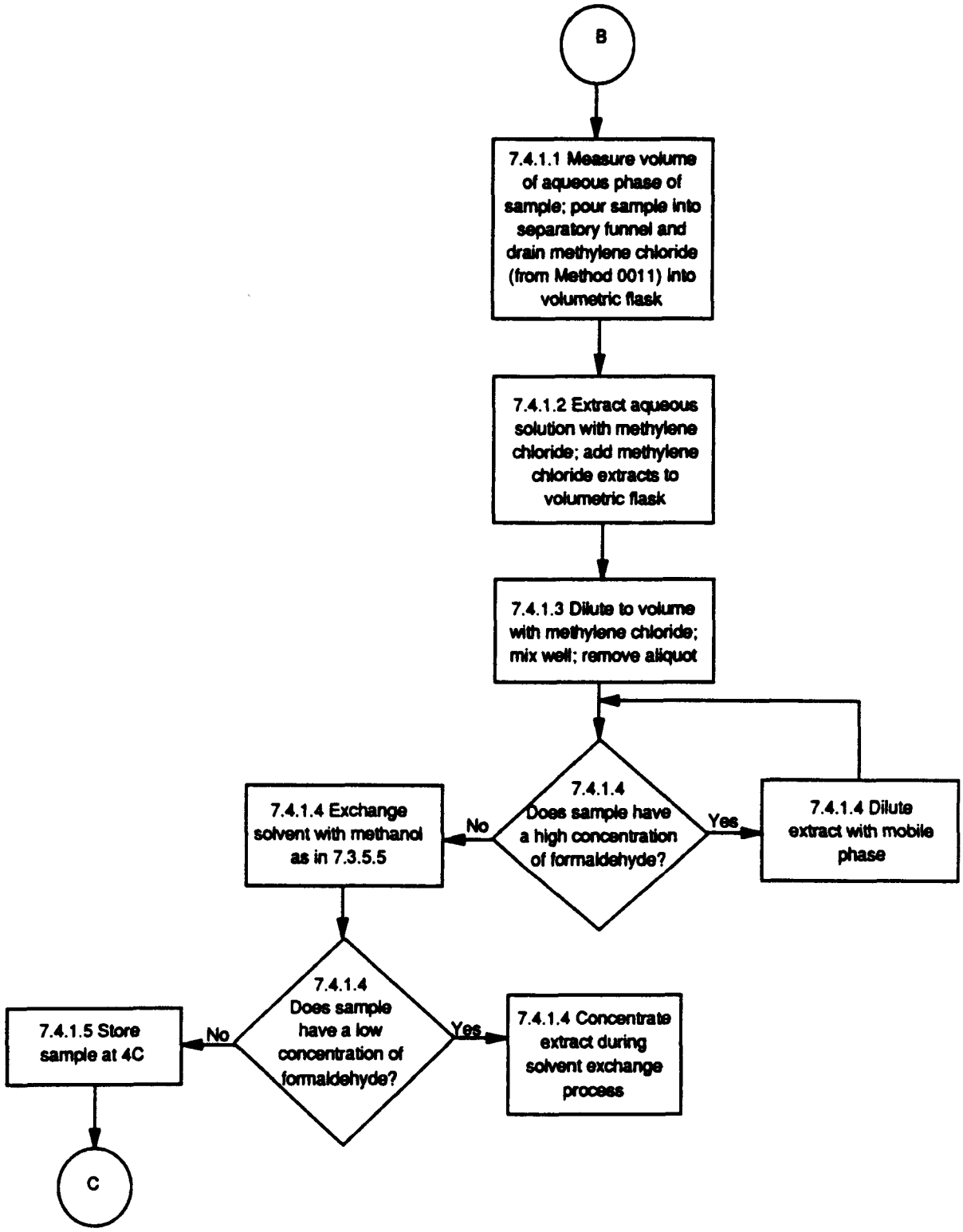


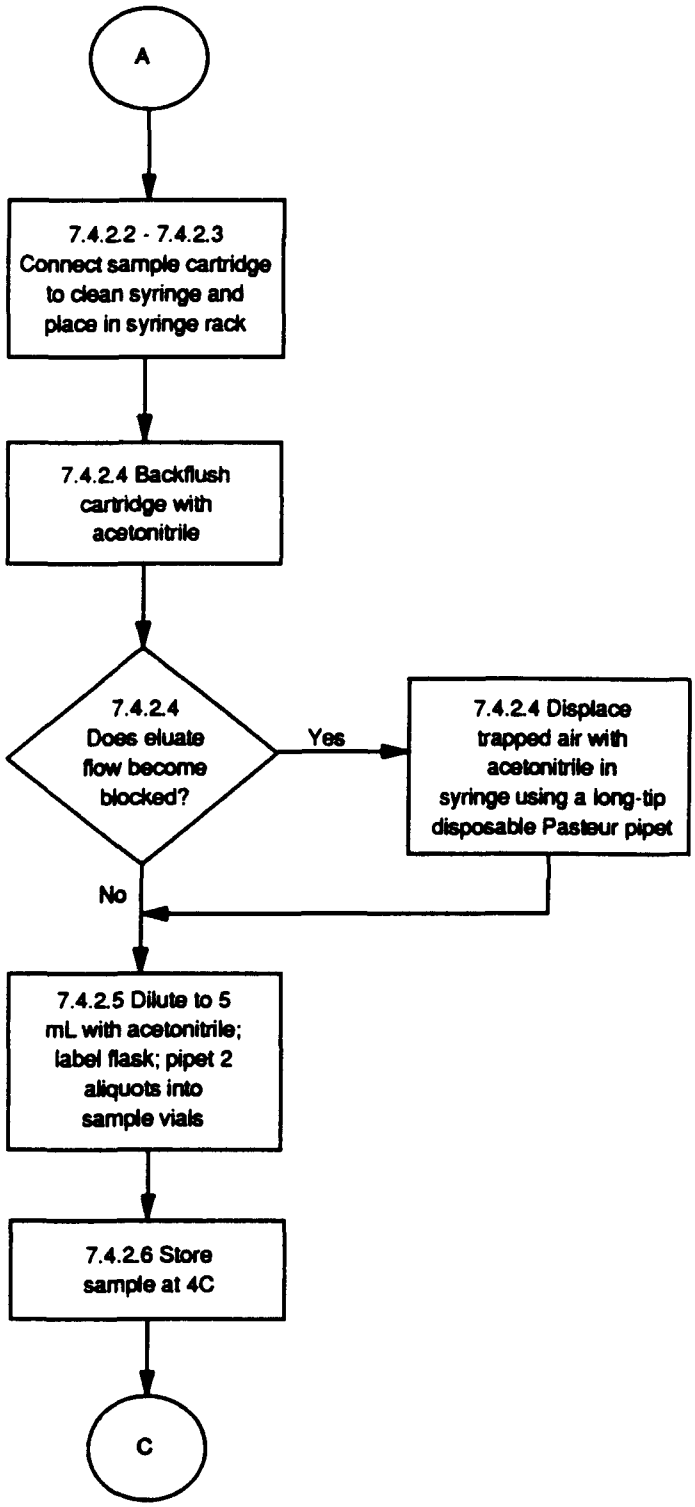
Peak Identification

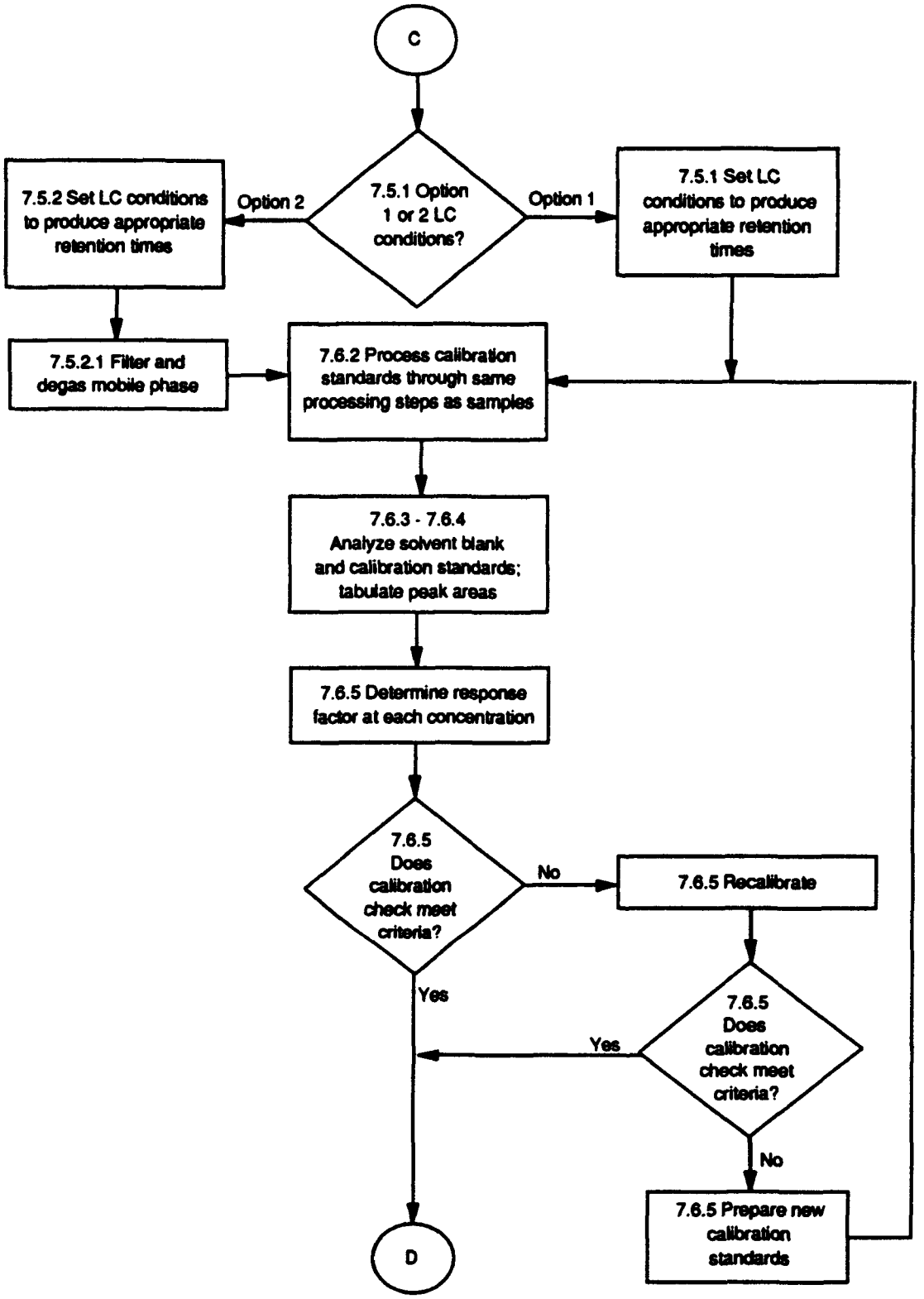
Number	Compound	Concentration(ng/µL)
1	Formaldehyde	1.140
2	Acetaldehyde	1.000
3	Acrolein	1.000
4	Acetone	1.000
5	Propanal	1.000
6	Crotonaldehyde	1.000
7	Butanal	0.905
8	Benzaldehyde	1.000
9	Isovaleraldehyde	0.450
10	Pentanal	0.485
11	o-Tolualdehyde	0.515
12	m-Tolualdehyde	0.505
13	p-Tolualdehyde	0.510
14	Hexanal	1.000
15	2,4-Dimethylbenzaldehyde	0.510

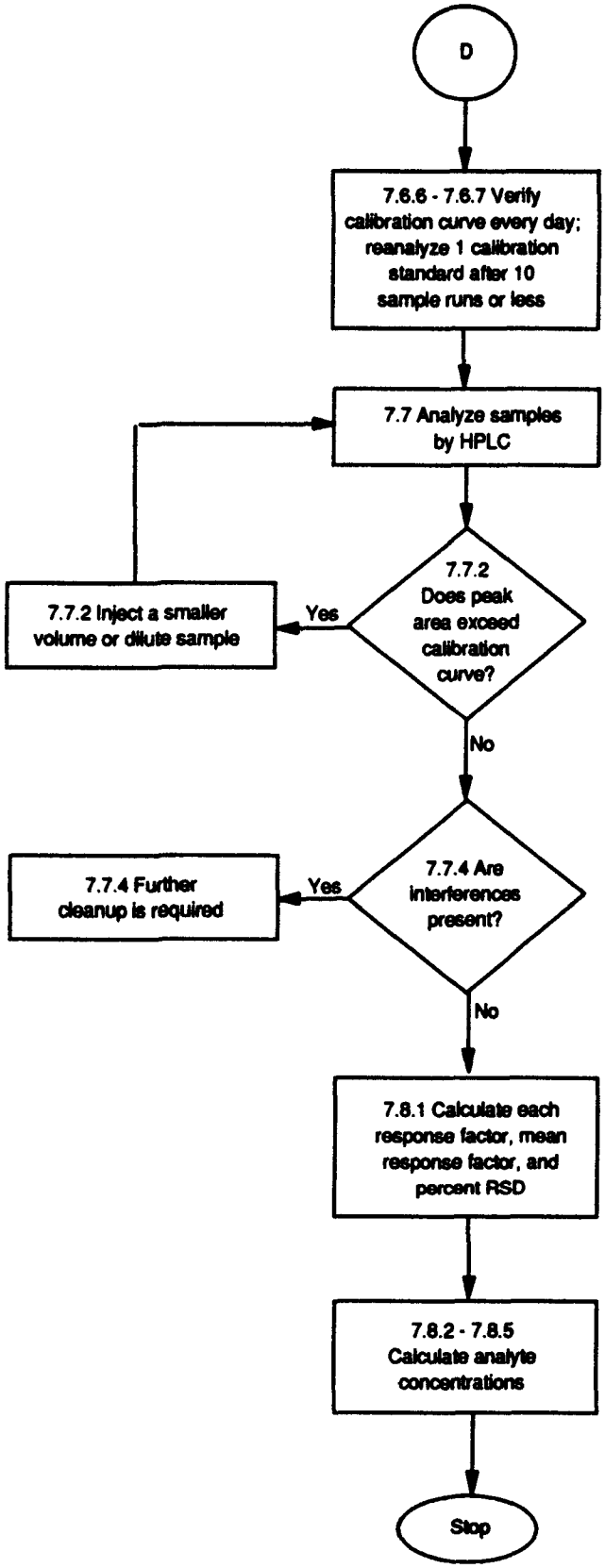
DETERMINATION OF CARBONYL COMPOUNDS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)




B
7.4.1.1 Measure volume of aqueous phase of sample; pour sample into separatory funnel and drain methylene chloride (from Method 0011) into volumetric flask
7.4.1.2 Extract aqueous solution with methylene chloride; add methylene chloride extracts to volumetric flask
7.4.1.3 Dilute to volume with methylene chloride; mix well; remove aliquot
7.4.1.4 Does sample have a high concentration of formaldehyde?
No
Yes
7.4.1.4 Exchange solvent with methanol as in 7.3.5.5
7.4.1.4 Dilute extract with mobile phase
7.4.1.4 Does sample have a low concentration of formaldehyde?
No
Yes
7.4.1.5 Store sample at 4C
7.4.1.4 Concentrate extract during solvent exchange process
C


A
7.4.2.2 - 7.4.2.3 Connect sample cartridge to clean syringe and place in syringe rack
7.4.2.4 Backflush cartridge with acetonitrile
7.4.2.4 Does eluate flow become blocked?
Yes
7.4.2.4 Displace trapped air with acetonitrile in syringe using a long-tip disposable Pasteur pipet
No
7.4.2.5 Dilute to 5 mL with acetonitrile; label flask; pipet 2 aliquots into sample vials
7.4.2.6 Store sample at 4C
C


C
7.5.1 Option 1 or 2 LC conditions?
Option 2
Option 1
7.5.2 Set LC conditions to produce appropriate retention times
7.5.1 Set LC conditions to produce appropriate retention times
7.5.2.1 Filter and degas mobile phase
7.6.2 Process calibration standards through same processing steps as samples
7.6.3 - 7.6.4 Analyze solvent blank and calibration standards; tabulate peak areas
7.6.5 Determine response factor at each concentration
7.6.5 Does calibration check meet criteria?
No
7.6.5 Recalibrate
Yes
7.6.5 Does calibration check meet criteria?
Yes
No
7.6.5 Prepare new calibration standards
D


D
7.6.6 - 7.6.7 Verify calibration curve every day; reanalyze 1 calibration standard after 10 sample runs or less
7.7 Analyze samples by HPLC
7.7.2 Does peak area exceed calibration curve?
Yes
7.7.2 Inject a smaller volume or dilute sample
No
7.7.4 Are interferences present?
Yes
7.7.4 Further cleanup is required
No
7.8.1 Calculate each response factor, mean response factor, and percent RSD
7.8.2 - 7.8.5 Calculate analyte concentrations
Stop

APPENDIX A

RECRYSTALLIZATION OF 2,4-DINITROPHENYLHYDRAZINE (DNPH)

NOTE: This procedure should be performed under a properly ventilated hood. Inhalation of acetonitrile can result in nose and throat irritation (brief exposure at 500 ppm) or more serious effects at higher concentration and/or longer exposures.

A.1 Prepare a saturated solution of DNPH by boiling excess DNPH in 200 mL of acetonitrile for approximately 1 hour.

A.2 After 1 hour, remove and transfer the supernatant to a covered beaker on a hot plate and allow gradual cooling to 40 to 60°C. Maintain this temperature range until 95% of the solvent has evaporated leaving crystals.

A.3 Decant the solution to waste and rinse the remaining crystals twice with three times their apparent volume of acetonitrile.

A.4 Transfer the crystals to a clean beaker, add 200 mL of acetonitrile, heat to boiling, and again let the crystals grow slowly at 40 to 60°C until 95% of the solvent has evaporated. Repeat the rinsing process as in Section A.3.

A.5 Take an aliquot of the second rinse, dilute 10 times with acetonitrile, acidify with 1 mL of 3.8 M perchloric acid per 100 mL of DNPH solution, and analyze with HPLC as in Section 7.0 for Option 2. An acceptable impurity level is less than 0.025 ng/μL of formaldehyde in recrystallized DNPH reagent or below the sensitivity (ppb, v/v) level indicated in Table 3 for the anticipated sample volume.

A.6 If the impurity level is not satisfactory, pipet off the solution to waste, repeat the recrystallization as in Section A.4 but rinse with two 25 mL portions of acetonitrile. Prep and analyze the second rinse as in Section A.5.

A.7 When the impurity level is satisfactory, place the crystals in an all-glass reagent bottle, add another 25 mL of acetonitrile, stopper, and shake the bottle. Use clean pipets when removing the saturated DNPH stock solution to reduce the possibility of contamination of the solution. Maintain only a minimum volume of the saturated solution adequate for day to day operation to minimize waste of the purified reagent.

METHOD 8316

ACRYLAMIDE, ACRYLONITRILE AND ACROLEIN BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

1.0 SCOPE AND APPLICATION

1.1 The following compounds can be determined by this method:

Compound Name	CAS No.[a]
Acrylamide	79-06-1
Acrylonitrile	107-13-1
Acrolein (Propenal)	107-02-8

a Chemical Abstract Services Registry Number.

1.2 The method detection limits (MDLs) for the target analytes in organic-free reagent water are listed in Table 1. The method may be applicable to other matrices.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatographs and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Water samples are analyzed by high pressure liquid chromatography (HPLC). A 200 µL aliquot is injected onto a C-18 reverse-phase column, and compounds in the effluent are detected with an ultraviolet (UV) detector.

3.0 INTERFERENCES

3.1 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 HPLC system

4.1.1 One high pressure pump.

4.1.2 Octadecyl Silane (ODS, C-18) reverse phase HPLC column, 25 cm x 4.6 mm, 10 μm, (Zorbax, or equivalent).

4.1.3 Variable wavelength UV detector.

4.1.4 Data system.

4.2 Other apparatus

4.2.1 Water degassing unit - 1 liter filter flask with stopper and pressure tubing.

4.2.2 Analytical balance - $\pm$ 0.0001 g.

4.2.3 Magnetic stirrer and magnetic stirring bar.

4.2.4 Sample filtration unit - syringe filter with 0.45 μm filter membrane, or equivalent disposable filter unit.

4.3 Materials

4.3.1 Syringes - 10, 25, 50 and 250 μL and 10 mL.

4.3.2 Volumetric pipettes, Class A, glass - 1, 5 and 10 mL.

4.3.3 Volumetric flasks - 5, 10, 50 and 100 mL.

4.3.4 Vials - 25 mL, 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 Acrylamide, CH_2:CHCONH$_2$, 99+% purity, electrophoresis reagent grade.

5.3 Acrylonitrile, H_2C:CHCN, 99+% purity.

5.4 Acrolein, CH_2:CHCHO, 99+% purity.

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

5.6 Stock standard solutions - Can be prepared from pure standard materials or can be purchased as certified solutions. Commercially prepared stock standards can be used if they are verified against EPA standards. If EPA

standards are not available for verification, then standards certified by the manufacturer and verified against a standard made from pure material is acceptable.

5.6.1 Acrylamide

5.6.1.1 Weigh 0.0100 g of acrylamide neat standard into a 100 mL volumetric flask, and dilute to the mark with organic-free reagent water. Calculate the concentration of the standard solution from the actual weight used. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard.

5.6.1.2 Transfer the stock solution into vials with Teflon lined screw caps or crimp tops. Store at 4°C, protected from light.

5.6.1.3 Stock solutions must be replaced after one year, or sooner if comparison with the check standards indicates a problem.

5.6.2 Acrylonitrile and Acrolein - Prepare separate stock solutions for acrylonitrile and acrolein.

5.6.2.1 Place about 9.8 mL of organic-free reagent water into a 10 mL volumetric flask before weighing the flask and stopper. Weigh the flask and record the weight to the nearest 0.0001 g. Add two drops of neat standard, using a 50 µL syringe, to the flask. The liquid must fall directly into the water, without contacting the inside wall of the flask.

CAUTION: Acrylonitrile and acrolein are toxic. Standard preparation should be performed in an laboratory fume hood.

5.6.2.2 Stopper the flask and then reweigh. Dilute to volume with organic-free reagent water. Calculate the concentration from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard.

5.6.2.3 Stock solutions must be replaced after one year, or sooner if comparison with the check standards indicates a problem.

5.7 Calibration standards

5.7.1 Prepare calibration standards at a minimum of five concentrations by diluting the stock solutions with organic-free reagent water.

5.7.2 One calibration standard should be prepared at a concentration near, but above, the method detection limit; the remaining standards

should correspond to the range of concentrations found in real samples, but should not exceed the working range of the HPLC system (1 mg/L to 10 mg/L).

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 HPLC Conditions

Mobile Phase:	Degassed organic-free reagent water
Injection Volume:	200 µL
Flow Rate:	2.0 mL/min
Pressure:	38 atm
Temperature:	25°C
Detector UV wavelength:	195 nm

7.2 Calibration:

7.2.1 Prepare standard solutions of acrylamide as described in Section 5.7.1. Inject 200 µL aliquots of each solution, in triplicate, into the chromatograph. See Method 8000 for additional guidance on calibration by the external standard method.

7.3 Chromatographic analysis:

7.3.1 Analyze the samples using the same chromatographic conditions used to prepare the standard curve. Suggested chromatographic conditions are given in Section 7.1. Table 1 provides the retention times that were obtained under these conditions during method development.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 Before processing any samples, the analyst must demonstrate, through the analysis of a method blank, that all glassware and reagents are interference free.

9.0 METHOD PERFORMANCE

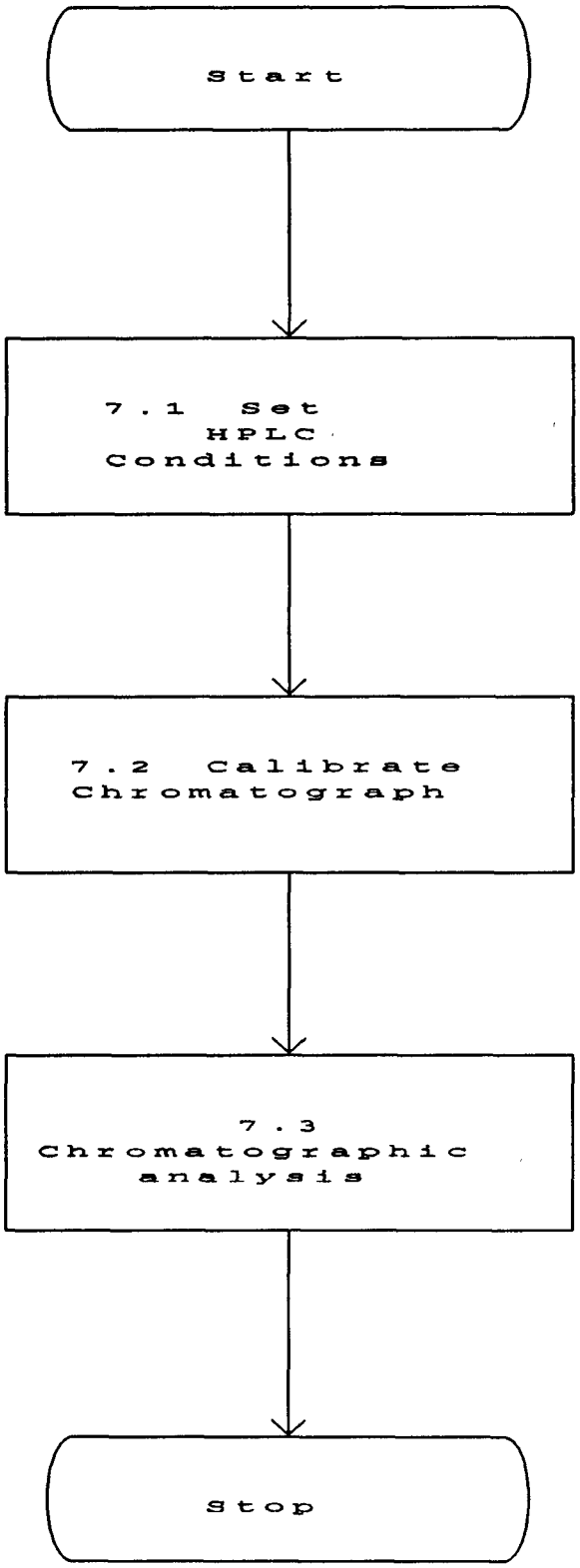
9.1 Method performance data are not available.

10.0 REFERENCES

1. Hayes, Samm "Acrylamide, Acrylonitrile, and Acrolein Determination in Water by High Pressure Liquid Chromatography," USEPA.

TABLE 1
ANALYTE RETENTION TIMES AND METHOD DETECTION LIMITS

Compound	Retention Time (min)	MDL (µg/L)
Acrylamide	3.5	10
Acrylonitrile	8.9	20
Acrolein (Propenal)	10.1	30


Start
7.1 Set HPLC Conditions
7.2 Calibrate Chromatograph
7.3 Chromatographic analysis
Stop

METHOD 8318

N-METHYLCARBAMATES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

1.0 SCOPE AND APPLICATION

1.1 Method 8318 is used to determine the concentration of N-methylcarbamates in soil, water and waste matrices. The following compounds can be determined by this method:

Compound Name	CAS No.[a]
Aldicarb (Temik)	116-06-3
Aldicarb Sulfone	1646-88-4
Carbaryl (Sevin)	63-25-2
Carbofuran (Furadan)	1563-66-2
Dioxacarb	6988-21-2
3-Hydroxycarbofuran	16655-82-6
Methiocarb (Mesurol)	2032-65-7
Methomyl (Lannate)	16752-77-5
Promecarb	2631-37-0
Propoxur (Baygon)	114-26-1

[a] Chemical Abstract Services Registry Number.

1.2 The method detection limits (MDLs) of Method 8318 for determining the target analytes in organic-free reagent water and in soil are listed in Table 1.

1.3 This method is restricted to use by, or under the supervision of, analysts experienced in the use of high performance liquid chromatography (HPLC) and skilled in the interpretation of chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 N-methylcarbamates are extracted from aqueous samples with methylene chloride, and from soils, oily solid waste and oils with acetonitrile. The extract solvent is exchanged to methanol/ethylene glycol, and then the extract is cleaned up on a C-18 cartridge, filtered, and eluted on a C-18 analytical column. After separation, the target analytes are hydrolyzed and derivatized post-column, then quantitated fluorometrically.

2.2 Due to the specific nature of this analysis, confirmation by a secondary method is not essential. However, fluorescence due to post-column derivatization may be confirmed by substituting the NaOH and o-phthalaldehyde

solutions with organic-free reagent water and reanalyzing the sample. If fluorescence is still detected, then a positive interference is present and care should be taken in the interpretation of the results.

2.3 The sensitivity of the method usually depends on the level of interferences present, rather than on the instrumental conditions. Waste samples with a high level of extractable fluorescent compounds are expected to yield significantly higher detection limits.

3.0 INTERFERENCES

3.1 Fluorescent compounds, primarily alkyl amines and compounds which yield primary alkyl amines on base hydrolysis, are potential sources of interferences.

3.2 Coeluting compounds that are fluorescence quenchers may result in negative interferences.

3.3 Impurities in solvents and reagents are additional sources of interferences. Before processing any samples, the analyst must demonstrate daily, through the analysis of solvent blanks, that the entire analytical system is interference free.

4.0 APPARATUS AND MATERIALS

4.1 HPLC system

4.1.1 An HPLC system capable of injecting 20 µL aliquots and performing multilinear gradients at a constant flow. The system must also be equipped with a data system to measure the peak areas.

4.1.2 C-18 reverse phase HPLC column, 25 cm x 4.6 mm (5 µm).

4.1.3 Post Column Reactor with two solvent delivery systems (Kratos PCRS 520 with two Kratos Spectroflow 400 Solvent Delivery Systems, or equivalent).

4.1.4 Fluorescence detector (Kratos Spectroflow 980, or equivalent).

4.2 Other apparatus

4.2.1 Centrifuge.

4.2.2 Analytical balance - ± 0.0001 g.

4.2.3 Top loading balance - ± 0.01 g.

4.2.4 Platform shaker.

4.2.5 Heating block, or equivalent apparatus, that can accommodate 10 mL graduated vials (Section 4.3.11).

4.3 Materials

4.3.1 HPLC injection syringe - 50 µL.

4.3.2 Filter paper, (Whatman #113 or #114, or equivalent).

4.3.3 Volumetric pipettes, Class A, glass, assorted sizes.

4.3.4 Reverse phase cartridges, (C-18 Sep-Pak^{R} [Waters Associates], or equivalent).

4.3.5 Glass syringes - 5 mL.

4.3.6 Volumetric flasks, Class A - Sizes as appropriate.

4.3.7 Erlenmeyer flasks with teflon-lined screw caps, 250 mL.

4.3.8 Assorted glass funnels.

4.3.9 Separatory funnels, with ground glass stoppers and teflon stopcocks - 250 mL.

4.3.10 Graduated cylinders - 100 mL.

4.3.11 Graduated glass vials - 10 mL, 20 mL.

4.3.12 Centrifuge tubes - 250 mL.

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

4.3.14 Positive displacement micro-pipettor, 3 to 25 µL displacement, (Gilson Microman [Rainin #M-25] with tips, [Rainin #CP-25], or equivalent).

4.3.15 Nylon filter unit, 25 mm diameter, 0.45 µm pore size, disposable (Alltech Associates, #2047, or equivalent).

5.0 REAGENTS

5.1 HPLC grade chemicals shall be used in all tests. 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 lowering the accuracy of the determination.

5.2 General

5.2.1 Acetonitrile, CH_3CN - HPLC grade - minimum UV cutoff at 203 nm (EM Omnisolv #AX0142-1, or equivalent).

5.2.2 Methanol, CH_3OH - HPLC grade - minimum UV cutoff at 230 nm (EM Omnisolv #MX0488-1, or equivalent).

5.2.3 Methylene chloride, CH_2Cl_2 - HPLC grade - minimum UV cutoff at 230 nm (EM Omnisolv #DX0831-1, or equivalent).

5.2.4 Hexane, C_6H_{14} - pesticide grade - (EM Omnisolv #HX0298-1, or equivalent).

5.2.5 Ethylene glycol, $HOCH_2CH_2OH$ - Reagent grade - (EM Science, or equivalent).

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

5.2.7 Sodium hydroxide, NaOH - reagent grade - 0.05N NaOH solution.

5.2.8 Phosphoric acid, H_3PO_4 - reagent grade.

5.2.9 pH 10 borate buffer (J.T. Baker #5609-1, or equivalent).

5.2.10 o-Phthalaldehyde, o-$C_6H_4(CHO)_2$ - reagent grade (Fisher #O-4241, or equivalent).

5.2.11 2-Mercaptoethanol, $HSCH_2CH_2OH$ - reagent grade (Fisher #O-3446, or equivalent).

5.2.12 N-methylcarbamate neat standards (equivalence to EPA standards must be demonstrated for purchased solutions).

5.2.13 Chloroacetic acid, $ClCH_2COOH$, 0.1 N.

5.3 Reaction solution

5.3.1 Dissolve 0.500 g of o-phthalaldehyde in 10 mL of methanol, in a 1 L volumetric flask. To this solution, add 900 mL of organic-free reagent water, followed by 50 mL of the borate buffer (pH 10). After mixing well, add 1 mL of 2-mercaptoethanol, and dilute to the mark with organic-free reagent water. Mix the solution thoroughly. Prepare fresh solutions on a weekly basis, as needed. Protect from light and store under refrigeration.

5.4 Standard solutions

5.4.1 Stock standard solutions: prepare individual 1000 mg/L solutions by adding 0.025 g of carbamate to a 25 mL volumetric flask, and diluting to the mark with methanol. Store solutions, under refrigeration, in glass vials with Teflon lined screw caps or crimp tops. Replace every six months.

5.4.2 Intermediate standard solution: prepare a mixed 50.0 mg/L solution by adding 2.5 mL of each stock solution to a 50 mL volumetric flask, and diluting to the mark with methanol. Store solutions, under

refrigeration, in glass vials with Teflon lined screw caps or crimp tops. Replace every three months.

5.4.3 Working standard solutions: prepare 0.5, 1.0, 2.0, 3.0 and 5.0 mg/L solutions by adding 0.25, 0.5, 1.0, 1.5 and 2.5 mL of the intermediate mixed standard to respective 25 mL volumetric flasks, and diluting each to the mark with methanol. Store solutions, under refrigeration, in glass vials with Teflon lined screw caps or crimp tops. Replace every two months, or sooner if necessary.

5.4.4 Mixed QC standard solution: prepare a 40.0 mg/L solution from another set of stock standard solutions, prepared similarly to those described in Section 5.4.1. Add 2.0 mL of each stock solution to a 50 mL volumetric flask and dilute to the mark with methanol. Store the solution, under refrigeration, in a glass vial with a Teflon lined screw cap or crimp top. Replace every three months.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Due to the extreme instability of N-methylcarbamates in alkaline media, water, waste water and leachates should be preserved immediately after collection by acidifying to pH 4-5 with 0.1 N chloroacetic acid.

6.2 Store samples at 4°C and out of direct sunlight, from the time of collection through analysis. N-methylcarbamates are sensitive to alkaline hydrolysis and heat.

6.3 All samples must be extracted within seven days of collection, and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction

7.1.1 Water, domestic wastewater, aqueous industrial wastes, and leachates

7.1.1.1 Measure 100 mL of sample into a 250 mL separatory funnel and extract by shaking vigorously for about 2 minutes with 30 mL of methylene chloride. Repeat the extraction two more times. Combine all three extracts in a 100 mL volumetric flask and dilute to volume with methylene chloride. If cleanup is required, go to Section 7.2. If cleanup is not required, proceed directly to Section 7.3.1.

7.1.2 Soils, solids, sludges, and heavy aqueous suspensions

7.1.2.1 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.

7.1.2.1.1 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:

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

7.1.2.2 Extraction - Weigh out 20 ± 0.1 g of sample into a 250 mL erlenmeyer flask with a teflon-lined screw cap. Add 50 mL of acetonitrile and shake for 2 hours on a platform shaker. Allow the mixture to settle (5-10 min), then decant the extract into a 250 mL centrifuge tube. Repeat the extraction two more times with 20 mL of acetonitrile and 1 hour shaking each time. Decant and combine all three extracts. Centrifuge the combined extract at 200 rpm for 10 min. Carefully decant the supernatant into a 100 mL volumetric flask and dilute to volume with acetonitrile. (Dilution factor = 5) Proceed to Section 7.3.2.

7.1.3 Soils heavily contaminated with non-aqueous substances, such as oils

7.1.3.1 Determination of sample % dry weight - Follow Sections 7.1.2.1 through 7.1.2.1.1.

7.1.3.2 Extraction - Weigh out 20 ± 0.1 g of sample into a 250 mL erlenmeyer flask with a teflon-lined screw cap. Add 60 mL of hexane and shake for 1 hour on a platform shaker. Add 50 mL of acetonitrile and shake for an additional 3 hours. Allow the mixture to settle (5-10 min), then decant the solvent layers into a 250 mL separatory funnel. Drain the acetonitrile (bottom layer) through filter paper into a 100 mL volumetric flask. Add 60 mL of hexane and 50 mL of acetonitrile to the sample extraction flask and shake for 1 hour. Allow the mixture to settle, then decant the mixture into the separatory funnel containing the hexane from the first extraction. Shake the separatory funnel for 2 minutes, allow the phases to separate, drain the acetonitrile layer through filter paper into the volumetric flask, and dilute to volume with acetonitrile. (Dilution factor = 5) Proceed to Section 7.3.2.

7.1.4 Non-aqueous liquids such as oils

7.1.4.1 Extraction - Weigh out 20 ± 0.1 g of sample into a 125 mL separatory funnel. Add 40 mL of hexane and 25 mL of acetonitrile and vigorously shake the sample mixture for 2 minutes. Allow the phases to separate, then drain the acetonitrile (bottom layer) into a 100 mL volumetric flask. Add 25 mL of acetonitrile to the sample funnel, shake for 2 minutes, allow the phases to separate, drain the acetonitrile layer into the volumetric flask.

Repeat the extraction with another 25 mL portion of acetonitrile, combining the extracts. Dilute to volume with acetonitrile. (Dilution factor = 5). Proceed to Section 7.3.2.

7.2 Cleanup - Pipet 20.0 mL of the extract into a 20 mL glass vial containing 100 µL of ethylene glycol. Place the vial in a heating block set at 50° C, and gently evaporate the extract under a stream of nitrogen (in a fume hood) until only the ethylene glycol keeper remains. Dissolve the ethylene glycol residue in 2 mL of methanol, pass the extract through a pre-washed C-18 reverse phase cartridge, and collect the eluate in a 5 mL volumetric flask. Elute the cartridge with methanol, and collect the eluate until the final volume of 5.0 mL is obtained. (Dilution factor = 0.25) Using a disposable 0.45 µm filter, filter an aliquot of the clean extract directly into a properly labelled autosampler vial. The extract is now ready for analysis. Proceed to Section 7.4.

7.3 Solvent Exchange

7.3.1 Water, domestic wastewater, aqueous industrial wastes, and leachates:

Pipet 10.0 mL of the extract into a 10 mL graduated glass vial containing 100 µL of ethylene glycol. Place the vial in a heating block set at 50° C, and gently evaporate the extract under a stream of nitrogen (in a fume hood) until only the ethylene glycol keeper remains. Add methanol to the ethylene glycol residue, dropwise, until the total volume is 1.0 mL. (Dilution factor = 0.1). Using a disposable 0.45 µm filter, filter this extract directly into a properly labelled autosampler vial. The extract is now ready for analysis. Proceed to Section 7.4.

7.3.2 Soils, solids, sludges, heavy aqueous suspensions, and non-aqueous liquids:

Elute 15 mL of the acetonitrile extract through a C-18 reverse phase cartridge, prewashed with 5 mL of acetonitrile. Discard the first 2 mL of eluate and collect the remainder. Pipet 10.0 mL of the clean extract into a 10 mL graduated glass vial containing 100 µL of ethylene glycol. Place the vial in a heating block set at 50° C, and gently evaporate the extract under a stream of nitrogen (in a fume hood) until only the ethylene glycol keeper remains. Add methanol to the ethylene glycol residue, dropwise, until the total volume is 1.0 mL. (Additional dilution factor = 0.1; overall dilution factor = 0.5). Using a disposable 0.45 µm filter, filter this extract directly into a properly labelled autosampler vial. The extract is now ready for analysis. Proceed to Section 7.4.

7.4 Sample Analysis

7.4.1 Analyze the samples using the chromatographic conditions, post-column reaction parameters and instrument parameters given in Sections 7.4.1.1, 7.4.1.2, 7.4.1.3 and 7.4.1.4. Table 2 provides the retention times that were obtained under these conditions during method development. A chromatogram of the separation is shown in Figure 1.

7.4.1.1 Chromatographic Conditions (Recommended)

Solvent A: Organic-free reagent water, acidified with 0.4 mL of phosphoric acid per liter of water
Solvent B: Methanol/acetonitrile (1:1, v/v)
Flow rate: 1.0 mL/min
Injection Volume: 20 µL
Solvent delivery system program:

Time (min)	Function	Value	Duration (min)	File
0.00	FR	1.0		0
0.00	B%	10%		0
0.02	B%	80%	20	0
20.02	B%	100%	5	0
25.02	B%	100%	5	0
30.02	B%	10%	3	0
33.02	B%	10%	7	0
36.02	ALARM		0.01	0

7.4.1.2 Post-column Hydrolysis Parameters (Recommended)

Solution: 0.05 N aqueous sodium hydroxide
Flow Rate: 0.7 mL/min
Temperature: 95° C
Residence Time: 35 seconds (1 mL reaction coil)

7.4.1.3 Post-column Derivatization Parameters (Recommended)

Solution: o-phthalaldehyde/2-mercaptoethanol(Section 5.3.1)
Flow Rate: 0.7 mL/min
Temperature: 40° C
Residence time: 25 seconds (1 mL reaction coil)

7.4.1.4 Fluorometer Parameters (Recommended)

Cell: 10 µL
Excitation wavelength: 340 nm
Emission wavelength: 418 nm cutoff filter
Sensitivity wavelength: 0.5 µA
PMT voltage: -800 V
Time constant: 2 sec

7.4.2 If the peak areas of the sample signals exceed the calibration range of the system, dilute the extract as necessary and reanalyze the diluted extract.

7.5 Calibration:

7.5.1 Analyze a solvent blank (20 µL of methanol) to ensure that the system is clean. Analyze the calibration standards (Section 5.4.3),

starting with the 0.5 mg/L standards and ending with the 5.0 mg/L standard. If the percent relative standard deviation (%RSD) of the mean response factor (RF) for each analyte does not exceed 20%, the system is calibrated and the analysis of samples may proceed. If the %RSD for any analyte exceeds 20%, recheck the system and/or recalibrate with freshly prepared calibration solutions.

7.5.2 Using the established calibration mean response factors, check the calibration of the instrument at the beginning of each day by analyzing the 2.0 mg/L mixed standard. If the concentration of each analyte falls within the range of 1.70 to 2.30 mg/L (i.e., within $\pm$ 15% of the true value), the instrument is considered to be calibrated and the analysis of samples may proceed. If the observed value of any analyte exceeds its true value by more than $\pm$ 15%, the instrument must be recalibrated (Section 7.5.1).

7.5.3 After 10 sample runs, or less, the 2.0 mg/L standards must be analyzed to ensure that the retention times and response factors are still within acceptable limits. Significant variations (i.e., observed concentrations exceeding the true concentrations by more than $\pm$ 15%) may require a re-analysis of the samples.

7.6 Calculations

7.6.1 Calculate each response factor as follows (mean value based on 5 points):

$$RF = \frac{\text{concentration of standard}}{\text{area of the signal}}$$

$$\text{mean RF} = \overline{RF} = \frac{(\sum_{i}^{5} RF_i)}{5}$$

$$\%RSD \text{ of } \overline{RF} = \frac{[(\sum_{i}^{5} RF_i - \overline{RF})^2]^{1/2} / 4}{\overline{RF}} \times 100\%$$

7.6.2 Calculate the concentration of each N-methylcarbamate as follows:

μg/g or mg/L = ($\overline{RF}$) (area of signal) (dilution factor)

8.0 QUALITY CONTROL

8.1 Before processing any samples, the analyst must demonstrate, through the analysis of a method blank for each matrix type, that all glassware and reagents are interference free. Each time there is a change of reagents, a method blank must be processed as a safeguard against laboratory contamination.

8.2 A QC check solution must be prepared and analyzed with each sample batch that is processed. Prepare this solution, at a concentration of 2.0 mg/L of each analyte, from the 40.0 mg/L mixed QC standard solution (Section 5.4.4). The acceptable response range is 1.7 to 2.3 mg/L for each analyte.

8.3 Negative interference due to quenching may be examined by spiking the extract with the appropriate standard, at an appropriate concentration, and examining the observed response against the expected response.

8.4 Confirm any detected analytes by substituting the NaOH and OPA reagents in the post column reaction system with deionized water, and reanalyze the suspected extract. Continued fluorescence response will indicate that a positive interference is present (since the fluorescence response is not due to the post column derivatization). Exercise caution in the interpretation of the chromatogram.

9.0 METHOD PERFORMANCE

9.1 Table 1 lists the single operator method detection limit (MDL) for each compound in organic-free reagent water and soil. Seven/ten replicate samples were analyzed, as indicated in the table. See reference 7 for more details.

9.2 Tables 2, 3 and 4 list the single operator average recoveries and standard deviations for organic-free reagent water, wastewater and soil. Ten replicate samples were analyzed at each indicated spike concentration for each matrix type.

9.3 The method detection limit, accuracy and precision obtained will be determined by the sample matrix.

10.0 REFERENCES

1. California Department of Health Services, Hazardous Materials Laboratory, "N-Methylcarbamates by HPLC", Revision No. 1.0, September 14, 1989.

2. Krause, R.T. Journal of Chromatographic Science, 1978, vol. 16, pg 281.

3. Klotter, Kevin, and Robert Cunico, "HPLC Post Column Detection of Carbamate Pesticides", Varian Instrument Group, Walnut Creek, CA 94598.

4. USEPA, "Method 531. Measurement of N-Methylcarbomyloximes and N-Methylcarbamates in Drinking Water by Direct Aqueous Injection HPLC with Post Column Derivatization", EPA 600/4-85-054, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268.

5. USEPA, "Method 632. The Determination of Carbamate and Urea Pesticides in Industrial and Municipal Wastewater", EPA 600/4-21-014, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268.

6. Federal Register, "Appendix B to Part 136 - Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11", Friday, October 26, 1984, 49, No. 209, 198-199.

7. Okamoto, H.S., D. Wijekoon, C. Esperanza, J. Cheng, S. Park, J. Garcha, S. Gill, K. Perera "Analysis for N-Methylcarbamate Pesticides by HPLC in Environmental Samples", Proceedings of the Fifth Annual USEPA Symposium on Waste Testing and Quality Assurance, July 24-28, 1989, Vol. II, 57-71.

TABLE 1
ELUTION ORDER, RETENTION TIMES[a] AND
SINGLE OPERATOR METHOD DETECTION LIMITS

Compound	Retention Time (min)	Method Detection Limits[b] Organic-free Reagent Water (µg/L)	Soil (µg/kg)
Aldicarb Sulfone	9.59	1.9[c]	44[c]
Methomyl (Lannate)	9.59	1.7	12
3-Hydroxycarbofuran	12.70	2.6	10[c]
Dioxacarb	13.50	2.2	>50[c]
Aldicarb (Temik)	16.05	9.4[c]	12[c]
Propoxur (Baygon)	18.06	2.4	17
Carbofuran (Furadan)	18.28	2.0	22
Carbaryl (Sevin)	19.13	1.7	31
α-Naphthol[d]	20.30	-	-
Methiocarb (Mesurol)	22.56	3.1	32
Promecarb	23.02	2.5	17

[a] See Section 7.4 for chromatographic conditions

[b] MDL for organic-free reagent water, sand, soil were determined by analyzing 10 low concentration spike replicate for each matrix type (except where noted). See reference 7 for more details.

[c] MDL determined by analyzing 7 spiked replicates.

[d] Breakdown product of Carbaryl.

TABLE 2
SINGLE OPERATOR AVERAGE RECOVERY AND
PRECISION DATA[a] FOR ORGANIC-FREE REAGENT WATER

Compound	Recovered	% Recovery	SD	%RSD
Aldicarb Sulfone	225	75.0	7.28	3.24
Methomyl (Lannate)	244	81.3	8.34	3.42
3-Hydroxycarbofuran	210	70.0	7.85	3.74
Dioxacarb	241	80.3	8.53	3.54
Aldicarb (Temik)	224	74.7	13.5	6.03
Propoxur (Baygon)	232	77.3	10.6	4.57
Carbofuran (Furadan)	239	79.6	9.23	3.86
Carbaryl (Sevin)	242	80.7	8.56	3.54
Methiocarb (Mesurol)	231	77.0	8.09	3.50
Promecarb	227	75.7	9.43	4.1

[a] Spike Concentration = 300 μg/L of each compound, n = 10

TABLE 3
SINGLE OPERATOR AVERAGE RECOVERY AND
PRECISION DATA[a] FOR WASTEWATER

Compound	Recovered	% Recovery	SD	%RSD
Aldicarb Sulfone	235	78.3	17.6	7.49
Methomyl (Lannate)	247	82.3	29.9	12.10
3-Hydroxycarbofuran	251	83.7	25.4	10.11
Dioxacarb	[b]	-	-	-
Aldicarb (Temik)	258	86.0	16.4	6.36
Propoxur (Baygon)	263	87.7	16.7	6.47
Carbofuran (Furadan)	262	87.3	15.7	5.99
Carbaryl (Sevin)	262	87.3	17.2	6.56
Methiocarb (Mesurol)	254	84.7	19.9	7.83
Promecarb	263	87.7	15.1	5.74

[a] Spike Concentration = 300 µg/L of each compound, n = 10

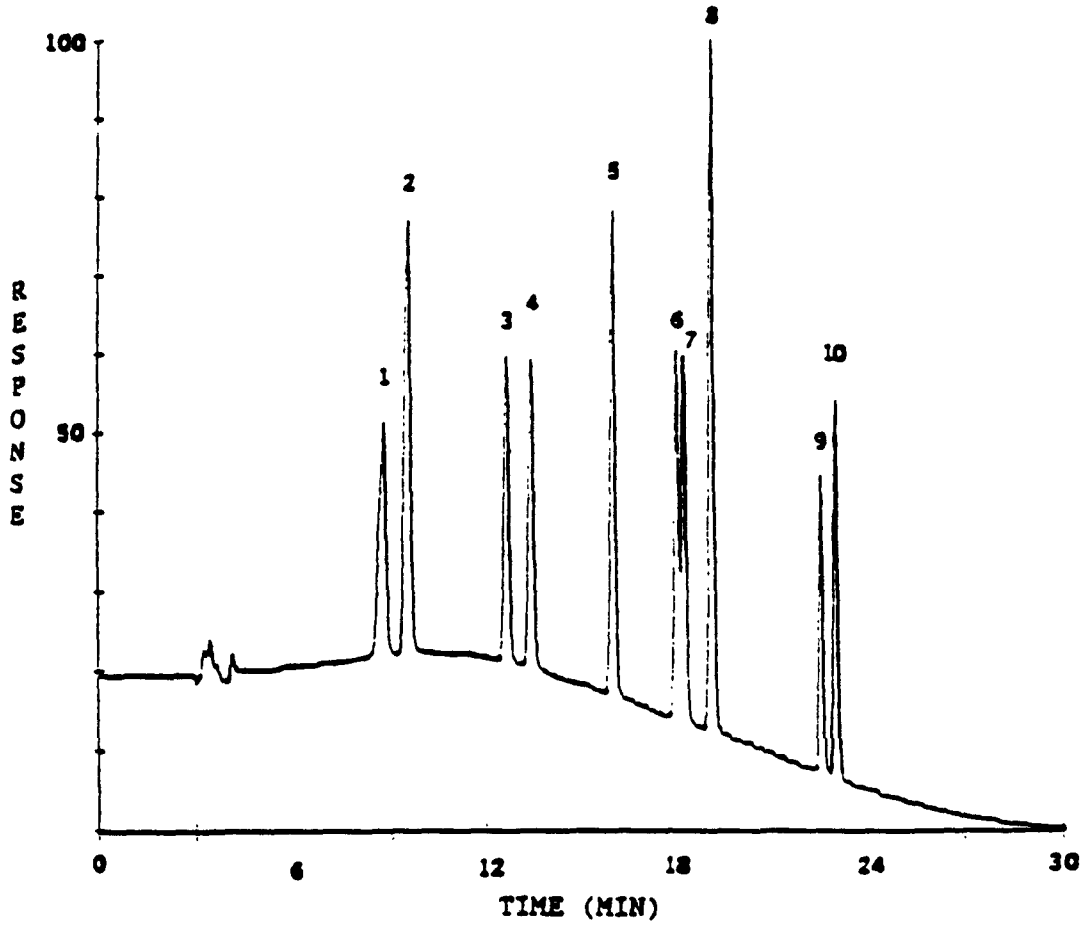
[b] No recovery

TABLE 4
SINGLE OPERATOR AVERAGE RECOVERY AND
PRECISION DATA[a] FOR SOIL

Compound	Recovered	% Recovery	SD	%RSD
Aldicarb Sulfone	1.57	78.5	0.069	4.39
Methomyl (Lannate)	1.48	74.0	0.086	5.81
3-Hydroxycarbofuran	1.60	80.0	0.071	4.44
Dioxacarb	1.51	75.5	0.073	4.83
Aldicarb (Temik)	1.29	64.5	0.142	11.0
Propoxur (Baygon)	1.33	66.5	0.126	9.47
Carbofuran (Furadan)	1.46	73.0	0.092	6.30
Carbaryl (Sevin)	1.53	76.5	0.076	4.90
Methiocarb (Mesurol)	1.45	72.5	0.071	4.90
Promecarb	1.29	64.7	0.124	9.61

[a] Spike Concentration = 2.00 mg/kg of each compound, n = 10

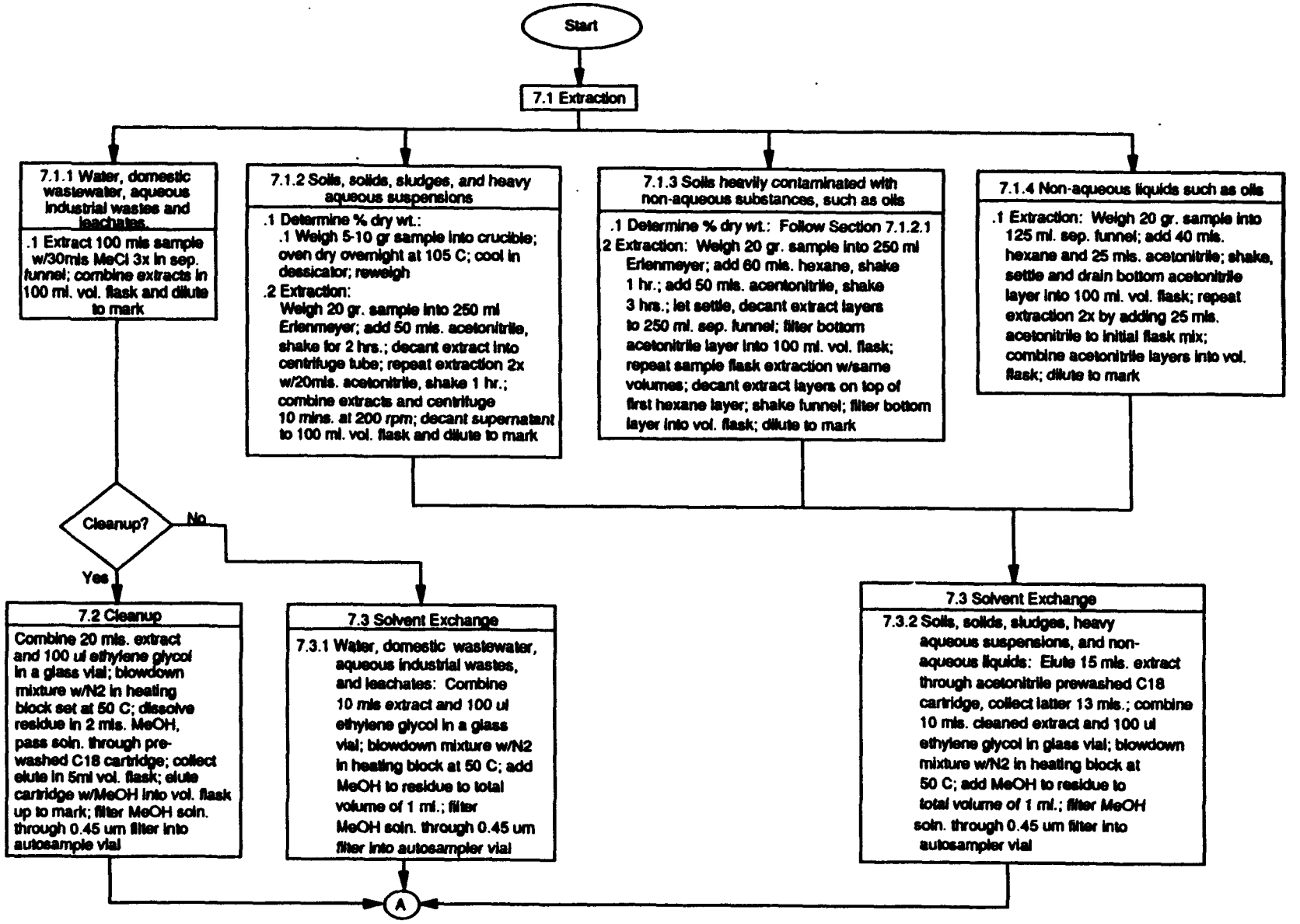
FIGURE 1

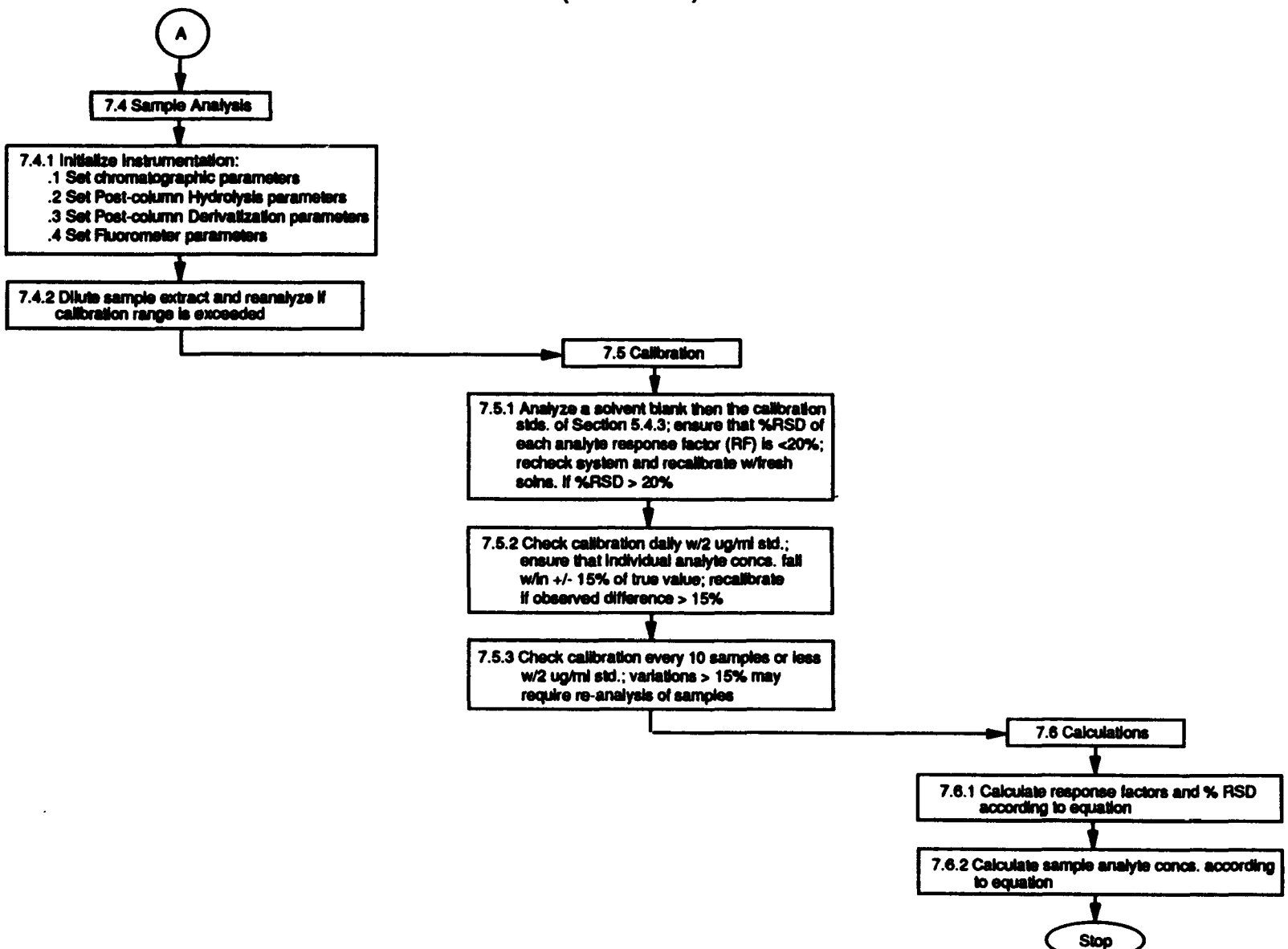


1.00 ug/mL EACH OF:

1. ALDICARB SULFONE
2. METHOMYL
3. 3-HYDROXYCARBOFURAN
4. DIOXACARB
5. ALDICARB
6. PROPOXUR
7. CARBOFURAN
8. CARBARYL
9. METHIOCARB
10. PROMECARB

METHOD 8318
N-METHYLCARBAMATES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)




A
7.4 Sample Analysis
7.4.1 Initialize Instrumentation:
.1 Set chromatographic parameters
.2 Set Post-column Hydrolysis parameters
.3 Set Post-column Derivatization parameters
.4 Set Fluorometer parameters
7.4.2 Dilute sample extract and reanalyze if calibration range is exceeded
7.5 Calibration
7.5.1 Analyze a solvent blank then the calibration stds. of Section 5.4.3; ensure that %RSD of each analyte response factor (RF) is <20%; recheck system and recalibrate w/fresh solns. If %RSD > 20%
7.5.2 Check calibration daily w/2 ug/ml std.; ensure that individual analyte concs. fall w/in +/- 15% of true value; recalibrate if observed difference > 15%
7.5.3 Check calibration every 10 samples or less w/2 ug/ml std.; variations > 15% may require re-analysis of samples
7.6 Calculations
7.6.1 Calculate response factors and % RSD according to equation
7.6.2 Calculate sample analyte concs. according to equation
Stop

METHOD 8321

SOLVENT EXTRACTABLE NON-VOLATILE COMPOUNDS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY/THERMOSPRAY/MASS SPECTROMETRY (HPLC/TSP/MS) OR ULTRAVIOLET (UV) DETECTION

1.0 SCOPE AND APPLICATION

1.1 This method covers the use of high performance liquid chromatography (HPLC), coupled with either thermospray-mass spectrometry (TSP-MS), and/or ultraviolet (UV), for the determination of disperse azo dyes, organophosphorus compounds, and Tris-(2,3-dibromopropyl)phosphate in wastewater, ground water, sludge, and soil/sediment matrices, and chlorinated phenoxyacid compounds and their esters in wastewater, ground water, and soil/sediment matrices. Data is also provided for chlorophenoxy acid herbicides in fly ash (Table 15), however, recoveries for most compounds are very poor indicating poor extraction efficiency for these analytes using the extraction procedure included in this method. Additionally, it may apply to other non-volatile compounds that are solvent extractable, are amenable to HPLC, and are ionizable under thermospray introduction for mass spectrometric detection. The following compounds can be determined by this method:

Compound Name	CAS No.[a]
Azo Dyes	
Disperse Red 1	2872-52-8
Disperse Red 5	3180-81-2
Disperse Red 13	2832-40-8
Disperse Yellow 5	6439-53-8
Disperse Orange 3	730-40-5
Disperse Orange 30	5261-31-4
Disperse Brown 1	17464-91-4
Solvent Red 3	6535-42-8
Solvent Red 23	85-86-9
Anthraquinone Dyes	
Disperse Blue 3	2475-46-9
Disperse Blue 14	2475-44-7
Disperse Red 60	17418-58-5
Coumarin Dyes	
(Fluorescent Brighteners)	
Fluorescent Brightener 61	8066-05-5
Fluorescent Brightener 236	63590-17-0
Alkaloids	
Caffeine	58-08-2
Strychnine	57-24-9

Compound Name	CAS No.[a]
Organophosphorus Compounds	
Methomyl	16752-77-5
Thiofanox	39196-18-4
Famphur	52-85-7
Asulam	3337-71-1
Dichlorvos	62-73-7
Dimethoate	60-51-5
Disulfoton	298-04-4
Fensulfothion	115-90-2
Merphos	150-50-5
Methyl parathion	298-00-0
Monocrotophos	919-44-8
Naled	300-76-5
Phorate	298-02-2
Trichlorfon	52-68-6
Tris-(2,3-Dibromopropyl) phosphate, (Tris-BP)	126-72-7
Chlorinated Phenoxyacid Compounds	
Dalapon	75-99-0
Dicamba	1918-00-9
2,4-D	94-75-7
MCPA	94-74-6
MCPP	7085-19-0
Dichlorprop	120-36-5
2,4,5-T	93-76-5
Silvex (2,4,5-TP)	93-72-1
Dinoseb	88-85-7
2,4-DB	94-82-6
2,4-D, butoxyethanol ester	1929-73-3
2,4-D, ethylhexyl ester	1928-43-4
2,4,5-T, butyl ester	93-79-8
2,4,5-T, butoxyethanol ester	2545-59-7

[a] Chemical Abstract Services Registry Number.

1.2 This method may be applicable to the analysis of other non-volatile or semivolatile compounds.

1.3 Tris-BP has been classified as a carcinogen. Purified standard material and stock standard solutions should be handled in a hood.

1.4 Method 8321 is designed to detect the chlorinated phenoxyacid compounds (free acid form) and their esters without the use of hydrolysis and esterification in the extraction procedure.

1.5 The compounds were chosen for analysis by HPLC/MS because they have been designated as problem compounds that are hard to analyze by traditional

chromatographic methods (e.g. gas chromatography). The sensitivity of this method is dependent upon the level of interferants within a given matrix, and varies with compound class and even with compounds within that class. Additionally, the limit of detection (LOD) is dependent upon the mode of operation of the mass spectrometer. For example, the LOD for caffeine in the selected reaction monitoring (SRM) mode is 45 pg of standard injected (10 µL injection), while for Disperse Red 1 the LOD is 180 pg. The LOD for caffeine under single quadrupole scanning is 84 pg and is 600 pg for Disperse Red 1 under similar scanning conditions.

1.6 The experimentally determined limits of detection (LOD) for the target analytes are presented in Tables 3, 10, 13, and 14. For further compound identification, MS/MS (CAD - collision activated dissociation) can be used as an optional extension of this method.

1.7 This method is restricted to use by or under the supervision of analysts experienced in the use of high performance liquid chromatographs/mass spectrometers and skilled in the interpretation of liquid chromatograms and mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 This method provides reverse phase high performance liquid chromatographic (RP/HPLC) and thermospray (TSP) mass spectrometric (MS) conditions for the detection of the target analytes. Quantitative analysis is performed by TSP/MS, using an external standard approach. Sample extracts can be analyzed by direct injection into the thermospray or onto a liquid chromatographic-thermospray interface. A gradient elution program is used on the chromatograph to separate the compounds. Detection is achieved both by negative ionization (discharge electrode) and positive ionization, with a single quadrupole mass spectrometer. Since this method is based on an HPLC technique, the use of ultraviolet (UV) detection is optional on routine samples.

2.2 Prior to the use of this method, appropriate sample preparation techniques must be used.

2.2.1 Samples for analysis of chlorinated phenoxyacid compounds are prepared by a modification of Method 8150 (see Section 7.1.2). In general, one liter of aqueous sample or fifty grams of solid sample are pH adjusted, extracted with diethyl ether, concentrated and solvent exchanged to acetonitrile.

2.2.2 Samples for analysis of the other target analytes are prepared by established extraction techniques. In general, water samples are extracted at a neutral pH with methylene chloride, using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Soxhlet (Method 3540) or ultrasonic (Method 3550) extraction using methylene chloride/acetone (1:1) is used for solid samples. A micro-extraction technique is included for the extraction of Tris-BP from aqueous and non-aqueous matrices.

2.3 An optional thermospray-mass spectrometry/mass spectrometry (TS-MS/MS) confirmatory method is provided. Confirmation is obtained by using MS/MS collision activated dissociation (CAD) or wire-repeller CAD.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, 8000 and 8150/8151.

3.2 The use of Florisil Column Cleanup (Method 3620) has been demonstrated to yield recoveries less than 85% for some of the compounds in this method, and is therefore not recommended for all compounds. Refer to Table 2 of Method 3620 for recoveries of organophosphorus compounds as a function of Florisil fractions.

3.3 Compounds with high proton affinity may mask some of the target analytes. Therefore, an HPLC must be used as a chromatographic separator, for quantitative analysis.

3.4 Analytical difficulties encountered with specific organophosphorus compounds, as applied in this method, may include (but are not limited to) the following:

3.4.1 Methyl parathion shows some minor degradation upon analysis.

3.4.2 Naled can undergo debromination to form dichlorvos.

3.4.3 Merphos often contains contamination from merphos oxide. Oxidation of merphos can occur during storage, and possibly upon introduction into the mass spectrometer.

Refer to Method 8141 for other compound problems as related to the various extraction methods.

3.5 The chlorinated phenoxy acid compounds, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware and glass wool must be acid-rinsed, and sodium sulfate must be acidified with sulfuric acid prior to use to avoid this possibility.

3.6 Due to the reactivity of the chlorinated herbicides, the standards must be prepared in acetonitrile. Methylation will occur if prepared in methanol.

3.7 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts or elevated baselines, or both, causing misinterpretation of chromatograms or spectra. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running reagent blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.8 Interferants co-extracted from the sample will vary considerably from source to source. Retention times of target analytes must be verified by using reference standards.

3.9 The optional use of HPLC/MS/MS methods aids in the confirmation of specific analytes. These methods are less subject to chemical noise than other mass spectrometric methods.

4.0 APPARATUS AND MATERIALS

4.1 HPLC/MS

4.1.1 High Performance Liquid Chromatograph (HPLC) - An analytical system with programmable solvent delivery system and all required accessories including 10 µL injection loop, analytical columns, purging gases, etc. The solvent delivery system must be capable, at a minimum, of a binary solvent system. The chromatographic system must be capable of interfacing with a Mass Spectrometer (MS).

4.1.1.1 HPLC Post-Column Addition Pump - A pump for post column addition should be used. Ideally, this pump should be a syringe pump, and does not have to be capable of solvent programming.

4.1.1.2 Recommended HPLC Columns - A guard column and an analytical column are required.

4.1.1.2.1 Guard Column - C_{18} reverse phase guard column, 10 mm x 2.6 mm ID, 0.5 µm frit, or equivalent.

4.1.1.2.2 Analytical Column - C_{18} reverse phase column, 100 mm x 2 mm ID, 5 µm particle size of ODS-Hypersil; or C_8 reversed phase column, 100 mm x 2 mm ID, 3 µm particle size of MOS2-Hypersil, or equivalent.

4.1.2 HPLC/MS interface(s)

4.1.2.1 Micromixer - 10 µL, interfaces HPLC column system with HPLC post-column addition solvent system.

4.1.2.2 Interface - Thermospray ionization interface and source that will give acceptable calibration response for each analyte of interest at the concentration required. The source must be capable of generating both positive and negative ions, and have a discharge electrode or filament.

4.1.3 Mass spectrometer system - A single quadrupole mass spectrometer capable of scanning from 1 to 1000 amu. The spectrometer must also be capable of scanning from 150 to 450 amu in 1.5 sec or less, using 70 volts (nominal) electron energy in the positive or negative electron impact modes. In addition, the mass spectrometer must be capable of producing a calibrated mass spectrum for PEG 400, 600, or 800 (see Section 5.14).

4.1.3.1 Optional triple quadrupole mass spectrometer - capable of generating daughter ion spectra with a collision gas in the second quadrupole and operation in the single quadrupole mode.

4.1.4 Data System - A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows any MS data file to be searched for ions of a specified mass, and such ion abundances to be plotted 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 integration of the abundances in any EICP between specified time or scan-number limits. There must be computer software available to operate the specific modes of the mass spectrometer.

4.2 HPLC with UV detector - An analytical system with solvent programmable pumping system for at least a binary solvent system, and all required accessories including syringes, 10 µL injection loop, analytical columns, purging gases, etc. An automatic injector is optional, but is useful for multiple samples. The columns specified in Section 4.1.1.2 are also used with this system.

4.2.1 If the UV detector is to be used in tandem with the thermospray interface, then the detector cell must be capable of withstanding high pressures (up to 6000 psi). However, the UV detector may be attached to an HPLC independent of the HPLC/TS/MS and in that case standard HPLC pressures are acceptable.

4.3 Purification Equipment for Azo Dye Standards

4.3.1 Soxhlet extraction apparatus.

4.3.2 Extraction thimbles, single thickness, 43 x 123 mm.

4.3.3 Filter paper, 9.0 cm (Whatman qualitative No. 1 or equivalent).

4.3.4 Silica-gel column - 3 in. x 8 in., packed with Silica gel (Type 60, EM reagent 70/230 mesh).

4.4 Extraction equipment for Chlorinated Phenoxyacid Compounds

4.4.1 Erlenmeyer flasks - 500-mL wide-mouth Pyrex, 500-mL Pyrex, with 24/40 ground glass joint, 1000-mL pyrex.

4.4.2 Separatory funnel - 2000 mL.

4.4.3 Graduated cylinder - 1000 mL.

4.4.4 Funnel - 75 mm diameter.

4.4.5 Wrist shaker - Burrell Model 75 or equivalent.

4.4.6 pH meter.

4.5 Kuderna-Danish (K-D) apparatus (optional).

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

4.5.4 Springs - 1/2 in. (Kontes K-662750 or equivalent).

4.6 Disposable serological pipets - 5 mL x 1/10, 5.5 mm ID.

4.7 Collection tube - 15 mL conical, graduated (Kimble No. 45165 or equivalent).

4.8 Vials - 5 mL conical, glass, with Teflon lined screw-caps or crimp tops.

4.9 Glass wool - Supelco No. 2-0411 or equivalent.

4.10 Microsyringes - 100 µL, 50 µL, 10 µL (Hamilton 701 N or equivalent), and 50 µL (Blunted, Hamilton 705SNR or equivalent).

4.11 Rotary evaporator - Equipped with 1000 mL receiving flask.

4.12 Balances - Analytical, 0.0001 g, Top-loading, 0.01 g.

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

4.14 Graduated cylinder - 100 mL.

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

5.4 Ammonium acetate, NH_4OOCCH_3, solution (0.1 M). Filter through a 0.45 micron membrane filter (Millipore HA or equivalent).

5.5 Acetic acid, CH_3CO_2H

5.6 Sulfuric acid solution

5.6.1 ((1:1) (v/v)) - Slowly add 50 mL H_2SO_4 (sp. gr. 1.84) to 50 mL of water.

5.6.2 ((1:3) (v/v)) - slowly add 25 mL H_2SO_4 (sp. gr. 1.84) to 75 mL of water.

5.7 Argon gas, 99+% pure.

5.8 Solvents

5.8.1 Methylene chloride, CH_2Cl_2 - Pesticide quality or equivalent.

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

5.8.3 Acetone, CH_3COCH_3 - Pesticide quality or equivalent.

5.8.4 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.

5.8.5 Methanol, CH_3OH - HPLC quality or equivalent.

5.8.6 Acetonitrile, CH_3CN - HPLC quality or equivalent.

5.8.7 Ethyl acetate $CH_3CO_2C_2H_5$ - Pesticide quality or equivalent.

5.9 Standard Materials - pure standard materials or certified solutions of each analyte targeted for analysis. Disperse azo dyes must be purified before use according to Section 5.10.

5.10 Disperse Azo Dye Purification

5.10.1 Two procedures are involved. The first step is the Soxhlet extraction of the dye for 24 hours with toluene and evaporation of the liquid extract to dryness, using a rotary evaporator. The solid is then recrystallized from toluene, and dried in an oven at approximately 100°C. If this step does not give the required purity, column chromatography should be employed. Load the solid onto a 3 x 8 inch silica gel column (Section 4.3.4), and elute with diethyl ether. Separate impurities chromatographically, and collect the major dye fraction.

5.11 Stock standard solutions - Can be prepared from pure standard materials or can be purchased as certified solutions. Commercially prepared stock standards can be used if they are verified against EPA standards. If EPA

standards are not available for verification, then standards certified by the manufacturer and verified against a standard made from pure material is acceptable.

5.11.1 Prepare stock standard solutions by accurately weighing 0.0100 g of pure material. Dissolve the material in methanol or other suitable solvent (e.g. prepare Tris-BP in ethyl acetate), and dilute to known volume in a volumetric flask.

NOTE: Due to the reactivity of the chlorinated herbicides, the standards must be prepared in acetonitrile. Methylation will occur if prepared in methanol.

If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.11.2 Transfer the stock standard solutions into glass vials with Teflon lined screw-caps or crimp-tops. 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.

5.12 Calibration standards - A minimum of five concentrations for each parameter of interest should be prepared through dilution of the stock standards with methanol (or other suitable solvent). One of these concentrations should be near, but above, the MDL. The remaining concentrations should correspond to the expected range of concentrations found in real samples, or should define the working range of the HPLC-UV/VIS or HPLC-TSP/MS. Calibration standards must be replaced after one or two months, or sooner if comparison with check standards indicates a problem.

5.13 Surrogate standards - The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system, along with the effectiveness of the method in dealing with each sample matrix, by spiking each sample, standard, and blank with one or two surrogates (e.g., organophosphorus or chlorinated phenoxyacid compounds not expected to be present in the sample).

5.14 HPLC/MS tuning standard - Polyethylene glycol 400 (PEG-400), PEG-600 or PEG-800. Dilute to 10 percent (v/v) in methanol. Dependent upon analyte molecular weight range: m.w. < 500 amu, use PEG-400; m.w. > 500 amu, use PEG-600, or PEG-800.

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 for analysis of disperse azo dyes and organophosphorus compounds must be prepared by one of the following methods prior to HPLC/MS analysis:

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

Samples for the analysis of Tris-(2,3-dibromopropyl)phosphate wastewater must be prepared according to Section 7.1.1 prior to HPLC/MS analysis. Samples for the analysis of chlorinated phenoxyacid compounds and their esters must be prepared according to Section 7.1.2 prior to HPLC/MS analysis.

7.1.1 Microextraction for Tris-BP:

7.1.1.1 Solid Samples

7.1.1.1.1 Weigh a 1 gram portion of the sample into a tared beaker. If the sample appears moist, add an equivalent amount of anhydrous sodium sulfate and mix well. Add 100 µL of Tris-BP (approximate concentration 1000 mg/L) to the sample selected for spiking; the amount added should result in a final concentration of 100 ng/µL in the 1 mL extract.

7.1.1.1.2 Remove the glass wool plug from a disposable serological pipet. Insert a 1 cm plug of clean silane treated glass wool to the bottom (narrow end) of the pipet. Pack 2 cm of anhydrous sodium sulfate onto the top of the glass wool. Wash pipet and contents with 3 - 5 mL of methanol.

7.1.1.1.3 Pack the sample into the pipet prepared according to Section 7.1.1.1.2. If packing material has dried, wet with a few mL of methanol first, then pack sample into the pipet.

7.1.1.1.4 Extract the sample with 3 mL of methanol followed by 4 mL of 50% (v/v) methanol/methylene chloride (rinse the sample beaker with each volume of extraction solvent prior to adding it to the pipet containing the sample). Collect the extract in a 15 mL graduated glass tube.

7.1.1.1.5 Evaporate the extract to 1 mL using the nitrogen blowdown technique (Section 7.1.1.1.6). Record the volume. It may not be possible to evaporate some sludge samples to a reasonable concentration.

7.1.1.1.6 Nitrogen Blowdown Technique

7.1.1.1.6.1 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.

7.1.1.1.6.2 The internal wall of the tube must be rinsed down several times with methylene chloride 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. Proceed to Section 7.1.1.1.7.

7.1.1.1.7 Transfer the extract to a glass vial with a Teflon lined screw-cap or crimp-top and store refrigerated at 4°C. Proceed with HPLC analysis.

7.1.1.1.8 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.

7.1.1.1.9 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:

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

7.1.1.2 Aqueous Samples

7.1.1.2.1 Using a 100 mL graduated cylinder, measure 100 mL of sample and transfer it to a 250 mL separatory funnel. Add 200 µL of Tris-BP (approximate concentration

1000 mg/L) to the sample selected for spiking; the amount added should result in a final concentration of 200 ng/µL in the 1 mL extract.

7.1.1.2.2 Add 10 mL of methylene chloride to the separatory funnel. Seal and shake the separatory funnel three times, approximately 30 seconds each time, with periodic venting to release excess pressure. NOTE: Methylene chloride creates excessive pressure rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once. Methylene chloride is a suspected carcinogen, use necessary safety precautions.

7.1.1.2.3 Allow the organic layer to separate from the water 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 phase separation. See Section 7.5, Method 3510.

7.1.1.2.4 Collect the extract in a 15 mL graduated glass tube. Proceed as in Section 7.1.1.1.4.

7.1.2 Extraction for chlorinated phenoxyacid compounds - Preparation of soil, sediment, and other solid samples must follow Method 8150, with the exception of no hydrolysis or esterification. Section 7.1.2.1 presents an outline of the procedure with the appropriate changes necessary for determination by Method 8321. Section 7.1.2.2 describes the extraction procedure for aqueous samples.

7.1.2.1 Extraction of solid samples

7.1.2.1.1 Add 50 g of soil/sediment sample to a 500 mL, wide mouth Erlenmeyer. Add spiking solutions if required, mix well and allow to stand for 15 minutes. Add 50 mL of organic-free reagent water and stir for 30 minutes. Determine the pH of the sample with a glass electrode and pH meter, while stirring. Adjust the pH to 2 with cold H_2SO_4 (1:1) and monitor the pH for 15 minutes, with stirring. If necessary, add additional H_2SO_4 until the pH remains at 2.

7.1.2.1.2 Add 20 mL of acetone to the flask, and mix the contents with the wrist shaker for 20 minutes. Add 80 mL of diethyl ether to the same flask, and shake again for 20 minutes. Decant the extract and measure the volume of solvent recovered.

7.1.2.1.3 Extract the sample twice more using 20 mL of acetone followed by 80 mL of diethyl ether. After addition of each solvent, the mixture should be shaken with the wrist shaker for 10 minutes and the acetone-ether extract decanted.

7.1.2.1.4 After the third extraction, the volume of extract recovered should be at least 75% of the volume of added solvent. If this is not the case, additional extractions may be necessary. Combine the extracts in a 2000 mL separatory funnel containing 250 mL of 5% acidified sodium sulfate. If an emulsion forms, slowly add 5 g of acidified sodium sulfate (anhydrous) until the solvent-water mixture separates. A quantity of acidified sodium sulfate equal to the weight of the sample may be added, if necessary.

7.1.2.1.5 Check the pH of the extract. If it is not at or below pH 2, add more concentrated HCl until the extract is stabilized at the desired pH. Gently mix the contents of the separatory funnel for 1 minute and allow the layers to separate. Collect the aqueous phase in a clean beaker, and the extract phase (top layer) in a 500 mL ground-glass Erlenmeyer flask. Place the aqueous phase back into the separatory funnel and re-extract using 25 mL of diethyl ether. Allow the layers to separate and discard the aqueous layer. Combine the ether extracts in the 500 mL Erlenmeyer flask.

7.1.2.1.6 Add 45 - 50 g acidified anhydrous sodium sulfate to the combined ether extracts. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hours.

NOTE: The drying step is very critical. Any moisture remaining in the ether will result in low recoveries. The amount of sodium sulfate used is adequate if some free flowing crystals are visible when swirling the flask. If all of the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate and again test by swirling. The 2 hour drying time is a minimum; however, the extracts may be held overnight in contact with the sodium sulfate.

7.1.2.1.7 Transfer the ether extract, through a funnel plugged with acid-washed glass wool, into a 500 mL K-D flask equipped with a 10 mL concentrator tube. Use a glass rod to crush caked sodium sulfate during the transfer. Rinse the Erlenmeyer flask and column with 20-30 mL of diethyl ether to complete the quantitative transfer. Reduce the volume of the extract using the macro K-D technique (Section 7.1.2.1.8).

7.1.2.1.8 Add one or two clean boiling chips to the flask and attach a three ball macro-Snyder column. Prewet the Snyder column by adding about 1 mL of diethyl ether to the top. Place the apparatus on a hot water bath (60°-65°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in vapor. 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 5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.1.2.1.9 Exchange the solvent of the extract to acetonitrile by quantitatively transferring the extract with acetonitrile to a blow-down apparatus. Add a total of 5 mL acetonitrile. Reduce the extract volume according to Section 7.1.1.1.6, and adjust the final volume to 1 mL.

7.1.2.2 Preparation of aqueous samples

7.1.2.2.1 Using a 1000 mL graduated cylinder, measure 1 liter (nominal) of sample, record the sample volume to the nearest 5 mL, and transfer it to a separatory funnel. If high concentrations are anticipated, a smaller volume may be used and then diluted with organic-free reagent water to 1 liter. Adjust the pH to less than 2 with sulfuric acid (1:1).

7.1.2.2.2 Add 150 mL of diethyl ether to the sample bottle, seal, and shake for 30 seconds to rinse the walls. Transfer the solvent wash to the separatory funnel and extract the sample by shaking the funnel for 2 minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water layer 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. Drain the aqueous phase into a 1000 mL Erlenmeyer flask.

7.1.2.2.3 Repeat the extraction two more times using 100 mL of diethyl ether each time. Combine the extracts in a 500 mL Erlenmeyer flask. (Rinse the 1000 mL flask with each additional aliquot of extracting solvent to make a quantitative transfer.)

7.1.2.2.4 Proceed to Section 7.1.2.1.6 (drying, K-D concentration, solvent exchange, and final volume adjustment).

7.2 Prior to HPLC analysis, the extraction solvent must be exchanged to methanol or acetonitrile (Section 7.1.2.1.9). The exchange is performed using the K-D procedures listed in all of the extraction methods.

7.3 HPLC Chromatographic Conditions:

7.3.1 Analyte-specific chromatographic conditions are shown in Table 1. Chromatographic conditions which are not analyte-specific are as follows:

Flow rate:	0.4 mL/min
Post-column mobile phase:	0.1 M ammonium acetate (1% methanol) (0.1 M ammonium acetate for phenoxyacid compounds)
Post-column flow rate:	0.8 mL/min

7.3.2 If there is a chromatographic problem from compound retention when analyzing for disperse azo dyes, organophosphorus compounds, and Tris-(2,3-dibromopropyl)phosphate, a 2% constant flow of methylene chloride may be applied as needed. Methylene chloride/aqueous methanol solutions must be used with caution as HPLC eluants. Acetic acid (1%), another mobile phase modifier, can be used with compounds with acid functional groups.

7.3.3 A total flow rate of 1.0 to 1.5 mL/min is necessary to maintain thermospray ionization.

7.3.4 Retention times for organophosphorus compounds on the specified analytical column are presented in Table 9.

7.4 Recommended HPLC/Thermospray/MS operating conditions:

7.4.1 Positive Ionization mode

Repeller (wire or plate, optional): 170 to 250 v (sensitivity optimized). See Figure 2 for schematic of source with wire repeller.

Mass range: 150 to 450 amu (compound dependent, expect 1 to 18 amu higher than molecular weight of the compound).
Scan time: 1.50 sec/scan.

7.4.2 Negative Ionization mode

Discharge electrode:	on
Filament:	off
Mass Range:	135 to 450 amu
Scan time:	1.50 sec/scan.

7.4.3 Thermospray temperatures:

Vaporizer control	110°C to 130°C.
Vaporizer tip	200°C to 215°C.
Jet	210°C to 220°C.
Source block	230°C to 265°C. (Some compounds may degrade in the source block at higher temperatures, operator should use knowledge of chemical properties to estimate proper source temperature).

7.4.4 Sample injection volume: 20 µL is necessary in order to overfill the 10 µL injection loop. If solids are present in the extract, allow them to settle or centrifuge the extract and withdraw the injection volume from the clear layer.

7.5 Calibration:

7.5.1 Thermospray/MS system - Must be hardware-tuned on quadrupole 1 (and quadrupole 3 for triple quadrupoles) for accurate mass assignment, sensitivity, and resolution. This is accomplished using polyethylene glycol (PEG) 400, 600, or 800 (see Section 5.14) which has average molecular weights of 400, 600, and 800, respectively. A mixture of these PEGs can be made such that it will approximate the expected working mass range for the analyses. Use PEG 400 for analysis of chlorinated phenoxyacid compounds. The PEG is introduced via the thermospray interface, circumventing the HPLC.

7.5.1.1 The mass calibration parameters are as follows:

for PEG 400 and 600	for PEG 800
Mass range: 15 to 765 amu	Mass range: 15 to 900 amu
Scan time: 5.00 sec/scan	Scan time: 5.00 sec/scan

Approximately 100 scans should be acquired, with 2 to 3 injections made. The scan with the best fit to the accurate mass table (see Tables 7 and 8) should be used as the calibration table.

7.5.1.2 The low mass range from 15 to 100 amu is covered by the ions from the ammonium acetate buffer used in the thermospray process: NH_4^+ (18 amu), $NH_4^+ \cdot H_2O$ (36), $CH_3OH \cdot NH_4^+$ (50) (methanol), or $CH_3CN \cdot NH_4^+$ (59) (acetonitrile), and $CH_3COOH \cdot NH_4^+$ (78) (acetic acid). The appearance of the m/z 50 or 59 ion depends upon the use of methanol or acetonitrile as the organic modifier. The higher mass range is covered by the ammonium ion adducts of the various ethylene glycols (e.g. $H(OCH_2CH_2)_nOH$ where n=4, gives the $H(OCH_2CH_2)_4OH \cdot NH_4^+$ ion at m/z 212).

7.5.2 Liquid Chromatograph

7.5.2.1 Prepare calibration standards as outlined in Section 5.12.

7.5.2.2 Choose the proper ionization conditions, as outlined in Section 7.4. Inject each calibration standard onto the HPLC, using the chromatographic conditions outlined in Table 1. Calculate the area under the curve for the mass chromatogram of each quantitation ion. For example, Table 9 lists the retention times and the major ions (>5%) present in the positive ionization thermospray single quadrupole spectra of the organophosphorus compounds. In most cases the $(M^+H)^+$ and $(M^+NH_4)^+$ adduct ions are the only ions of significant abundance. Plot these ions as area response versus the amount injected. The points should fall on a straight line, with a correlation coefficient of at least 0.99 (0.97 for chlorinated phenoxyacid analytes).

7.5.2.3 If HPLC-UV detection is also being used, calibrate the instrument by preparing calibration standards as outlined in Section 5.12, and injecting each calibration standard onto the HPLC using the chromatographic conditions outlined in Table 1. Integrate the area under the full chromatographic peak for each concentration. Quantitation by HPLC-UV may be preferred if it is known that sample interference and/or analyte coelution are not a problem.

7.5.2.4 For the methods specified in Section 7.5.2.2 and 7.5.2.3, the retention time of the chromatographic peak is an important variable in analyte identification. Therefore, the ratio of the retention time of the sample analyte to the standard analyte should be 1.0 - 0.1.

7.5.2.5 The concentration of the sample analyte will be determined by using the calibration curves determined in Sections 7.5.2.2 and 7.5.2.3. These calibration curves must be generated on the same day as each sample is analyzed. At least duplicate determinations must be made for each sample extract. Samples whose concentrations exceed the standard calibration range should be diluted to fall within the range.

7.5.2.6 Refer to Method 8000 for further information on calculations.

7.5.2.7 Precision can also be calculated from the ratio of response (area) to the amount injected; this is defined as the calibration factor (CF) for each standard concentration. If the percent relative standard deviation (%RSD) of the CF is less than 20 percent over the working range, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve. The CF and %RSD can be calculated as follows:

CF = Total Area of Peak/Mass injected (ng)

$\%RSD = SD/\overline{CF} \times 100$

where:

SD = Standard deviation between CFs

$\overline{CF}$ = Average CF

7.5.2.8 The working calibration curve, or the CF, must be verified on each working day by the injection of one or more calibration standards. If the response varies from the predicted response by more than $\pm$ 20 percent, a new calibration curve must be prepared. The % Difference is calculated as follows:

$\%\ Difference = (R_1 - R_2)/R_1 \times 100.$

where:

R_1 = CF first analysis.
R_2 = CF from succeeding analyses.

7.6 Sample Analysis

7.6.1 Once the LC/MS system has been calibrated as outlined in Section 7.5, then it is ready for sample analysis. It is recommended that the samples be initially analyzed in the negative ionization mode. If low levels of compounds are suspected then the samples should also be screened in the positive ionization mode.

7.6.1.1 A blank 20 µL injection (methanol) must be analyzed after the standard(s) analyses, in order to determine any residual contamination of the Thermospray/HPLC/MS system.

7.6.1.2 Take a 20 µL aliquot of the sample extract from Section 7.4.4. Start the HPLC gradient elution, load and inject the sample aliquot, and start the mass spectrometer data system analysis.

7.7 Calculations

7.7.1 Using the external standard calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample reconstructed ion chromatogram which corresponds to the compounds used for calibration processes. See Method 8000 for calculation equations.

7.7.2 The retention time of the chromatographic peak is an important parameter for the identity of the analyte. However, because matrix interferences can change chromatographic column conditions, the retention times are not as significant, and the mass spectra confirmations are important criteria for analyte identification.

8.0 QUALITY CONTROL

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

8.2 Tables 4, 5, 6, 11, 12, and 15 indicate the single operator accuracy and precision for this method. Compare the results obtained with the results in the tables to determine if the data quality is acceptable. Tables 4, 5, and 6 provide single lab data for Disperse Red 1, Table 11 with organophoshorus pesticides, Table 12 with Tris-BP and Table 15 with chlorophenoxyacid herbicides.

8.2.1 If recovery is not acceptable, check the following:

8.2.1.1 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.

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

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

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

8.3 Instrument performance - Check the performance of the entire analytical system daily using data gathered from analyses of blanks, standards, and replicate samples.

8.3.1 See Section 7.5.2.7 for required HPLC/MS parameters for standard calibration curve %RSD limits.

8.3.2 See Section 7.5.2.4 regarding retention time window QC limits.

8.3.3 If any of the chromatographic QC limits are not met, the analyst should examine the LC system for:

- Leaks,
- Proper pressure delivery,
- A dirty guard column; may need replacing or repacking, and
- Possible partial thermospray plugging.

Any of the above items will necessitate shutting down the HPLC/TSP system, making repairs and/or replacements, and then restarting the analyses. The calibration standard should be reanalyzed before any sample analyses, as described in Section 7.5.

8.3.4 The experience of the analyst performing liquid chromatography is invaluable to the success of the method. Each day that analysis is performed, the daily calibration standard should be evaluated to determine if the chromatographic system is operating properly. If any changes are made to the system (e.g. column change), the system must be recalibrated.

8.4 Optional Thermospray HPLC/MS/MS confirmation

8.4.1 With respect to this method, MS/MS shall be defined as the daughter ion collision activated dissociation acquisition with quadrupole one set on one mass (parent ion), quadrupole two pressurized with argon and with a higher offset voltage than normal, and quadrupole three set to scan desired mass range.

8.4.2 Since the thermospray process often generates only one or two ions per compound, the use of MS/MS is a more specific mode of operation yielding molecular structural information. In this mode, fast screening of samples can be accomplished through direct injection of the sample into the thermospray.

8.4.3 For MS/MS experiments, the first quadrupole should be set to the protonated molecule or ammoniated adduct of the analyte of interest. The third quadrupole should be set to scan from 30 amu to just above the mass region of the protonated molecule.

8.4.4 The collision gas pressure (Ar) should be set at about 1.0 mTorr and the collision energy at 20 eV. If these parameters fail to give considerable fragmentation, they may be raised above these settings to create more and stronger collisions.

8.4.5 For analytical determinations, the base peak of the collision spectrum shall be taken as the quantification ion. For extra specificity, a second ion should be chosen as a backup quantification ion.

8.4.6 Generate a calibration curve as outlined in Section 7.5.2.

8.4.7 For analytical determinations, calibration blanks must be run in the MS/MS mode to determine specific ion interferences. If no calibration blanks are available, chromatographic separation must be performed to assure no interferences at specific masses. For fast screening, the MS/MS spectra of the standard and the analyte could be compared and the ratios of the three major (most intense) ions examined. These ratios should be approximately the same unless there is an interference. If an interference appears, chromatography must be utilized.

8.4.8 For unknown concentrations, the total area of the quantitation ion(s) is calculated and the calibration curves generated as in Section 7.5 are used to attain an injected weight number.

8.4.9 MS/MS techniques can also be used to perform structural analysis on ions represented by unassigned m/z ratios. The procedure for compounds of unknown structures is to set up a CAD experiment on the ion of interest. The spectrum generated from this experiment will reflect the structure of the compound by its fragmentation pattern. A trained mass spectroscopist and some history of the sample are usually needed to interpret the spectrum. (CAD experiments on actual standards of the expected compound are necessary for confirmation or denial of that substance.)

8.5 Optional wire-repeller CAD confirmation

8.5.1 See Figure 3 for the correct position of the wire-repeller in the thermospray source block.

8.5.2 Once the wire-repeller is inserted into the thermospray flow, the voltage can be increased to approximately 500 - 700 v. Enough voltage is necessary to create fragment ions, but not so much that shorting occurs.

8.5.3 Continue as outlined in Section 7.6.

9.0 METHOD PERFORMANCE

9.1 Single operator accuracy and precision studies have been conducted using spiked sediment, wastewater, sludge, and water samples. The results are presented in Tables 4, 5, 6, 11, 12, and 15. Tables 4, 5, and 6 provide single lab data for Disperse Red 1, Table 11 with organophoshorus pesticides, Table 12 with Tris-BP and Table 15 with chlorophenoxyacid herbicides.

9.2 LODs should be calculated for the known analytes, on each instrument to be used. Tables 3, 10, and 13 list limits of detection (LOD) and/or estimated quantitation limits (EQL) that are typical with this method.

9.2.1 The LODs presented in this method were calculated by analyzing three replicates of four standard concentrations, with the lowest concentration being near the instrument detection limit. A linear regression was performed on the data set to calculate the slope and intercept. Three times the standard deviation (3σ) of the lowest standard amount, along with the calculated slope and intercept, was used to find the LOD. The LOD was not calculated using the specifications in Chapter One, but according to the ACS guidelines specified in Reference 4.

9.2.2 Table 17 presents a comparison of the LODs from Method 8150 and Method 8321 for the chlorinated phenoxyacid compounds.

9.3 Table 16 presents multilaboratory accuracy and precision data for the chlorinated phenoxyacid herbicides. The data summary is based on data from three laboratories that analyzed duplicate solvent solutions at each concentration specified in the Table.

10.0 REFERENCES

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TABLE 1.
RECOMMENDED HPLC CHROMATOGRAPHIC CONDITIONS

Initial Mobile Phase (%)	Initial Time (min)	Gradient (linear) (min)	Final Mobile Phase (%)	Final Time (min)
Analytes:				
Organophosphorus Compounds				
50/50 (water/methanol)	0	10	100 (methanol)	5
Azo Dyes (e.g. Disperse Red 1)				
50/50 (water/CH_3CN)	0	5	100 (CH_3CN)	5
Tris-(2,3-dibromopropyl)phosphate				
50/50 (water/methanol)	0	10	100 (methanol)	5
Chlorinated phenoxyacid compounds				
75/25 (A/methanol)	2	15	40/60 (A/methanol)	
40/60 (A/methanol)	3	5	75/25 (A/methanol)	10

Where A = 0.01 M ammonium acetate (1% acetic acid)

TABLE 2.
COMPOUNDS AMENABLE TO THERMOSPRAY MASS SPECTROMETRY

Disperse Azo Dyes	Alkaloids
Methine Dyes	Aromatic ureas
Arylmethane Dyes	Amides
Coumarin Dyes	Amines
Anthraquinone Dyes	Amino acids
Xanthene Dyes	Organophosphorus Compounds
Flame retardants	Chlorinated Phenoxyacid Compounds

TABLE 3.
LIMITS OF DETECTION AND METHOD SENSITIVITIES
FOR DISPERSE RED 1 AND CAFFEINE

Compound	Mode	LOD pg	EQL(7s) pg	EQL(10s) pg
Disperse Red 1	SRM	180	420	600
	Single Quad	600	1400	2000
	CAD	2,000	4700	6700
Caffeine	SRM	45	115	150
	Single Quad	84	200	280
	CAD	240	560	800

EQL = Estimated Quantitation Limit

Data from Reference 16.

TABLE 4.
PRECISION AND ACCURACY COMPARISONS OF MS AND MS/MS WITH HPLC/UV FOR ORGANIC-FREE REAGENT WATER SPIKED WITH DISPERSE RED 1

	Percent Recovery			
Sample	HPLC/UV	MS	CAD	SRM
Spike 1	82.2 ± 0.2	92.5 ± 3.7	87.6 ± 4.6	95.5 ± 17.1
Spike 2	87.4 ± 0.6	90.2 ± 4.7	90.4 ± 9.9	90.0 ± 5.9
RPD	6.1%	2.5%	3.2%	5.9%

Data from Reference 16.

TABLE 5.
PRECISION AND ACCURACY COMPARISONS OF MS AND MS/MS WITH HPLC/UV FOR MUNICIPAL WASTEWATER SPIKED WITH DISPERSE RED 1

	Percent Recovery		
Sample	HPLC/UV	MS	CAD
Spike 1	93.4 ± 0.3	102.0 ± 31	82.7 ± 13
Spike 2	96.2 ± 0.1	79.7 ± 15	83.7 ± 5.2
RPD	3.0%	25%	1.2%

Data from Reference 16.

TABLE 6.
RESULTS FROM ANALYSES OF ACTIVATED SLUDGE PROCESS WASTEWATER

Sample	Recovery of Disperse Red 1 (mg/L) HPLC/UV	MS	CAD
5 mg/L Spiking Concentration			
1	0.721 ± 0.003	0.664 ± 0.030	0.796 ± 0.008
1-D	0.731 ± 0.021	0.600 ± 0.068	0.768 ± 0.093
2	0.279 ± 0.000	0.253 ± 0.052	0.301 ± 0.042
3	0.482 ± 0.001	0.449 ± 0.016	0.510 ± 0.091
RPD	1.3%	10.1%	3.6%
0 mg/L Spiking Concentration			
1	0.000	0.005 ± 0.0007	<0.001
1-D	0.000	0.006 ± 0.001	<0.001
2	0.000	0.002 ± 0.0003	<0.001
3	0.000	0.003 ± 0.0004	<0.001
RPD	--	18.2%	--

Data from Reference 16.

TABLE 7.
CALIBRATION MASSES AND % RELATIVE ABUNDANCES
OF PEG 400

Mass	% Relative Abundances[a]
18.0	32.3
35.06	13.5
36.04	40.5
50.06	94.6
77.04	27.0
168.12	5.4
212.14	10.3
256.17	17.6
300.20	27.0
344.22	45.9
388.25	64.9
432.28	100
476.30	94.6
520.33	81.1
564.35	67.6
608.38	32.4
652.41	16.2
653.41	4.1
696.43	8.1
697.44	2.7

[a] Intensity is normalized to mass 432.

TABLE 8.
CALIBRATION MASSES AND % RELATIVE ABUNDANCES
OF PEG 600

Mass	% Relative Abundances[a]
18.0	4.7
36.04	11.4
50.06	64.9
77.04	17.5
168.12	9.3
212.14	43.9
256.17	56.1
300.20	22.8
344.22	28.1
388.25	38.6
432.28	54.4
476.30	64.9
520.33	86.0
564.35	100
608.38	63.2
652.41	17.5
653.41	5.6
696.43	1.8

[a] Intensity is normalized to mass 564.

TABLE 9.
RETENTION TIMES AND THERMOSPRAY MASS SPECTRA
OF ORGANOPHOSPHORUS COMPOUNDS

Compound	Retention Time (minutes)	Mass Spectra (% Relative Abundance)[a]
Monocrotophos	1:09	241 (100), 224 (14)
Trichlorfon	1:22	274 (100), 257 (19), 238 (19)
Dimethoate	1:28	230 (100), 247 (20)
Dichlorvos	4:40	238 (100), 221 (40)
Naled	9:16	398 (100), 381 (23), 238 (5), 221 (2)
Fensulfothion	9:52	326 (10), 309 (100)
Methyl parathion	10:52	281 (100), 264 (8), 251 (21), 234 (48)
Phorate	13:30	278 (4), 261 (100)
Disulfoton	13:55	292 (10), 275 (100)
Merphos	18:51	315 (100), 299 (15)

[a] For molecules containing Cl, Br and S, only the base peak of the isotopic cluster is listed.

Data from Reference 17.

TABLE 10.
PRECISION AND LIMITS OF DETECTION FOR
ORGANOPHOSPHORUS COMPOUND STANDARDS

Compound	Ion	Standard Quantitation Concentration (ng/µL)	%RSD	MDL (ng)
Dichlorvos	238	2	16	
		12.5	13	
		25	5.7	
		50	4.2	4
Dimethoate	230	2	2.2	
		12.5	4.2	
		25	13	
		50	7.3	2
Phorate	261	2	0.84	
		12.5	14	
		25	7.1	
		50	4.0	2
Disulfoton	275	2	2.2	
		12.5	14	
		25	6.7	
		50	3.0	1
Fensulfothion	309	2	4.1	
		12.5	9.2	
		25	9.8	
		50	2.5	0.4
Naled	398	2	9.5	
		12.5	9.6	
		25	5.2	
		50	6.3	0.2
Merphos	299	2	5.5	
		12.5	17	
		25	3.9	
		50	5.3	1
Methyl parathion	281	2	--	
		12.5	7.1	
		25	4.8	
		50	1.5	30

Data from Reference 17.

TABLE 11.
SINGLE OPERATOR ACCURACY AND PRECISION FOR LOW CONCENTRATION DRINKING WATER (A), LOW CONCENTRATION SOIL (B), MEDIUM CONCENTRATION DRINKING WATER (C), MEDIUM CONCENTRATION SEDIMENT (D)

Compound	Average Recovery (%)	Standard Deviation	Spike Amount	Range of Recovery (%)	Number of Analyses
A			µg/L		
Dimethoate	70	7.7	5	85 - 54	15
Dichlorvos	40	12	5	64 - 14	15
Naled	0.5	1.0	5	2 - 0	15
Fensulfothion	112	3.3	5	119 - 106	15
Methyl parathion	50	28	10	105 - 0	15
Phorate	16	35	5	86 - 0	15
Disulfoton	3.5	8	5	19 - 0	15
Merphos	237	25	5	287 - 187	15
B			µg/g		
Dimethoate	16	4	50	24 - 7	15
Dichlorvos	ND		50		15
Naled	ND		50		15
Fensulfothion	45	5	50	56 - 34	15
Methyl parathion	ND		100		15
Phorate	78	15	50	109 - 48	15
Disulfoton	36	7	50	49 - 22	15
Merphos	118	19	50	155 - 81	15
C			µg/L		
Dimethoate	52	4	50	61 - 43	12
Dichlorvos	146	29	50	204 - 89	12
Naled	4	3	50	9 - 0	12
Fensulfothion	65	7	50	79 - 51	12
Methyl parathion	85	24	100	133 - 37	12
Phorate	10	15	50	41 - 0	12
Disulfoton	2	1	50	4 - 0	12
Merphos	101	13	50	126 - 75	12
D			mg/kg		
Dimethoate	74	8.5	2	91 - 57	15
Dichlorvos	166	25	2	216 - 115	15
Naled	ND		2		15
Fensulfothion	72	8.6	2	90 - 55	15
Methyl parathion	84	9	3	102 - 66	15
Phorate	58	6	2	70 - 46	15
Disulfoton	56	5	2	66 - 47	15
Merphos	78	4	2	86 - 70	12

Data from Reference 17.

TABLE 12.
SINGLE OPERATOR ACCURACY AND PRECISION FOR MUNICIPAL WASTE WATER (A), DRINKING WATER (B), CHEMICAL SLUDGE WASTE (C)

Compound		Average Recovery (%)	Standard Deviation	Spike Amount (ng/µL)	Range of % Recovery	Number of Analyses
Tris-BP	(A)	25	8.0	2	41 - 9.0	15
	(B)	40	5.0	2	50 - 30	12
	(C)	63	11	100	84 - 42	8

Data from Reference 18.

TABLE 13.
SINGLE OPERATOR EQL TABLE FOR TRIS-BP

Concentration (ng/µL)	Average Area	Standard Deviation	3*Std Dev.	7*Std Dev.	10*Std Dev.
50	2675	782	2347	5476	7823
100	5091	558			
150	7674	2090			
200	8379	2030			

LOD (ng/µL)	Lower EQL (ng/µL)	Upper EQL (ng/µL)
33	113	172

Data from Reference 18.
EQL = Estimated Quantitation Limit

TABLE 14
LIMITS OF DETECTION IN THE POSITIVE AND NEGATIVE ION MODES
FOR THE CHLORINATED PHENOXYACID HERBICIDES AND FOUR ESTERS

Compound	Positive Mode Quantitation Ion	LOD (ng)	Negative Mode Quantitation Ion	LOD (ng)
Dalapon	Not detected		141 $(M^-H)^-$	11
Dicamba	238 $(M^+NH_4)^+$	13	184 $(M^-HCl)^-$	3.0
2,4-D	238 $(M^+NH_4)^+$	2.9	184 $(M^-HCl)^-$	50
MCPA	218 $(M^+NH_4)^+$	120	199 $(M^-1)^-$	28
Dichlorprop	252 $(M^+NH_4)^+$	2.7	235 $(M^-1)^-$	25
MCPP	232 $(M^+NH_4)^+$	5.0	213 $(M^-1)^-$	12
2,4,5-T	272 $(M^+NH_4)^+$	170	218 $(M^-HCl)^-$	6.5
2,4,5-TP (Silvex)	286 $(M^+NH_4)^+$	160	269 $(M^-1)^-$	43
Dinoseb	228 $(M^+NH_4-NO)^+$	24	240 $(M)^-$	19
2,4-DB	266 $(M^+NH_4)^+$	3.4	247 $(M^-1)^-$	110
2,4-D,Butoxy ethanol ester	321 $(M^+H)^+$	1.4	185 $(M^-C_6H_{13}O_1)^-$	
2,4,5-T,Butoxy ethanol ester	372 $(M^+NH_4)^+$	0.6	195 $(M^-C_8H_{15}O_3)^-$	
2,4,5-T,Butyl ester	328 $(M^+NH_4)^+$	8.6	195 $(M^-C_6H_{11}O_2)^-$	
2,4-D,ethyl-hexyl ester	350 $(M^+NH_4)^+$	1.2	161 $(M^-C_{10}H_{19}O_3)^-$	

Data from Reference 19.

TABLE 15
SINGLE LABORATORY OPERATOR ACCURACY AND PRECISION
FOR THE CHLORINATED PHENOXYACID HERBICIDES

Compound	Average Recovery(%)[a]	Standard Deviation	Spike Amount	Range of Recovery (%)	Number of Analyses
	LOW LEVEL DRINKING WATER			µg/L	
Dicamba	63	22	5	86 - 33	9
2,4-D	26	13	5	37 - 0	9
MCPA	60	23	5	92 - 37	9
MCPP	78	21	5	116 - 54	9
Dichlorprop	43	18	5	61 - 0	9
2,4,5-T	72	31	5	138 - 43	9
Silvex	62	14	5	88 - 46	9
2,4-DB	29	24	5	62 - 0	9
Dinoseb	73	11	5	85 - 49	9
Dalapon	ND	ND	5	ND	9
2,4-D,ester	73	17	5	104 - 48	9
	HIGH LEVEL DRINKING WATER			µg/L	
Dicamba	54	30	50	103 - 26	9
2,4-D	60	35	50	119 - 35	9
MCPA	67	41	50	128 - 32	9
MCPP	66	33	50	122 - 35	9
Dichlorprop	66	33	50	116 - 27	9
2,4,5-T	61	23	50	99 - 44	9
Silvex	74	35	50	132 - 45	9
2,4-DB	83	25	50	120 - 52	9
Dinoseb	91	10	50	102 - 76	9
Dalapon	43	9.6	50	56 - 31	6
2,4-D,ester	97	19	50	130 - 76	9
	LOW LEVEL SAND			µg/g	
Dicamba	117	26	.1	147 - 82	10
2,4-D	147	23	.1	180 -118	10
MCPA	167	79	.1	280 - 78	10
MCPP	142	39	.1	192 - 81	10
Dichlorprop	ND	ND	.1	ND	10
2,4,5-T	134	27	.1	171 - 99	10
Silvex	121	23	.1	154 - 85	10
2,4-DB	199	86	.1	245 - 0	10
Dinoseb	76	74	.1	210 - 6	10
Dalapon	ND	ND	.1	ND	10
2,4-D,ester	180	58	.1	239 - 59	7

[a]All recoveries are in negative ionization mode, except for 2,4-D,ester.
ND = Not Detected.

TABLE 15 (cont.)
SINGLE LABORATORY OPERATOR ACCURACY AND PRECISION
FOR THE CHLORINATED PHENOXYACID HERBICIDES

Compound	Average Recovery(%)[a]	Standard Deviation	Spike Amount	Range of Recovery (%)	Number of Analyses
	HIGH LEVEL SAND			µg/g	
Dicamba	153	33	1	209 -119	9
2,4-D	218	27	1	276 -187	9
MCPA	143	30	1	205 -111	9
MCPP	158	34	1	226 -115	9
Dichlorprop	92	37	1	161 - 51	9
2,4,5-T	160	29	1	204 -131	9
Silvex	176	34	1	225 -141	9
2,4-DB	145	22	1	192 -110	9
Dinoseb	114	28	1	140 - 65	9
Dalapon	287	86	1	418 -166	9
2,4-D,ester	20	3.6	1	25 - 17	7
	LOW LEVEL MUNICIPAL ASH			µg/g	
Dicamba	83	22	.1	104 - 48	9
2,4-D	ND	ND	.1	ND	9
MCPA	ND	ND	.1	ND	9
MCPP	ND	ND	.1	ND	9
Dichlorprop	ND	ND	.1	ND	9
2,4,5-T	27	25	.1	60 - 0	9
Silvex	68	38	.1	128 - 22	9
2,4-DB	ND	ND	.1	ND	9
Dinoseb	44	13	.1	65 - 26	9
Dalapon	ND	ND	.1	ND	9
2,4-D,ester	29	23	.1	53 - 0	6
	HIGH LEVEL MUNICIPAL ASH			µg/g	
Dicamba	66	21	1	96 - 41	9
2,4-D	8.7	4.8	1	21 - 5	9
MCPA	3.2	4.8	1	10 - 0	9
MCPP	10	4.3	1	16 - 4.7	9
Dichlorprop	ND	ND	1	ND	9
2,4,5-T	2.9	1.2	1	3.6- 0	9
Silvex	6.0	3.1	1	12 - 2.8	9
2,4-DB	ND	ND	1	ND	9
Dinoseb	16	6.8	1	23 - 0	9
Dalapon	ND	ND	1	ND	9
2,4-D,ester	1.9	1.7	1	6.7- 0	6

[a]All recoveries are in negative ionization mode, except for 2,4-D,ester.
ND = Not Detected.

TABLE 16
MULTILABORATORY ACCURACY AND PRECISION DATA
FOR THE CHLORINATED PHENOXYACID HERBICIDES

Compounds	Spiking Concentration	Mean (% Recovery)[a]	% Relative Standard Deviation[b]
		500 mg/L	
2,4,5-T		90	23
2,4,5-T,butoxy		90	29
2,4-D		86	17
2,4-DB		95	22
Dalapon		83	13
Dicamba		77	25
Dichlorprop		84	20
Dinoseb		78	15
MCPA		89	11
MCPP		86	12
Silvex		96	27
		50 mg/L	
2,4,5-T		62	68
2,4,5-T,butoxy		85	9
2,4-D		64	80
2,4-DB		104	28
Dalapon		121	99
Dicamba		90	23
Dichlorprop		96	15
Dinoseb		86	57
MCPA		96	20
MCPP		76	74
Silvex		65	71
		5 mg/L	
2,4,5-T		90	28
2,4,5-T,butoxy		99	17
2,4-D		103	31
2,4-DB		96	21
Dalapon		150	4
Dicamba		105	12
Dichlorprop		102	22
Dinoseb		108	30
MCPA		94	18
MCPP		98	15
Silvex		87	15

Data from Reference 20.
[a] Mean of duplicate data from 3 laboratories.
[b] % RSD of duplicate data from 3 laboratories.

TABLE 17
COMPARISON OF LODs: METHOD 8150 vs. METHOD 8321

Ionization Compound	Method 8150 LOD(µg/L)	Method 8321 LOD (µg/L)	Mode
Dalapon	5.8	1.1	(-)
Dicamba	0.27	0.3	(-)
2,4-D	1.2	0.29	(+)
MCPA	249	2.8	(-)
Dichlorprop	0.65	0.27	(+)
MCPP	192	0.50	(+)
2,4,5-T	0.2	0.65	(-)
2,4,5-TP (Silvex)	0.17	4.3	(-)
2,4,-DB	0.91	0.34	(+)
Dinoseb	1.9	1.9	(-)

FIGURE 1.
SCHEMATIC OF THE THERMOSPRAY PROBE AND ION SOURCE

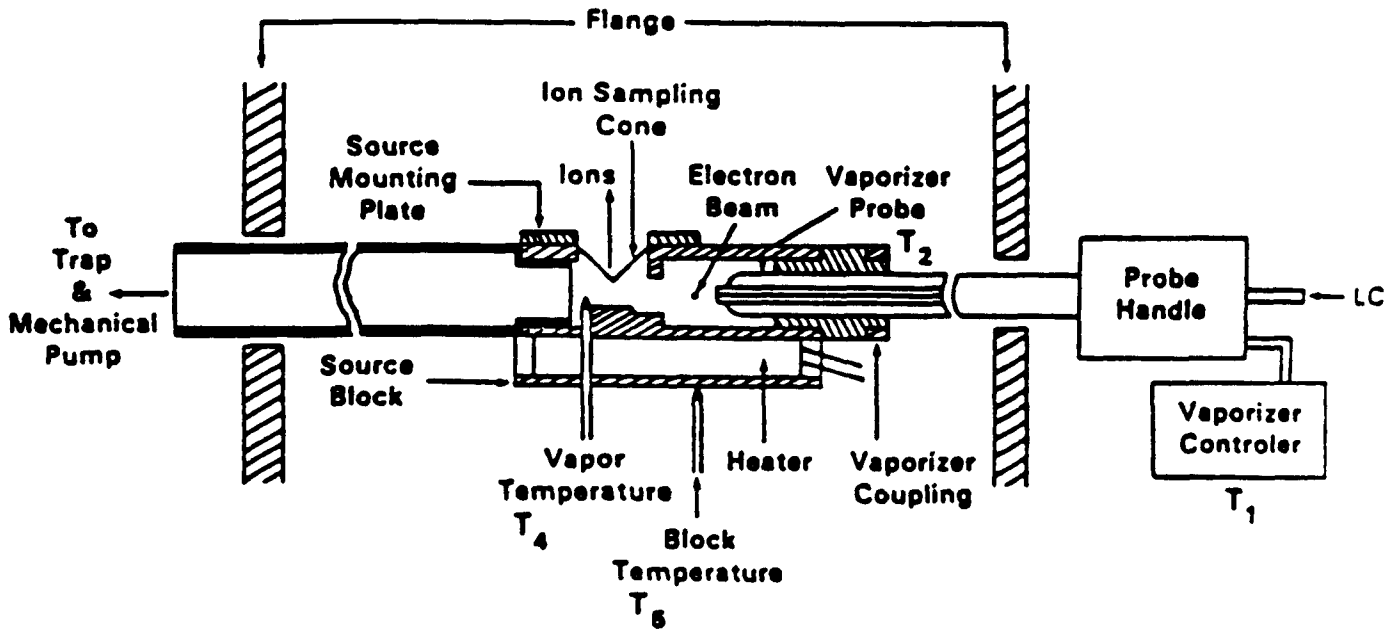


FIGURE 2.
THERMOSPRAY SOURCE WITH WIRE-REPELLER
(High sensitivity configuration)

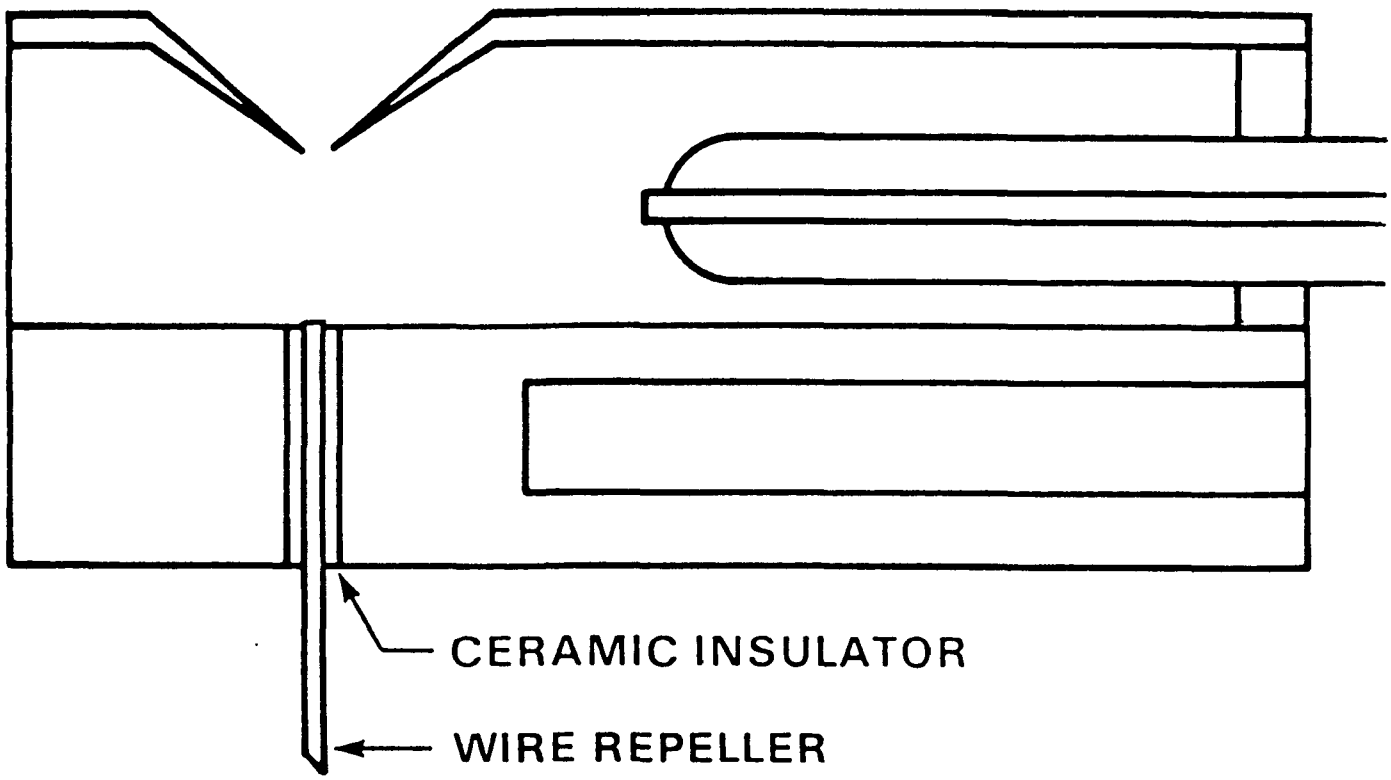
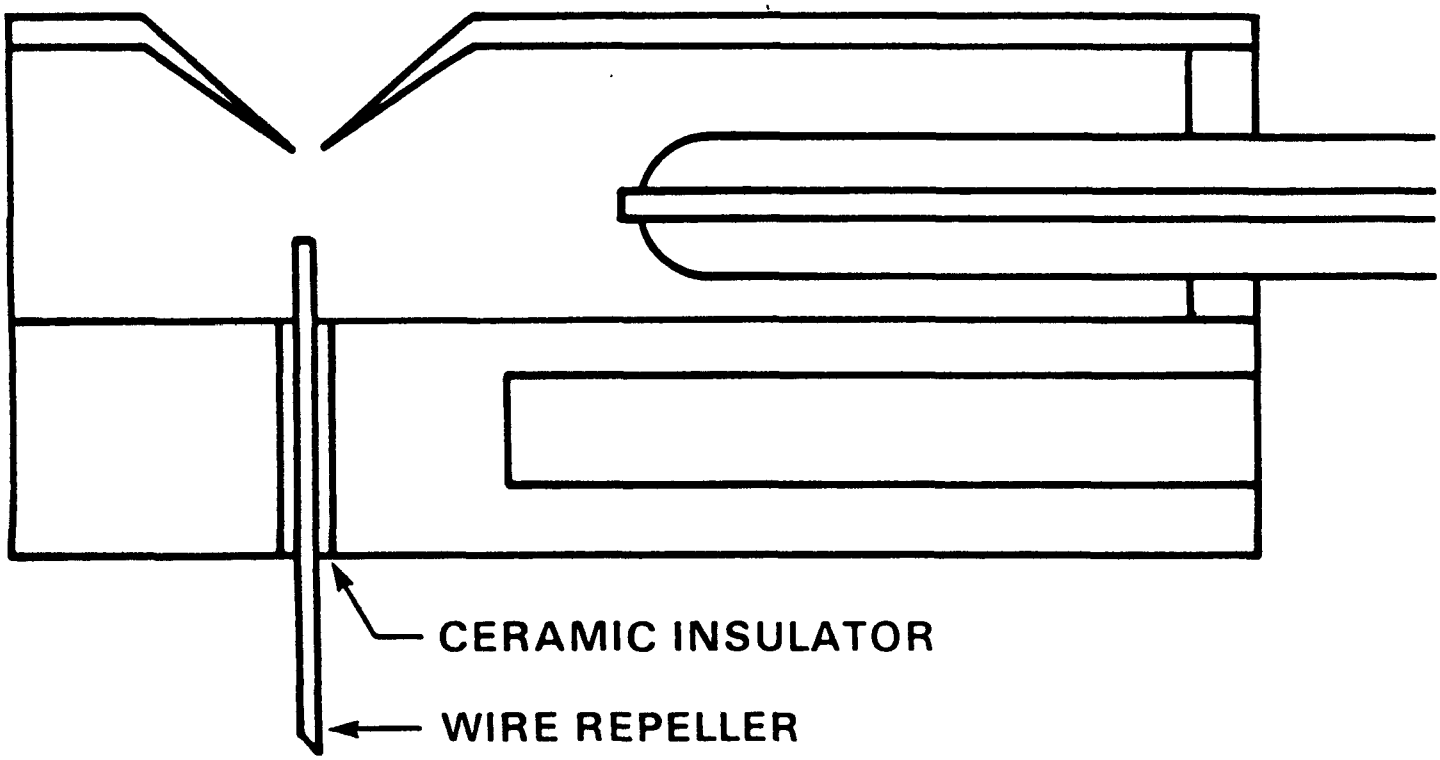
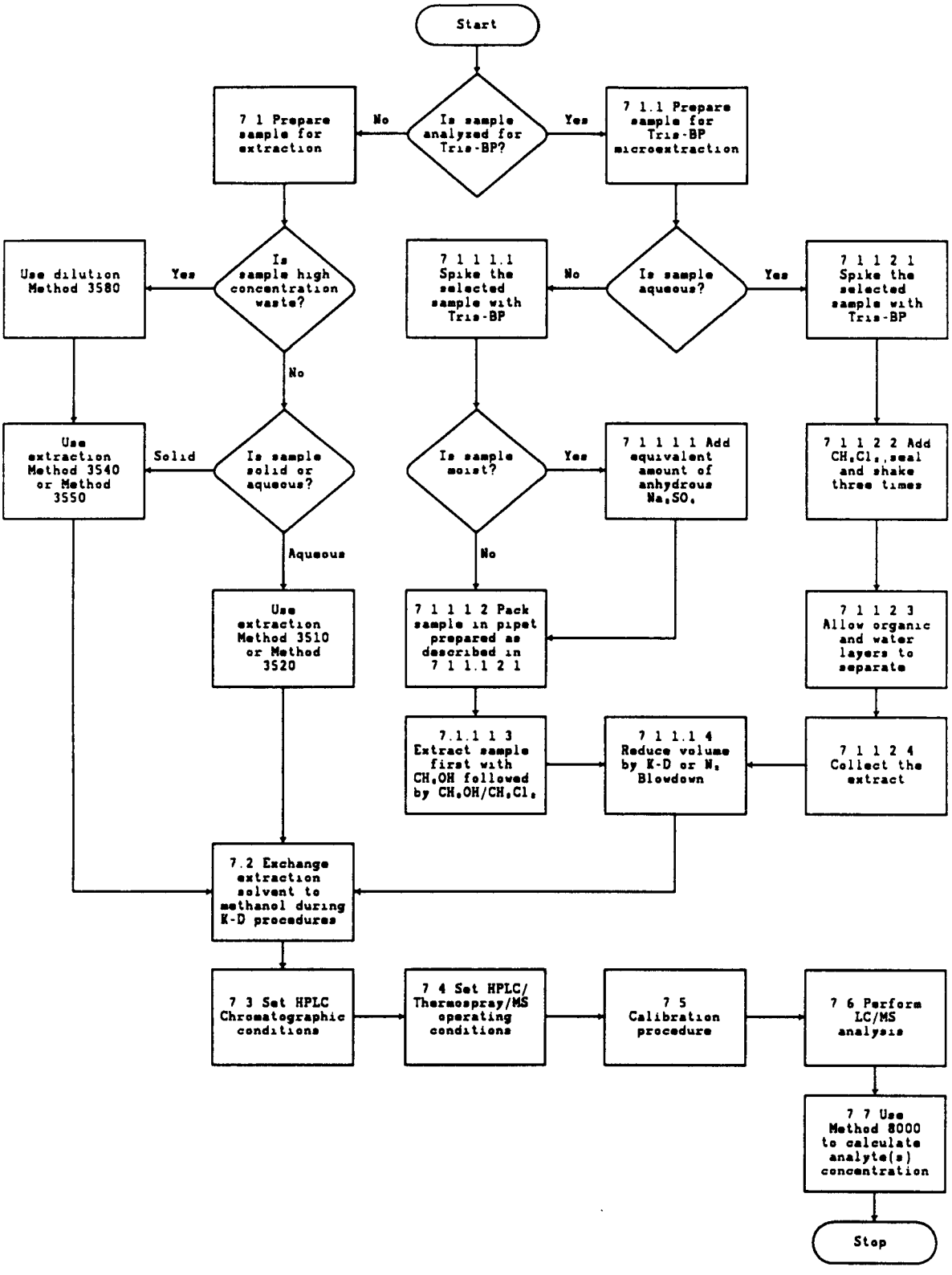


FIGURE 3.
THERMOSPRAY SOURCE WITH WIRE-REPELLER
(CAD configuration)



METHOD 8321
SOLVENT EXTRACTABLE NON-VOLATILE COMPOUNDS BY
HIGH PERFORMANCE LIQUID CHROMATOGRAPHY/THERMOSPRAY/MASS SPECTROMETRY
(HPLC/TSP/MS) OR ULTRAVIOLET (UV) DETECTION



METHOD 8330

NITROAROMATICS AND NITRAMINES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

1.0 SCOPE AND APPLICATION

1.1 Method 8330 is intended for the trace analysis of explosives residues by high performance liquid chromatography using a UV detector. This method is used to determine the concentration of the following compounds in a water, soil, or sediment matrix:

Compound	Abbreviation	CAS No[a]
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	HMX	2691-41-0
Hexahydro-1,3,5-trinitro-1,3,5-triazine	RDX	121-82-4
1,3,5-Trinitrobenzene	1,3,5-TNB	99-35-4
1,3-Dinitrobenzene	1,3-DNB	99-65-0
Methyl-2,4,6-trinitrophenylnitramine	Tetryl	479-45-8
Nitrobenzene	NB	98-95-3
2,4,6-Trinitrotoluene	2,4,6-TNT	118-96-7
4-Amino-2,6-dinitrotoluene	4-Am-DNT	1946-51-0
2-Amino-4, 6-dinitrotoluene	2-Am-DNT	355-72-78-2
2,4-Dinitrotoluene	2,4-DNT	121-14-2
2,6-Dinitrotoluene	2,6-DNT	606-20-2
2-Nitrotoluene	2-NT	88-72-2
3-Nitrotoluene	3-NT	99-08-1
4-Nitrotoluene	4-NT	99-99-0

a Chemical Abstracts Service Registry number

1.2 Method 8330 provides a salting-out extraction procedure for low concentration (parts per trillion or nanograms per liter) of explosives residues in surface or ground water. Direct injection of diluted and filtered water samples can be used for water samples of higher concentration (See Table 1).

1.3 All of these compounds are either used in the manufacture of explosives or are the degradation products of compounds used for that purpose. When making stock solutions for calibration, treat each explosive compound with caution. See NOTE in Section 5.3.1 and Section 11 on Safety.

1.4 The estimated quantitation limits (EQLs) of target analytes determined by Method 8330 in water and soil are presented in Table 1.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of HPLC, skilled in the interpretation of chromatograms, and experienced in handling explosive materials. (See Section 11.0 on SAFETY.) Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Method 8330 provides high performance liquid chromatographic (HPLC) conditions for the detection of ppb levels of certain explosives residues in water, soil and sediment matrix. Prior to use of this method, appropriate sample preparation techniques must be used.

2.2 Low-Level Salting-out Method With No Evaporation: Aqueous samples of low concentration are extracted by a salting-out extraction procedure with acetonitrile and sodium chloride. The small volume of acetonitrile that remains undissolved above the salt water is drawn off and transferred to a smaller volumetric flask. It is back-extracted by vigorous stirring with a specific volume of salt water. After equilibration, the phases are allowed to separate and the small volume of acetonitrile residing in the narrow neck of the volumetric flask is removed using a Pasteur pipet. The concentrated extract is diluted 1:1 with reagent grade water. An aliquot is separated on a C-18 reverse phase column, determined at 254 nm, and confirmed on a CN reverse phase column.

2.3 High-level Direct Injection Method: Aqueous samples of higher concentration can be diluted 1/1 (v/v) with methanol or acetonitrile, filtered, separated on a C-18 reverse phase column, determine at 254 nm, and confirmed on a CN reverse phase column. If HMX is an important target analyte, methanol is preferred.

2.4 Soil and sediment samples are extracted using acetonitrile in an ultrasonic bath, filtered and chromatographed as in Section 2.3.

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts and/or elevated baselines, causing misinterpretation of the chromatograms. All of these materials must be demonstrated to be free from interferences.

3.2 2,4-DNT and 2,6-DNT elute at similar retention times (retention time difference of 0.2 minutes). A large concentration of one isomer may mask the response of the other isomer. If it is not apparent that both isomers are present (or are not detected), an isomeric mixture should be reported.

3.3 Tetryl decomposes rapidly in methanol/water solutions, as well as with heat. All aqueous samples expected to contain tetryl should be diluted with acetonitrile prior to filtration. All samples expected to contain tetryl should not be exposed to temperatures above room temperature.

3.4 Degradation products of tetryl appear as a shoulder on the 2,4,6-TNT peak. Peak heights rather than peak areas should be used when tetryl is present in concentrations that are significant relative to the concentration of 2,4,6-TNT.

4.0 APPARATUS AND MATERIALS

4.1 HPLC system

4.1.1 HPLC - equipped with a pump capable of achieving 4000 psi, a 100 µl loop injector and a 254 nm UV detector (Perkin Elmer Series 3, or equivalent). For the low concentration option, the detector must be capable of a stable baseline at 0.001 absorbance units full scale.

4.1.2 Recommended Columns:

4.1.2.1 Primary column: C-18 Reverse phase HPLC column, 25 cm x 4.6 mm (5 µm), (Supelco LC-18, or equivalent).

4.1.2.2 Secondary column: CN Reverse phase HPLC column, 25 cm x 4.6 mm (5 µm), (Supelco LC-CN, or equivalent).

4.1.3 Strip chart recorder.

4.1.4 Digital integrator (optional).

4.1.5 Autosampler (optional).

4.2 Other Equipment

4.2.1 Temperature controlled ultrasonic bath.

4.2.2 Vortex mixer.

4.2.3 Balance ± 0.0001 g.

4.2.4 Magnetic stirrer with stirring pellets.

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

4.2.6 Oven - Forced air, without heating.

4.3 Materials

4.3.1 High pressure injection syringe - 500 µL, (Hamilton liquid syringe or equivalent).

4.3.2 Disposable cartridge filters - 0.45 µm Teflon filter.

4.3.3 Pipets - Class A, glass, Appropriate sizes.

4.3.4 Pasteur pipets.

4.3.5 Scintillation Vials - 20 mL, glass.

4.3.6 Vials - 15 mL, glass, Teflon-lined cap.

4.3.7 Vials- 40 mL, glass, Teflon-lined cap.

4.3.8 Disposable syringes - Plastipak, 3 mL and 10 mL or equivalent.

4.3.9 Volumetric flasks - Appropriate sizes with ground glass stoppers, Class A.

NOTE: The 100 mL and 1 L volumetric flasks used for magnetic stirrer extraction must be round.

4.3.10 Vacuum desiccator - Glass.

4.3.11 Mortar and pestle - Steel.

4.3.12 Sieve - 30 mesh.

4.3.13 Graduated cylinders - Appropriate sizes.

4.4 Preparation of Materials

4.4.1 Prepare all materials to be used as described in Chapter 4 for semivolatile organics.

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 lowering the accuracy of the determination.

5.1.1 Acetonitrile, CH_3CN - HPLC grade.

5.1.2 Methanol, CH_3OH - HPLC grade.

5.1.3 Calcium chloride, $CaCl_2$ - Reagent grade. Prepare an aqueous solution of 5 g/L.

5.1.4 Sodium chloride, NaCl, shipped in glass bottles - reagent grade.

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

5.3.1 Dry each solid analyte standard to constant weight in a vacuum desiccator in the dark. Place about 0.100 g (weighed to 0.0001 g) of a single analyte into a 100 mL volumetric flask and dilute to volume with acetonitrile. Invert flask several times until dissolved. Store in refrigerator at 4°C in the dark. Calculate the concentration of the stock

solution from the actual weight used (nominal concentration = 1,000 mg/L). Stock solutions may be used for up to one year.

NOTE: The HMX, RDX, Tetryl, and 2,4,6-TNT are explosives and the neat material should be handled carefully. See SAFETY in Section 11 for guidance. HMX, RDX, and Tetryl reference materials are shipped under water. Drying at ambient temperature requires several days. DO NOT DRY AT HEATED TEMPERATURES!

5.4 Intermediate Standards Solutions

5.4.1 If both 2,4-DNT and 2,6-DNT are to be determined, prepare two separate intermediate stock solutions containing (1) HMX, RDX, 1,3,5-TNB, 1,3-DNB, NB, 2,4,6-TNT, and 2,4-DNT and (2) Tetryl, 2,6-DNT, 2-NT, 3-NT, and 4-NT. Intermediate stock standard solutions should be prepared at 1,000 µg/L, in acetonitrile when analyzing soil samples, and in methanol when analyzing aqueous samples.

5.4.2 Dilute the two concentrated intermediate stock solutions, with the appropriate solvent, to prepare intermediate standard solutions that cover the range of 2.5 - 1,000 µg/L. These solutions should be refrigerated on preparation, and may be used for 30 days.

5.4.3 For the low-level method, the analyst must conduct a detection limit study and devise dilution series appropriate to the desired range. Standards for the low level method must be prepared immediately prior to use.

5.5 Working standards

5.5.1 Calibration standards at a minimum of five concentration levels should be prepared through dilution of the intermediate standards solutions by 50% (v/v) with 5 g/L calcium chloride solution (Section 5.1.3). These solutions must be refrigerated and stored in the dark, and prepared fresh on the day of calibration.

5.6 Surrogate Spiking Solution

5.6.1 The analyst should monitor the performance of the extraction and analytical system as well as the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard and reagent water blank with one or two surrogates (e.g., analytes not expected to be present in the sample).

5.7 Matrix Spiking Solutions

5.7.1 Prepare matrix spiking solutions in methanol such that the concentration in the sample is five times the Estimated Quantitation Limit (Table 1). All target analytes should be included.

5.8 HPLC Mobile Phase

5.8.1 To prepare 1 liter of mobile phase, add 500 mL of methanol to 500 mL of organic-free reagent water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Follow conventional sampling and sample handling procedures as specified for semivolatile organics in Chapt. 4.

6.2 Samples and sample extracts must be stored in the dark at 4°C. Holding times are the same as for semivolatile organics.

7.0 PROCEDURE

7.1 Sample Preparation

7.1.1 Aqueous Samples: It is highly recommended that process waste samples be screened with the high-level method to determine if the low level method (1-50 µg/L) is required. Most groundwater samples will fall into the low level method.

7.1.1.1 Low-Level Method (salting-out extraction)

7.1.1.1.1 Add 251.3 g of sodium sulfate to a 1 L volumetric flask (round). Measure out 770 mL of a water sample (using a 1 L graduated cylinder) and transfer it to the volumetric flask containing the salt. Add a stir bar and mix the contents at maximum speed on a magnetic stirrer until the salt is completely dissolved.

7.1.1.1.2 Add 164 mL of acetonitrile (measured with a 250 mL graduated cylinder) while the solution is being stirred and stir for an additional 15 minutes. Turn off the stirrer and allow the phases to separate for 10 minutes.

7.1.1.1.3 Remove the acetonitrile (upper) layer (about 8 mL) with a Pasteur pipet and transfer it to a 100 mL volumetric flask (round). Add 10 mL of fresh acetonitrile to the water sample in the 1 L flask. Again stir the contents of the flask for 15 minutes followed by 10 minutes for phase separation. Combine the second acetonitrile portion with the initial extract. The inclusion of a few drops of salt water at this point is unimportant.

7.1.1.1.4 Add 84 mL of salt water (325 g NaCl per 1000 mL of reagent water) to the acetonitrile extract in the 100 mL volumetric flask. Add a stir bar and stir the contents on a magnetic stirrer for 15 minutes followed by 10 minutes for phase separation. Carefully transfer the acetonitrile phase to a 10 mL graduated cylinder using a Pasteur pipet. At this

stage the amount of water transferred with the acetonitrile must be minimized. The water contains a high concentration of NaCl that produces a large peak at the beginning of the chromatogram where it could interfere with the HMX determination.

7.1.1.1.5 Add an additional 1.0 mL of acetonitrile to the 100 mL volumetric flask. Again stir the contents of the flask for 15 minutes followed by 10 minutes for phase separation. Combine the second acetonitrile portion with the initial extract in the 10 mL graduated cylinder (transfer to a 25 mL graduated cylinder if the volume exceeds 5 mL). Record the total volume of acetonitrile extract to the nearest 0.1 mL. (Use this as the volume of total extract [V_t] in the calculation of concentration after converting to µL). The resulting extract, about 5 - 6 mL, is then diluted 1:1 with reagent water prior to analysis.

7.1.1.1.6 If the diluted extract is turbid, filter it through a 0.45 - µm Teflon filter using a disposable syringe. Discard the first 0.5 mL of filtrate, and retain the remainder in a Teflon-capped vial for RP-HPLC analysis as in Section 7.4.

7.1.1.2 High-Level Method

7.1.1.2.1 Sample filtration: Place a 5 mL aliquot of each water sample in a scintillation vial, add 5 mL of acetonitrile, shake thoroughly, and filter through a 0.45-µm Teflon filter using a disposable syringe. Discard the first 3 mL of filtrate, and retain the remainder in a Teflon-capped vial for RP-HPLC analysis as in Section 7.4. HMX quantitation can be improved with the use of methanol rather than acetonitrile for dilution before filtration.

7.1.2 Soil and Sediment Samples

7.1.2.1 Sample homogenization: Dry soil samples in air at room temperature or colder to a constant weight, being careful not to expose the samples to direct sunlight. Grind and homogenize the dried sample thoroughly in an acetonitrile rinsed mortar to pass a 30 mesh sieve.

NOTE: Soil samples should be screened by Method 8510 prior to grinding in a mortar and pestle (See Safety Section 11.2).

7.1.2.2 Sample extraction

7.1.2.2.1 Place a 2.0 g subsample of each soil sample in a 15 mL glass vial. Add 10.0 mL of acetonitrile, cap with Teflon-lined cap, vortex swirl for one minute, and place in a cooled ultrasonic bath for 18 hours.

7.1.2.2.2 After sonication, allow sample to settle for 30 minutes. Remove 5.0 mL of supernatant, and combine with 5.0 mL of calcium chloride solution (Section 5.1.3) in a 20 mL vial. Shake, and let stand for 15 minutes.

7.1.2.2.3 Place supernatant in a disposable syringe and filter through a 0.45-µm Teflon filter. Discard first 3 mL and retain remainder in a Teflon-capped vial for RP-HPLC analysis as in Section 7.4.

7.2 Chromatographic Conditions (Recommended)

Primary Column:	C-18 reverse phase HPLC column, 25-cm x 4.6-mm, 5 µm, (Supelco LC-18 or equivalent).
Secondary Column:	CN reverse phase HPLC column, 25-cm x 4.6-mm, 5 µm, (Supelco LC-CN or equivalent).
Mobile Phase:	50/50 (v/v) methanol/organic-free reagent water.
Flow Rate:	1.5 mL/min
Injection volume:	100-µL
UV Detector:	254 nm

7.3 Calibration of HPLC

7.3.1 All electronic equipment is allowed to warm up for 30 minutes. During this period, at least 15 void volumes of mobile phase are passed through the column (approximately 20 min at 1.5 mL/min) and continued until the baseline is level at the UV detector's greatest sensitivity.

7.3.2 Initial Calibration. Triplicate injections of each calibration standard over the concentration range of interest are sequentially injected into the HPLC in random order. Peak heights or peak areas are obtained for each analyte. Experience indicates that a linear calibration curve with zero intercept is appropriate for each analyte. Therefore, a response factor for each analyte can be taken as the slope of the best-fit regression line.

7.3.3 Daily Calibration. Analyze midpoint calibration standards, at a minimum, in triplicate at the beginning of the day, singly at the midpoint of the run and singly after the last sample of the day (assuming a sample group of 10 samples or less). Obtain the response factor for each analyte from the mean peak heights or peak areas and compare it with the response factor obtained for the initial calibration. The mean response factor for the daily calibration must agree within ±15% of the response factor of the initial calibration. The same criteria is required

for subsequent standard responses compared to the mean response of the triplicate standards beginning the day. If this criterion is not met, a new initial calibration must be obtained.

7.4 HPLC Analysis

7.4.1 Analyze the samples using the chromatographic conditions given in Section 7.2. All positive measurements observed on the C-18 column must be confirmed by injection onto the CN column.

7.4.2 Follow Section 7.0 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence. If column temperature control is not employed, special care must be taken to ensure that temperature shifts do not cause peak misidentification.

7.4.3 Table 2 summarizes the estimated retention times on both C-18 and CN columns for a number of analytes analyzable using this method. An example of the separation achieved by Column 1 is shown in Figure 1.

7.4.4 Record the resulting peak sizes in peak heights or area units. The use of peak heights is recommended to improve reproducibility of low level samples.

7.4.5 Calculation of concentration is covered in Section 7.0 of Method 8000.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500.

8.2 Quality control required to validate the HPLC system operation is found in Method 8000, Section 8.0.

8.3 Prior to preparation of stock solutions, acetonitrile, methanol, and water blanks should be run to determine possible interferences with analyte peaks. If the acetonitrile, methanol, or water blanks show contamination, a different batch should be used.

9.0 METHOD PERFORMANCE

9.1 Table 3 presents the single laboratory precision based on data from the analysis of blind duplicates of four spiked soil samples and four field contaminated samples analyzed by seven laboratories.

9.2 Table 4 presents the multilaboratory error based on data from the analysis of blind duplicates of four spiked soil samples and four field contaminated samples analyzed by seven laboratories.

9.3 Table 5 presents the multilaboratory variance of the high concentration method for water based on data from nine laboratories.

9.4 Table 6 presents multilaboratory recovery data from the analysis of spiked soil samples by seven laboratories.

9.5 Table 7 presents a comparison of method accuracy for soil and aqueous samples (high concentration method).

9.6 Table 8 contains precision and accuracy data for the salting-out extraction method.

10.0 REFERENCES

1. Bauer, C.F., T.F. Jenkins, S.M. Koza, P.W. Schumacher, P.H. Miyares and M.E. Walsh (1989). Development of an analytical method for the determination of explosive residues in soil. Part 3. Collaborative test results and final performance evaluation. USA Cold Regions Research and Engineering Laboratory, CRREL Report 89-9.

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3. Jenkins, T.F., C.F. Bauer, D.C. Leggett and C.L. Grant (1984) Reversed-phased HPLC method for analysis of TNT, RDX, HMX and 2,4-DNT in munitions wastewater. USA Cold Regions Research and Engineering Laboratory, CRREL Report 84-29.

4. Jenkins, T.F. and M.E. Walsh (1987) Development of an analytical method for explosive residues in soil. USA Cold Regions Research and Engineering Laboratory, CRREL Report 87-7.

5. Jenkins, T.F., P.H. Miyares and ME. Walsh (1988a) An improved RP-HPLC method for determining nitroaromatics and nitramines in water. USA Cold Regions Research and Engineering Laboratory, Special Report 88-23.

6. Jenkins, T.F. and P.H. Miyares (1992) Comparison of Cartridge and Membrane Solid-Phase Extraction with Salting-out Solvent Extraction for Preconcentration of Nitroaromatic and Nitramine Explosives from Water. USA Cold Regions Research and Engineering Laboratory, Draft CRREL Special Report.

7. Jenkins, T.F., P.W. Schumacher, M.E. Walsh and C.F. Bauer (1988b) Development of an analytical method for the determination of explosive residues in soil. Part II: Further development and ruggedness testing. USA Cold Regions Research and Engineering Laboratory, CRREL Report 88-8.

8. Leggett, D.C., T.F. Jenkins and P.H. Miyares (1990) Salting-out solvent extraction for preconcentration of neutral polar organic solutes from water. Analytical Chemistry, 62: 1355-1356.

9. Miyares, P.H. and T.F. Jenkins (1990) Salting-out solvent extraction for determining low levels of nitroaromatics and nitramines in water. USA Cold Regions Research and Engineering Laboratory, Special Report 90-30.

11.0 SAFETY

11.1 Standard precautionary measures used for handling other organic compounds should be sufficient for the safe handling of the analytes targeted by Method 8330. The only extra caution that should be taken is when handling the analytical standard neat material for the explosives themselves and in rare cases where soil or waste samples are highly contaminated with the explosives. Follow the note for drying the neat materials at ambient temperatures.

11.2 It is advisable to screen soil or waste samples using Method 8510 to determine whether high concentrations of explosives are present. Soil samples as high as 2% 2,4,6-TNT have been safely ground. Samples containing higher concentrations should not be ground in the mortar and pestle. Method 8510 is for 2,4,6-TNT, however, the other nitroaromatics will also cause a color to be developed and provide a rough estimation of their concentrations. 2,4,6-TNT is the analyte most often detected in high concentrations in soil samples. Visual observation of a soil sample is also important when taken from a site expected to contain explosives. Lumps of material that have a chemical appearance should be suspect and not ground. Explosives are generally a very finely ground grayish-white material.

TABLE 1
ESTIMATED QUANTITATION LIMITS

Compounds	Water (µg/L) Low-Level	Water (µg/L) High-Level	Soil (mg/kg)
HMX	-	13.0	2.2
RDX	0.84	14.0	1.0
1,3,5-TNB	0.26	7.3	0.25
1,3-DNB	0.11	4.0	0.25
Tetryl	-	4.0	0.65
NB	-	6.4	0.26
2,4,6-TNT	0.11	6.9	0.25
4-Am-DNT	0.060	-	-
2-Am-DNT	0.035	-	-
2,6-DNT	0.31	9.4	0.26
2,4-DNT	0.020	5.7	0.25
2-NT	-	12.0	0.25
4-NT	-	8.5	0.25
3-NT	-	7.9	0.25

TABLE 2
RETENTION TIMES AND CAPACITY FACTORS ON LC-18 AND LC-CN COLUMNS

	Retention time (min)		Capacity factor (k)*	
Compound	LC-18	LC-CN	LC-18	LC-CN
HMX	2.44	8.35	0.49	2.52
RDX	3.73	6.15	1.27	1.59
1,3,5-TNB	5.11	4.05	2.12	0.71
1,3-DNB	6.16	4.18	2.76	0.76
Tetryl	6.93	7.36	3.23	2.11
NB	7.23	3.81	3.41	0.61
2,4,6-TNT	8.42	5.00	4.13	1.11
4-Am-DNT	8.88	5.10	4.41	1.15
2-Am-DNT	9.12	5.65	4.56	1.38
2,6-DNT	9.82	4.61	4.99	0.95
2,4-DNT	10.05	4.87	5.13	1.05
2-NT	12.26	4.37	6.48	0.84
4-NT	13.26	4.41	7.09	0.86
3-NT	14.23	4.45	7.68	0.88

* Capacity factors are based on an unretained peak for nitrate at 1.71 min on LC-18 and 2.00 min on LC-CN

TABLE 3
SINGLE LABORATORY PRECISION OF METHOD FOR SOIL SAMPLES

	Spiked Soils			Field-Contaminated Soils		
	Mean Conc. (mg/kg)	SD	%rsd	Mean Conc. (mg/kg)	SD	%rsd
HMX	46	1.7	3.7	14	1.8	12.8
				153	21.6	14.1
RDX	60	1.4	2.3	104	12	11.5
				877	29.6	3.4
1,3,5-TNB	8.6	0.4	4.6	2.8	0.2	7.1
	46	1.9	4.1	72	6.0	8.3
1,3-DNB	3.5	0.14	4.0	1.1	0.11	9.8
Tetryl	17	3.1	17.9	2.3	0.41	18.0
2,4,6-TNT	40	1.4	3.5	7.0	0.61	9.0
				669	55	8.2
2,4-DNT	5.0	0.17	3.4	1.0	0.44	42.3

TABLE 4
MULTILABORATORY ERROR OF METHOD FOR SOIL SAMPLES

	Spiked Soils			Field-Contaminated Soils		
	Mean Conc. (mg/kg)	SD	%rsd	Mean Conc. (mg/kg)	SD	%rsd
HMX	46	2.6	5.7	14	3.7	26.0
				153	37.3	24.0
RDX	60	2.6	4.4	104	17.4	17.0
				877	67.3	7.7
1,3,5-TNB	8.6	0.61	7.1	2.8	0.23	8.2
	46	2.97	6.5	72	8.8	12.2
1,3-DNB	3.5	0.24	6.9	1.1	0.16	14.5
Tetryl	17	5.22	30.7	2.3	0.49	21.3
2,4,6-TNT	40	1.88	4.7	7.0	1.27	18.0
				669	63.4	9.5
2,4-DNT	5.0	0.22	4.4	1.0	0.74	74.0

TABLE 5
MULTILABORATORY VARIANCE OF METHOD FOR WATER SAMPLES[a]

Compounds	Mean Conc. (µg/L)	SD	%rsd
HMX	203	14.8	7.3
RDX	274	20.8	7.6
2,4-DNT	107	7.7	7.2
2,4,6-TNT	107	11.1	10.4

[a] Nine Laboratories

TABLE 6
MULTILABORATORY RECOVERY DATA FOR SPIKED SOIL SAMPLES

	Concentration (µg/g)						
Laboratory	HMX	RDX	1,3,5-TNB	1,3-DNB	Tetryl	2,4,6-TNT	2,4-DNT
1	44.97	48.78	48.99	49.94	32.48	49.73	51.05
3	50.25	48.50	45.85	45.96	47.91	46.25	48.37
4	42.40	44.00	43.40	49.50	31.60	53.50	50.90
5	46.50	48.40	46.90	48.80	32.10	55.80	49.60
6	56.20	55.00	41.60	46.30	13.20	56.80	45.70
7	41.50	41.50	38.00	44.50	2.60	36.00	43.50
8	52.70	52.20	48.00	48.30	44.80	51.30	49.10
true conc	50.35	50.20	50.15	50.05	50.35	50.65	50.05
mean	47.79	48.34	44.68	47.67	29.24	49.91	48.32
std dev	5.46	4.57	3.91	2.09	16.24	7.11	2.78
% rsd	11.42	9.45	8.75	4.39	55.53	14.26	5.76
% diff*	5.08	3.71	10.91	4.76	41.93	1.46	3.46
mean % recovery	95	96	89	95	58	98	96

* Between true value and mean determined value.

TABLE 7
COMPARISON OF METHOD ACCURACY FOR SOIL AND AQUEOUS SAMPLES
(HIGH CONCENTRATION METHOD)

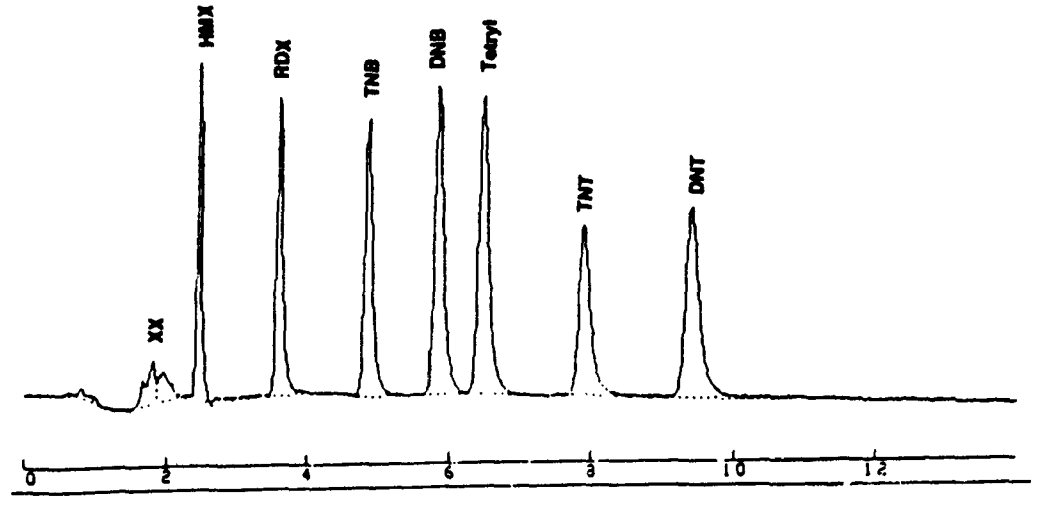
Analyte	Recovery (%) Soil Method*	Aqueous Method**
2,4-DNT	96.0	98.6
2,4,6-TNT	96.8	94.4
RDX	96.8	99.6
HMX	95.4	95.5

* Taken from Bauer et al. (1989), Reference 1.
** Taken from Jenkins et al. (1984), Reference 3.

TABLE 8
PRECISION AND ACCURACY DATA FOR THE SALTING-OUT EXTRACTION METHOD

Analyte	No. of Samples[1]	Precision (% RSD)	Ave. Recovery (%)	Conc. Range (µg/L)
HMX	20	10.5	106	0-1.14
RDX	20	8.7	106	0-1.04
1,3,5-TNB	20	7.6	119	0-0.82
1,3-DNB	20	6.6	102	0-1.04
Tetryl	20	16.4	93	0-0.93
2,4,6-TNT	20	7.6	105	0-0.98
2-Am-DNT	20	9.1	102	0-1.04
2,4-DNT	20	5.8	101	0-1.01
1,2-NT	20	9.1	102	0-1.07
1,4-NT	20	18.1	96	0-1.06
1,3-NT	20	12.4	97	0-1.23

[1]Reagent water



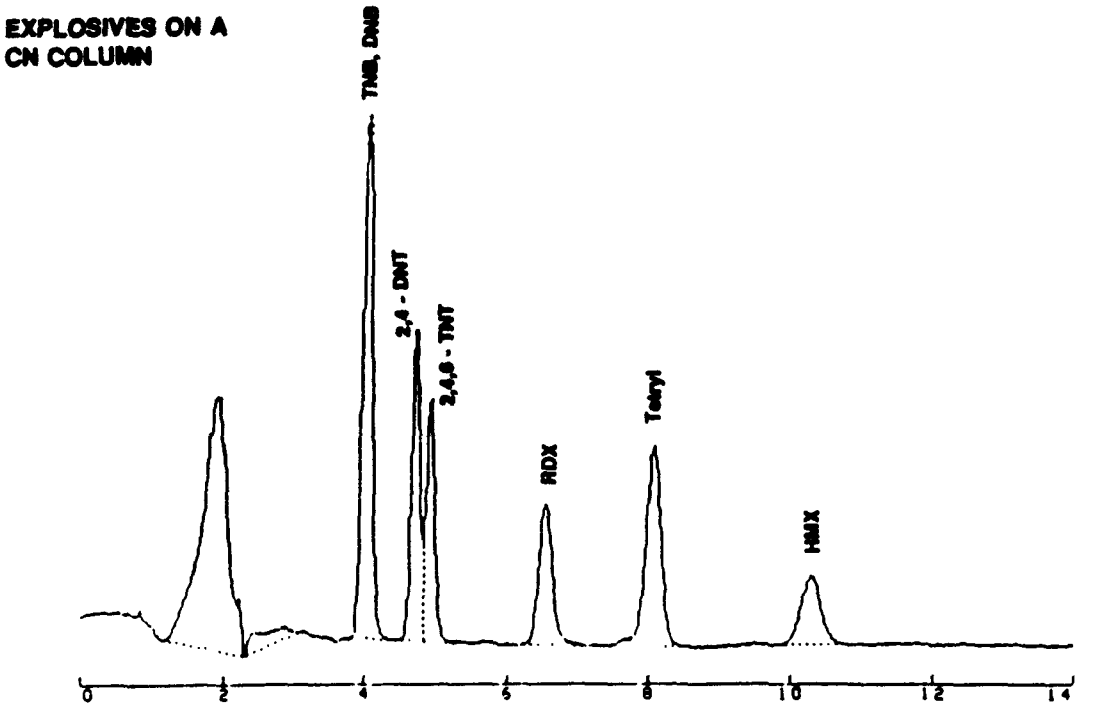
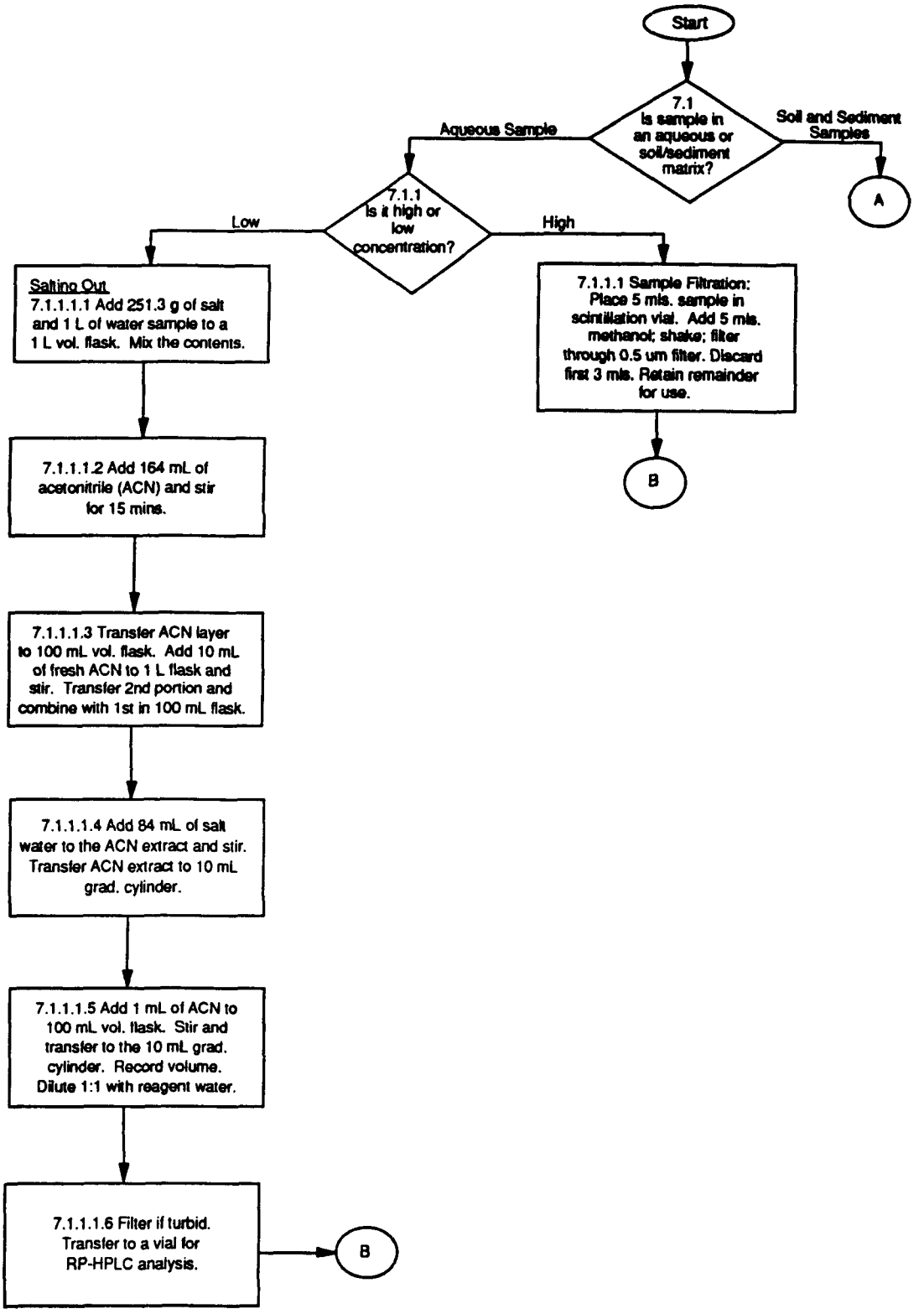
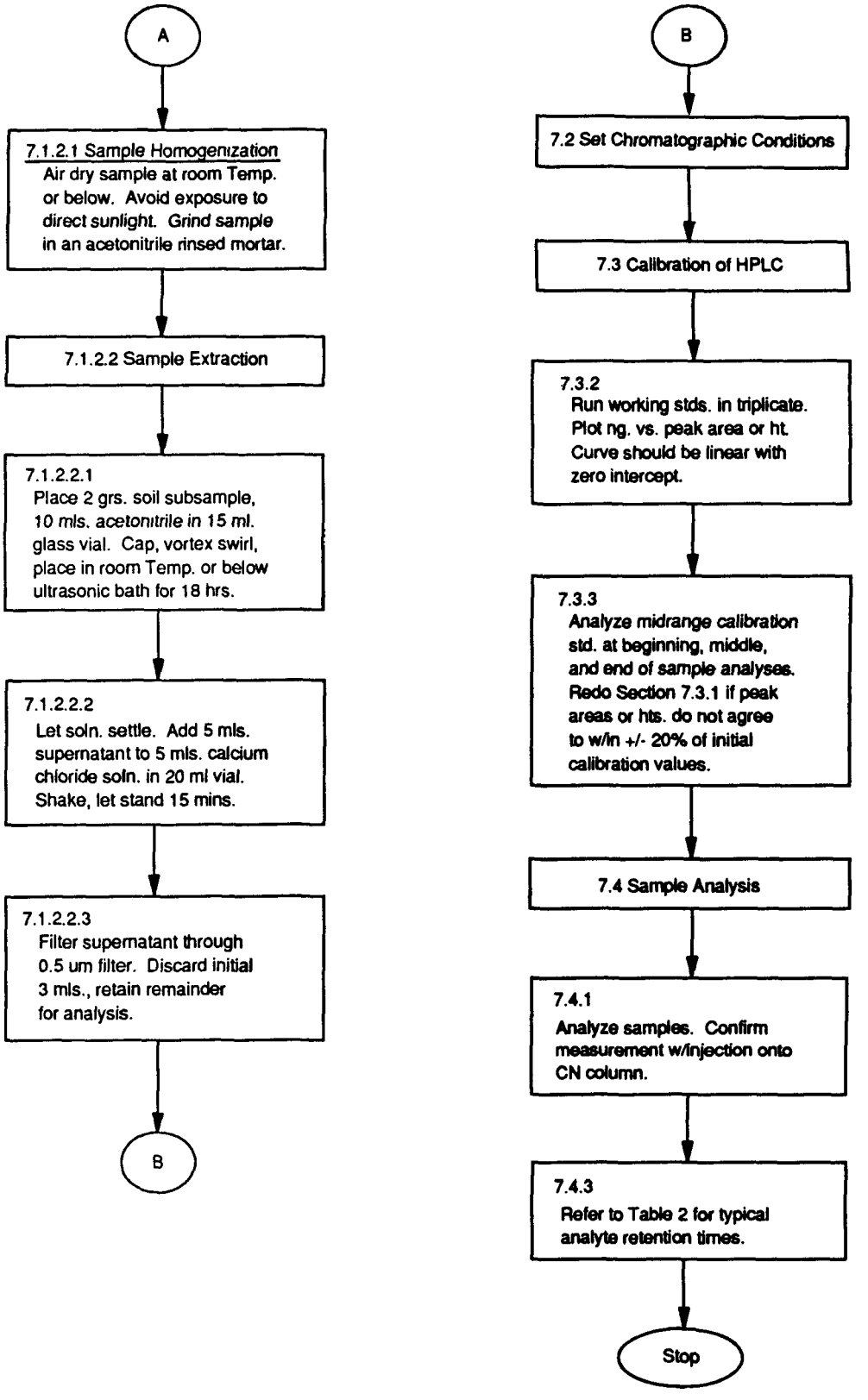


FIGURE 1
CHROMATOGRAMS FOR COLUMNS DESCRIBED IN SECTION 4.1.2.
COURTESY OF U.S. ARMY CORPS OF ENGINEERS, OMAHA, NE.


Start
7.1
Is sample in an aqueous or soil/sediment matrix?
Aqueous Sample
Soil and Sediment Samples
A
7.1.1
Is it high or low concentration?
Low
High
Salting Out
7.1.1.1.1 Add 251.3 g of salt and 1 L of water sample to a 1 L vol. flask. Mix the contents.
7.1.1.1 Sample Filtration: Place 5 mls. sample in scintillation vial. Add 5 mls. methanol; shake; filter through 0.5 um filter. Discard first 3 mls. Retain remainder for use.
B
7.1.1.1.2 Add 164 mL of acetonitrile (ACN) and stir for 15 mins.
7.1.1.1.3 Transfer ACN layer to 100 mL vol. flask. Add 10 mL of fresh ACN to 1 L flask and stir. Transfer 2nd portion and combine with 1st in 100 mL flask.
7.1.1.1.4 Add 84 mL of salt water to the ACN extract and stir. Transfer ACN extract to 10 mL grad. cylinder.
7.1.1.1.5 Add 1 mL of ACN to 100 mL vol. flask. Stir and transfer to the 10 mL grad. cylinder. Record volume. Dilute 1:1 with reagent water.
7.1.1.1.6 Filter if turbid. Transfer to a vial for RP-HPLC analysis.
B


A
7.1.2.1 Sample Homogenization
Air dry sample at room Temp. or below. Avoid exposure to direct sunlight. Grind sample in an acetonitrile rinsed mortar.
7.1.2.2 Sample Extraction
7.1.2.2.1
Place 2 grs. soil subsample, 10 mls. acetonitrile in 15 ml. glass vial. Cap, vortex swirl, place in room Temp. or below ultrasonic bath for 18 hrs.
7.1.2.2.2
Let soln. settle. Add 5 mls. supernatant to 5 mls. calcium chloride soln. in 20 ml vial. Shake, let stand 15 mins.
7.1.2.2.3
Filter supernatant through 0.5 um filter. Discard initial 3 mls., retain remainder for analysis.
B
B
7.2 Set Chromatographic Conditions
7.3 Calibration of HPLC
7.3.2
Run working stds. in triplicate. Plot ng. vs. peak area or ht. Curve should be linear with zero intercept.
7.3.3
Analyze midrange calibration std. at beginning, middle, and end of sample analyses. Redo Section 7.3.1 if peak areas or hts. do not agree to w/in +/- 20% of initial calibration values.
7.4 Sample Analysis
7.4.1
Analyze samples. Confirm measurement w/injection onto CN column.
7.4.3
Refer to Table 2 for typical analyte retention times.
Stop

METHOD 8331

TETRAZENE BY REVERSE PHASE
HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

1.0 SCOPE AND APPLICATION

1.1 This method is intended for the analysis of tetrazene, an explosive residue, in soil and water. This method is limited to use by analysts experienced in handling and analyzing explosive materials. The following compounds can be determined by this method:

Compound	CAS No[a]
Tetrazene	31330-63-9

[a] Chemical Abstracts Service Registry number

1.2 Tetrazene degrades rapidly in water and methanol at room temperature. Special care must be taken to refrigerate or cool all solutions throughout the analytical process.

1.3 Tetrazene, in its dry form, is extremely explosive. Caution must be taken during preparation of standards.

1.4 The estimated quantitation limit (EQL) of Method 8331 for determining the concentration of tetrazene is approximately 7 µg/L in water and approximately 1 mg/kg in soil.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of HPLC, skilled in the interpretation of chromatograms, and experienced in handling explosive materials. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A 10 mL water sample is filtered, eluted on a C-18 column using ion pairing reverse phase HPLC, and quantitated at 280 nm.

2.2 2 g of soil are extracted with 55:45 v/v methanol-water and 1-decanesulfonic acid on a platform shaker, filtered, and eluted on a C-18 column using ion pairing reverse phase HPLC, and quantitated at 280 nm.

3.0 INTERFERENCES

3.1 No interferences are known. Tetrazene elutes early, however, and if a computing integrator is used for peak quantification, the baseline setting may

have to be set to exclude baseline aberrations. Baseline setting is particularly important at low concentrations of analyte.

4.0 APPARATUS AND MATERIALS

4.1 HPLC system

4.1.1 HPLC - Pump capable of achieving 4000 psi.

4.1.2 100 µL loop injector.

4.1.3 Variable or fixed wavelength detector capable of reading 280 nm.

4.1.4 C-18 reverse phase HPLC column, 25 cm x 4.6 mm (5 µm) (Supelco LC-18, or equivalent).

4.1.5 Digital integrator - HP 3390A (or equivalent)

4.1.6 Strip chart recorder.

4.2 Other apparatus

4.2.1 Platform orbital shaker.

4.2.2 Analytical balance - ± 0.0001 g.

4.2.3 Desiccator.

4.3 Materials

4.3.1 Injection syringe - 500 µL.

4.3.2 Filters - 0.5 µm Millex-SR and 0.5 µm Millex-HV, disposable, or equivalent.

4.3.3 Pipets - volumetric, glass, Class A.

4.3.4 Scintillation vials - 20 mL, glass.

4.3.5 Syringes - 10 mL.

4.3.6 Volumetric flasks, Class A - 100 mL, 200 mL.

4.3.7 Erlenmeyer flasks with ground glass stoppers - 125 mL.

4.4 Preparation

4.4.1 Prepare all materials as described in Chapter 4 for volatile organics.

5.0 REAGENTS

5.1 HPLC grade chemicals shall be used in all tests. 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 lowering the accuracy of the determination.

5.2 General

5.2.1 Methanol, CH_3OH - HPLC grade.

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

5.2.3 1-Decanesulfonic acid, sodium salt, $C_{10}H_{21}SO_3Na$ - HPLC grade.

5.2.4 Acetic acid (glacial), CH_3COOH - reagent grade.

5.3 Standard Solutions

5.3.1 Tetrazene - Standard Analytical Reference Material.

5.3.2 Stock standard solution - Dry tetrazene to constant weight in a vacuum desiccator in the dark. (Tetrazene is extremely explosive in the dry state. Do not dry more reagent than is necessary to prepare stock solutions.) Place about 0.0010 g (weighed to 0.0001 g) into a 100-ml volumetric flask and dilute to volume with methanol. Invert flask several times until tetrazene is dissolved. Store in freezer at -10°C. Stock solution is about 100 mg/L. Replace stock standard solution every week.

5.3.3 Intermediate standard solutions

5.3.3.1 Prepare a 4 mg/L standard by diluting the stock solution 1/25 v/v with methanol.

5.3.3.2 Pipet 0.5, 1.0, 2.0, 5.0, 10.0, and 20.0 mL of the 4 mg/L standard solution into 6 separate 100 mL volumetric flasks, and make up to volume with methanol. Pipet 25.0 mL of the 4 mg/L standard solution into a 50 mL volumetric flask, and make up to volume with methanol. This results in intermediate standards of about 0.02, 0.04, 0.08, 0.2, 0.4, 0.8, 2 and 4 mg/L.

5.3.3.3 Cool immediately on preparation in refrigerator or ice bath.

5.3.4 Working standard solutions

5.3.4.1 Inject 4 mL of each of the intermediate standard solutions into 6.0 mL of water. This results in concentrations of about 0.008, 0.016, 0.032, 0.08, 0.16, 0.3, 0.8 and 1.6 mg/L.

5.3.4.2 Cool immediately on preparation in refrigerator or ice bath.

5.5 QC spike concentrate solution

5.5.1 Dry tetrazene to constant weight in a vacuum desiccator in the dark. (Tetrazene is extremely explosive in the dry state. Do not dry any more than necessary to prepare standards.) Place about 0.0011 g (weighed to 0.0001 g) into a 200-ml volumetric flask and dilute to volume with methanol. Invert flask several times until tetrazene is dissolved. Store in freezer at -10°C. QC spike concentrate solution is about 55 mg/L. Replace stock standard solution every week.

5.5.2 Prepare spiking solutions, at concentrations appropriate to the concentration range of the samples being analyzed, by diluting the QC spike concentrate solution with methanol. Cool on preparation in refrigerator or ice bath.

5.6 Eluent

5.6.1 To make about 1 liter of eluent, add 2.44 g of 1-decanesulfonic acid, sodium salt to 400/600 v/v methanol/water, and add 2.0 mL of glacial acetic acid.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

6.2 Samples must be collected and stored in glass containers. Follow conventional sampling procedures.

6.3 Samples must be kept below 4°C from the time of collection through analysis.

7.0 PROCEDURE

7.1 Sample Preparation

7.1.1 Filtration of Water Samples

7.1.1.1 Place a 10 mL portion of each water sample in a syringe and filter through a 0.5 μm Millex-HV filter unit. Discard first 5 mL of filtrate, and retain 5 mL for analysis.

7.1.2 Extraction and Filtration of Soil Samples

7.1.2.1 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.

7.1.2.1.1 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:

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

7.1.2.2 Weigh 2 g soil subsamples into 125 mL Erlenmeyer flasks with ground glass stoppers.

7.1.2.3 Add 50 mL of 55/45 v/v methanol-water with 1-decanesulfonic acid, sodium salt added to make a 0.1 M solution.

7.1.2.4 Vortex for 15 seconds.

7.1.2.5 Shake for 5 hr at 2000 rpm on platform shaker.

7.1.2.6 Place a 10 mL portion of each soil sample extract in a syringe and filter through a 0.5 μm Millex-SR filter unit. Discard first 5 mL of filtrate, and retain 5 mL for analysis.

7.2 Sample Analysis

7.2.1 Analyze the samples using the chromatographic conditions given in Section 7.2.1.1. Under these conditions, the retention time of tetrazene is 2.8 min. A sample chromatogram, including other compounds likely to be present in samples containing tetrazene, is shown in Figure 1.

7.2.1.1 Chromatographic Conditions

Solvent:	0.01 M 1-decanesulfonic acid, in acidic methanol/water (Section 5.5)
Flow rate:	1.5 mL/min
Injection volume:	100 μL
UV Detector:	280 nm

7.3 Calibration of HPLC

7.3.1 Initial Calibration - Analyze the working standards (Section 5.3.4), starting with the 0.008 mg/L standards and ending with the 0.30 mg/L standard. If the percent relative standard deviation (%RSD) of the mean response factor (RF) for each analyte does not exceed 20%, the system is calibrated and the analysis of samples may proceed. If the %RSD for any analyte exceeds 20%, recheck the system and/or recalibrate with freshly prepared calibration solutions.

7.3.2 Continuing Calibration - On a daily basis, inject 250 µL of stock standard into 20 mL water. Keep solution in refrigerator until analysis. Analyze in triplicate (by overfilling loop) at the beginning of the day, singly after each five samples, and singly after the last sample of the day. Compare response factors from the mean peak area or peak height obtained over the day with the response factor at initial calibration. If these values do not agree within 10%, recalibrate.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 Prior to preparation of stock solutions, methanol should be analyzed to determine possible interferences with the tetrazene peak. If the methanol shows contamination, a different batch of methanol should be used.

8.3 Method Blanks

8.3.1 Method blanks for the analysis of water samples should be organic-free reagent water carried through all sample storage and handling procedures.

8.3.2 Method blanks for the analysis of soil samples should be uncontaminated soil carried through all sample storage, extraction, and handling procedures.

9.0 METHOD PERFORMANCE

9.1 Method 8331 was tested in a laboratory over a period of four days. Spiked organic-free reagent water and standard soil were analyzed in duplicate each day for four days. The HPLC was calibrated daily according to the procedures given in Section 7.1. Method performance data are presented in Tables 1 and 2.

10.0 REFERENCES

1. Walsh, M.E., and T.F. Jenkins, "Analytical Method for Determining Tetrazene in Water," U.S. Army Corps of Engineers, Cold Regions Research & Engineering Laboratory, Special Report 87-25, 1987.

2. Walsh, M.E., and T.F. Jenkins, "Analytical Method for Determining Tetrazene in Soil," U.S. Army Corps of Engineers, Cold Regions Research & Engineering Laboratory, Special Report 88-15, 1988.

11.0 SAFETY

11.1 Standard precautionary measures used for handling other organic compounds should be sufficient for safe handling of the analytes targeted by Method 8331.

FIGURE 1

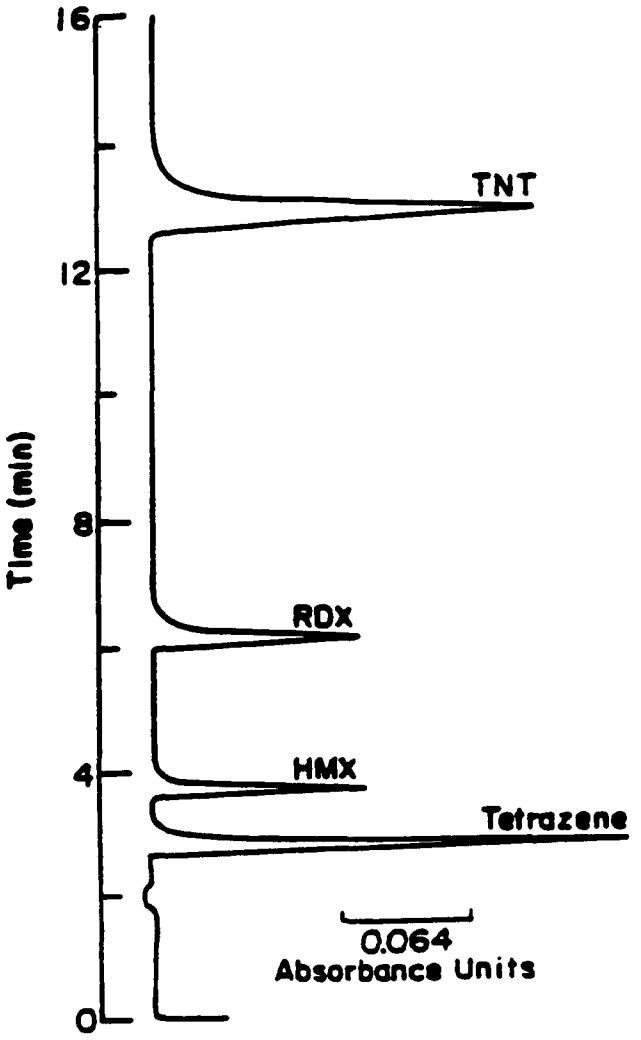

16
12
8
4
0
Time (min)
TNT
RDX
HMX
Tetrazene
0.064
Absorbance Units

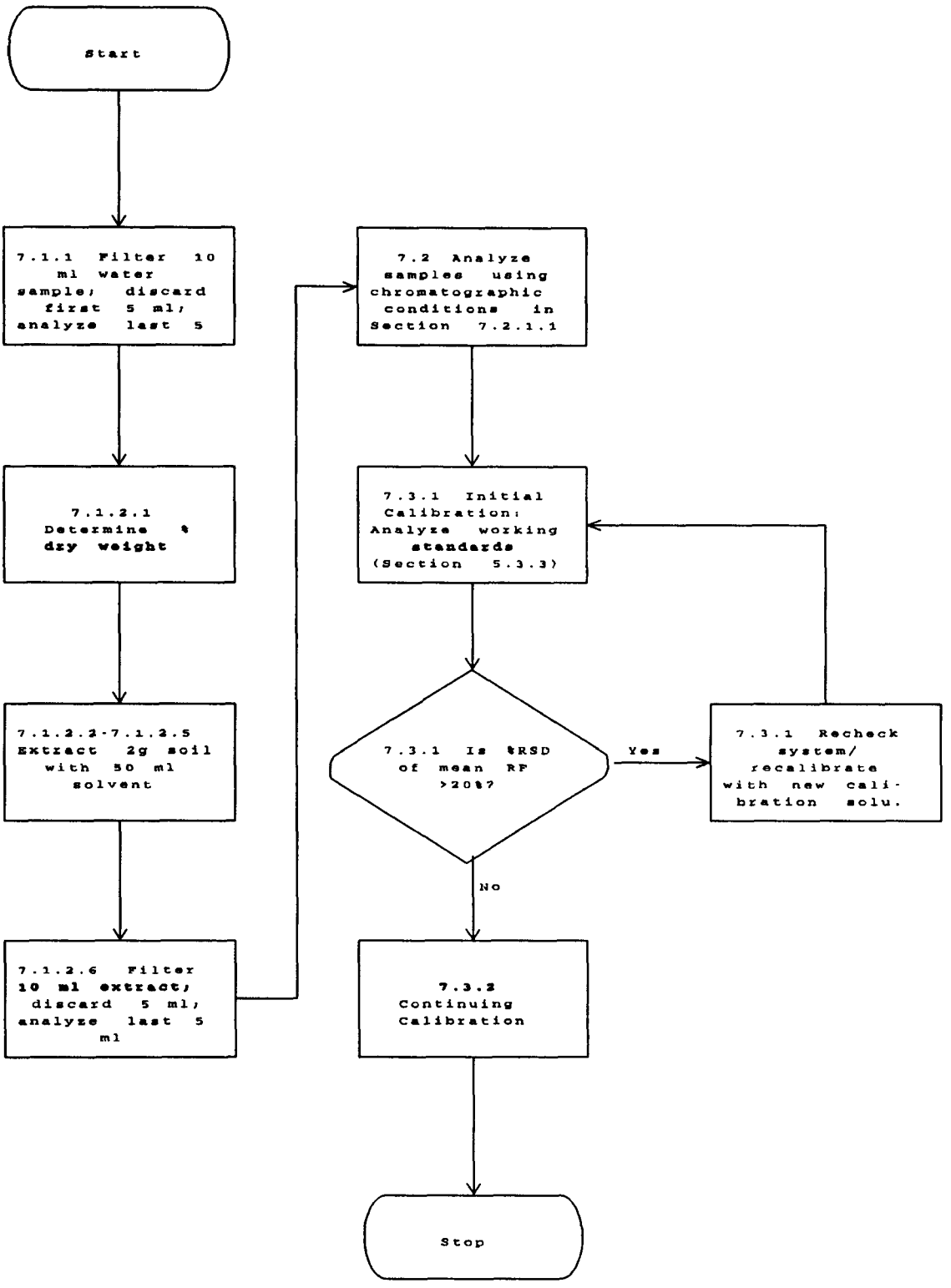
TABLE 1.
METHOD PERFORMANCE, WATER MATRIX

Spike Conc. (µg/L)	Replicate	Avg % Recovery Day 1	Day 2	Day 3	Day 4	Average % Recovery
0.00	Replicate 1	0.0	0.0	0.0	0.0	
	% Recovery	NA	NA	NA	NA	NA
	Replicate 2	0.0	0.0	0.0	0.0	
	% Recovery	NA	NA	NA	NA	NA
7.25	Replicate 1	8.9	7.8	7.4	9.4	
	% Recovery	122	108	102	130	116
	Replicate 2	6.6	9.9	8.5	6.7	
	% Recovery	91	137	117	92	109
14.5	Replicate 1	14.6	14.6	13.8	14.6	
	% Recovery	101	101	95	101	99
	Replicate 2	14.8	14.1	14.1	15.2	
	% Recovery	102	97	98	105	100
29	Replicate 1	31.8	30.0	30.8	28.7	
	% Recovery	110	103	106	99	105
	Replicate 2	29.5	29.7	30.4	30.7	
	% Recovery	102	102	105	106	104
72.5	Replicate 1	71.1	73.6	75.7	73.9	
	% Recovery	98	102	104	102	101
	Replicate 2	71.2	71.3	70.7	71.6	
	% Recovery	98	98	98	99	98
145	Replicate 1	140.6	143.8	144.7	142.1	
	% Recovery	97	99	100	98	98
	Replicate 2	138.5	140.8	140.9	136.9	
	% Recovery	96	97	97	94	96
290	Replicate 1	289.4	288.5	291.0	289.8	
	% Recovery	100	99	100	100	100
	Replicate 2	282.0	284.2	281.9	282.5	
	% Recovery	97	98	97	97	97
725	Replicate 1	737.6	707.2	714.3	722.0	
	% Recovery	102	98	99	100	99
	Replicate 2	700.2	695.8	714.2	716.3	
	% Recovery	97	96	99	99	97
OVERALL						102

TABLE 2
METHOD PERFORMANCE, SOIL MATRIX

Spike Conc. (µg/L)	Replicate	Avg % Recovery Day 1	Day 2	Day 3	Day 4	Average % Recovery
0.00	Replicate 1	0.0	0.0	0.0	0.0	
	% Recovery	NA	NA	NA	NA	NA
	Replicate 2	0.0	0.0	0.0	0.0	
	% Recovery	NA	NA	NA	NA	NA
1.28	Replicate 1	0.6	0.9	0.6	1.0	
	% Recovery	49	73	48	74	61
	Replicate 2	1.2	0.7	0.8	0.7	
	% Recovery	92	56	63	56	67
2.56	Replicate 1	1.4	1.5	1.6	1.6	
	% Recovery	56	58	61	61	59
	Replicate 2	1.5	2.0	1.4	1.3	
	% Recovery	59	79	56	50	61
5.12	Replicate 1	2.9	3.0	2.9	2.9	
	% Recovery	57	58	56	56	57
	Replicate 2	3.0	3.0	3.5	3.1	
	% Recovery	58	59	69	60	61
12.8	Replicate 1	7.8	7.6	7.8	8.1	
	% Recovery	61	59	61	63	61
	Replicate 2	8.0	8.4	7.7	8.2	
	% Recovery	62	66	60	64	63
25.6	Replicate 1	17.2	16.7	17.4	17.3	
	% Recovery	67	65	68	68	67
	Replicate 2	16.7	16.8	17.6	17.2	
	% Recovery	65	66	69	67	67
OVERALL						62

METHOD 8331
TETRAZENE BY REVERSE PHASE
HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)



METHOD 8410

GAS CHROMATOGRAPHY/FOURIER TRANSFORM INFRARED (GC/FT-IR) SPECTROMETRY FOR SEMIVOLATILE ORGANICS: CAPILLARY COLUMN

1.0 SCOPE AND APPLICATION

1.1 This method covers the automated identification, or compound class assignment of unidentifiable compounds, of solvent extractable semivolatile organic compounds which are amenable to gas chromatography, by GC/FT-IR. GC/FT-IR can be a useful complement to GC/MS analysis (Method 8270). It is particularly well suited for the identification of specific isomers that are not differentiated using GC/MS. Compound class assignments are made using infrared group absorption frequencies. The presence of an infrared band in the appropriate group frequency region may be taken as evidence of the possible presence of a particular compound class, while its absence may be construed as evidence that the compound class in question is not present. This evidence will be further strengthened by the presence of confirmatory group frequency bands. Identification limits of the following compounds have been demonstrated by this method.

Compound Name	CAS No.[a]
Acenaphthene	83-32-9
Acenaphthylene	208-96-8
Anthracene	120-12-7
Benzo(a)anthracene	56-55-3
Benzo(a)pyrene	50-32-8
Benzoic acid	65-85-0
Bis(2-chloroethoxy)methane	111-91-1
Bis(2-chloroethyl) ether	111-44-4
Bis(2-chloroisopropyl) ether	39638-32-9
Bis(2-ethylhexyl) phthalate	117-81-7
4-Bromophenyl phenyl ether	101-55-3
Butyl benzyl phthalate	85-68-7
4-Chloroaniline	106-47-8
4-Chloro-3-methylphenol	59-50-7
2-Chloronaphthalene	91-58-7
2-Chlorophenol	95-57-8
4-Chlorophenol	106-48-9
4-Chlorophenyl phenyl ether	7005-72-3
Chrysene	218-01-9
Dibenzofuran	132-64-9
Di-n-butyl phthalate	84-74-2
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
2,4-Dichlorophenol	120-83-2
Dimethyl phthalate	131-11-3

Compound Name	CAS No.[a]
Diethyl phthalate	84-66-2
4,6-Dinitro-2-methylphenol	534-52-1
2,4-Dinitrophenol	51-28-5
2,4-Dinitrotoluene	121-14-2
2,6-Dinitrotoluene	606-20-2
Di-n-octyl phthalate	117-84-0
Di-n-propyl phthalate	131-16-8
Fluoranthene	206-44-0
Fluorene	86-73-7
Hexachlorobenzene	118-74-1
1,3-Hexachlorobutadiene	87-68-3
Hexachlorocyclopentadiene	77-47-4
Hexachloroethane	67-72-1
Isophorone	78-59-1
2-Methylnaphthalene	91-57-6
2-Methylphenol	95-48-7
4-Methylphenol	106-44-5
Naphthalene	91-20-3
2-Nitroaniline	88-74-4
3-Nitroaniline	99-09-2
4-Nitroaniline	100-01-6
Nitrobenzene	98-95-3
2-Nitrophenol	88-75-5
4-Nitrophenol	100-02-7
N-Nitrosodimethylamine	62-75-9
N-Nitrosodiphenylamine	86-30-9
N-Nitroso-di-n-propylamine	621-64-7
Pentachlorophenol	87-86-5
Phenanthrene	85-01-8
Phenol	108-95-2
Pyrene	129-00-0
1,2,4-Trichlorobenzene	120-82-1
2,4,5-Trichlorophenol	95-95-4
2,4,6-Trichlorophenol	88-06-2

[a] Chemical Abstract Services Registry Number.

1.2 This method is applicable to the determination of most extractable, semivolatile-organic compounds in wastewater, soils and sediments, and solid wastes. Benzidine can be subject to losses during solvent concentration and GC analysis; α-BHC, β-BHC, endosulfan I and II, and endrin are subject to decomposition under the alkaline conditions of the extraction step; endrin is subject to decomposition during GC analysis; and hexachlorocyclopentadiene and N-nitrosodiphenylamine may decompose during extraction and GC analysis. Other extraction and/or instrumentation procedures should be considered for unstable analytes.

1.3 The identification limit of this method may depend strongly upon the level and type of gas chromatographable (GC) semivolatile extractants. The values listed in Tables 1 and 2 represent the minimum quantities of semivolatile organic compounds which have been identified by the specified GC/FT-IR system, using this method and under routine environmental analysis conditions. Capillary GC/FT-IR wastewater identification limits of 25 μg/L may be achieved for weak infrared absorbers with this method, while the corresponding identification limits for strong infrared absorbers is 2 μg/L. Identification limits for other sample matrices can be calculated from the wastewater values after choice of the proper sample workup procedure (see Section 7.1).

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 and uses FT-IR for detection and quantitation of the target analytes.

3.0 INTERFERENCES

3.1 Glassware and other sample processing hardware must be thoroughly cleaned to prevent contamination and misinterpretation. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents or purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interference will vary considerably from source to source, depending upon the diversity of the residual waste being sampled. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup to isolate the analytes of interest from interferences in order to achieve maximum sensitivity.

3.3 4-Chlorophenol and 2-nitrophenol are subject to interference from co-eluting compounds.

3.4 Clean all glassware as soon as possible after use by rinsing with the last solvent used. Glassware should be sealed/stored in a clean environment immediately after drying to prevent any accumulation of dust or other contaminants.

4.0 APPARATUS AND MATERIALS

4.1 Gas Chromatographic/Fourier Transform Infrared Spectrometric Equipment

4.1.1 Fourier Transform-Infrared Spectrometer - A spectrometer capable of collecting at least one scan set per second at 8 cm^{-1} resolution is required. In general, a spectrometer purchased after 1985, or retrofitted to meet post-1985 FT-IR improvements, will be necessary to

meet the detection limits of this protocol. A state-of-the-art A/D converter is required, since it has been shown that the signal-to-noise ratio of single beam GC/FT-IR systems is A/D converter limited.

4.1.2 GC/FT-IR Interface - The interface should be lightpipe volume-optimized for the selected chromatographic conditions (lightpipe volume of 100-200 μL for capillary columns). The shortest possible inert transfer line (preferably fused silica) should be used to interface the end of the chromatographic column to the lightpipe. If fused silica capillary columns are employed, the end of the GC column can serve as the transfer line if it is adequately heated. It has been demonstrated that the optimum lightpipe volume is equal to the full width at half height of the GC eluate peak.

4.1.3 Capillary Column - A fused silica DB-5 30 m x 0.32 mm capillary column with 1.0 μm film thickness (or equivalent).

4.1.4 Data Acquisition - A computer system dedicated to the GC/FT-IR system to allow the continuous acquisition of scan sets for a full chromatographic run. Peripheral data storage systems should be available (magnetic tape and/or disk) for the storage of all acquired data. Software should be available to allow the acquisition and storage of every scan set to locate the file numbers and transform high S/N scan sets, and to provide a real time reconstructed chromatogram.

4.1.5 Detector - A cryoscopic, medium-band HgCdTe (MCT) detector with the smallest practical focal area. Typical narrow-band MCT detectors operate from 3800-800 cm^{-1} but medium-band MCT detectors can reach 650 cm^{-1}. A 750 cm^{-1} cutoff (or lower) is desirable since it allows the detection of typical carbon-chlorine stretch and aromatic out-of-plane carbon-hydrogen vibrations of environmentally important organo-chlorine and polynuclear aromatic compounds. The MCT detector sensitivity $(D)^*$ should be $\geq 1 \times 10^{10}$ cm.

4.1.6 Lightpipe - Constructed of inert materials, gold coated, and volume-optimized for the desired chromatographic conditions (see Section 7.3).

4.1.7 Gas Chromatograph - The FT-IR spectrometer should be interfaced to a temperature programmable gas chromatograph equipped with a Grob-type (or equivalent) purged splitless injection system suitable for capillary glass columns or an on-column injector system.

A short, inert transfer line should interface the gas chromatograph to the FT-IR lightpipe and, if applicable, to the GC detector. Fused silica GC columns may be directly interfaced to the lightpipe inlet and outlet.

4.2 Dry Purge Gas - If the spectrometer is the purge-type, provisions should be made to provide a suitable continuous source of dry purge-gas to the FT-IR spectrometer.

4.3 Dry Carrier Gas - The carrier gas should be passed through an efficient cartridge-type drier.

4.4 Syringes - 1-μL, 10-μL.

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 Solvents

5.3.1 Acetone, CH_3COCH_3 - Pesticide quality, or equivalent.

5.3.2 Methylene chloride, CH_2Cl_2 - Pesticide quality, or equivalent.

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

5.4.1 Prepare stock standard solutions by accurately weighing 0.1000 $\pm$ 0.0010 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 100 mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96 percent 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.

5.4.2 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.

5.4.3 Stock standard solutions must be replaced after 6 months or sooner if comparison with quality control reference samples indicates a problem.

5.5 Calibration Standards and Internal Standards - For use in situations where GC/FT-IR will be used for primary quantitation of analytes rather than confirmation of GC/MS identification.

5.5.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations that will completely bracket the working range of the chromatographic system (at least one order of magnitude is suggested).

5.5.2 Prepare internal standard solutions. Suggested internal standards are 1-fluoronaphthalene, terphenyl, 2-chlorophenol, phenol, bis(2-chloroethoxy)methane, 2,4-dichlorophenol, phenanthrene, anthracene, and butyl benzyl phthalate. Determine the internal standard concentration levels from the minimum identifiable quantities.

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/FT-IR analysis.

Matrix	Methods
Water	3510, 3520
Soil/sediment	3540, 3541, 3550
Waste	3540, 3541, 3550, 3580

7.2 Extracts may be cleaned up by Method 3640, Gel-Permeation Cleanup.

7.3 Initial Calibration - Recommended GC/FT-IR conditions:

Scan time:	At least 2 scan/sec.
Initial column temperature and hold time:	40°C for 1 minute.
Column temperature program:	40-280°C at 10°C/min.
Final column temperature hold:	280°C.
Injector temperature:	280-300°C.
Transfer line temperature:	270°C.
Lightpipe:	280°C.
Injector:	Grob-type, splitless or on-column.
Sample volume:	2-3 µL.
Carrier gas:	Dry helium at about 1 mL/min.

7.4 With an oscilloscope, check the detector centerburst intensity versus the manufacturer's specifications. Increase the source voltage, if necessary, to meet these specifications. For reference purposes, laboratories should prepare a plot of time versus detector voltage over at least a 5 day period.

7.5 Capillary Column Interface Sensitivity Test - Install a 30 m x 0.32 mm fused silica capillary column coated with 1.0 µm of DB-5 (or equivalent). Set the lightpipe and transfer lines at 280°C, the injector at 225°C and the GC detector at 280°C (if used). Under splitless Grob-type or on-column injection conditions, inject 25 ng of nitrobenzene, dissolved in 1 µL of methylene chloride. The nitrobenzene should be identified by the on-line library software search within the first five hits (nitrobenzene should be contained within the search library).

7.6 Interferometer - If the interferometer is air-driven, adjust the interferometer drive air pressure to manufacturer's specifications.

7.7 MCT Detector Check - If the centerburst intensity is 75 percent or less of the mean intensity of the plot maximum obtained by the procedure of Section 7.4, install a new source and check the MCT centerburst with an oscilloscope versus the manufacturer's specifications (if available). Allow at least five hours of new source operation before data acquisition.

7.8 Frequency Calibration - At the present time, no consensus exists within the spectroscopic community on a suitable frequency reference standard for vapor-phase FT-IR. One reviewer has suggested the use of indene as an on-the-fly standard.

7.9 Minimum Identifiable Quantities - Using the GC/FT-IR operating parameters specified in Section 7.3, determine the minimum identifiable quantities for the compounds of interest.

7.9.1 Prepare a plot of lightpipe temperature versus MCT centerburst intensity (in volts or other vertical height units). This plot should span the temperature range between ambient and the lightpipe thermal limit in increments of about 20°C. Use this plot for daily QA/QC (see Section 8.4). Note that modern GC/FT-IR interfaces (1985 and later) may have eliminated most of this temperature effect.

7.10 GC/FT-IR Extract Analysis

7.10.1 Analysis - Analyze the dried methylene chloride extract using the chromatographic conditions specified in Section 7.3 for capillary column interfaces.

7.10.2 GC/FT-IR Identification - Visually compare the analyte infrared (IR) spectrum versus the search library spectrum of the most promising on-line library search hits. Report, as identified, those analytes with IR frequencies for the five (maximum number) most intense IR bands (S/N $\geq$ 5) which are within $\pm$ 5.0 cm^{-1} of the corresponding bands in the library spectrum. Choose IR bands which are sharp and well resolved. The software used to locate spectral peaks should employ the peak "center of gravity" technique. In addition, the IR frequencies of the analyte and library spectra should be determined with the same computer software.

7.10.3 Retention Time Confirmation - After visual comparison of the analyte and library spectrum as described in Section 7.10.2, compare the relative retention times (RRT) of the analyte and an authentic standard of the most promising library search hit. The standard and analyte RRT should agree within $\pm$ 0.01 RRT units when both are determined at the same chromatographic conditions.

7.10.4 Compound Class or Functionality Assignment - If the analyte cannot be unequivocally identified, report its compound class or functionality. See Table 3 for gas-phase group frequencies to be used as an aid for compound class assignment. It should be noted that FT-IR gas-phase group stretching frequencies are 0-30 cm^{-1} higher in frequency than those of the condensed phase.

7.10.5 Quantitation - Although this protocol can be used to confirm GC/MS identifications, with subsequent quantitation, FT-IR quantitation guidelines are also provided.

7.10.6 Integrated Absorbance Technique - After analyte identification, construct a standard calibration curve of concentration versus integrated infrared absorbance. For this purpose, choose for integration only those FT-IR scans which are at or above the peak half-height. The calibration curve should span at least one order of magnitude and the working range should bracket the analyte concentration.

7.10.7 Maximum Absorbance Infrared Band Technique - Following analyte identification, construct a standard calibration curve of concentration versus maximum infrared band intensity. For this purpose, choose an intense, symmetrical and well resolved IR absorbance band.

(Note that IR transmission is not proportional to concentration). Select the FT-IR scan with the highest absorbance to plot against concentration. The calibration curve should span at least one order of magnitude and the working range should bracket the analyte concentration. This method is most practical for repetitive, target compound analyses. It is more sensitive than the integrated absorbance technique.

7.10.8 Supplemental GC Detector Technique - If a GC detector is used in tandem with the FT-IR detector, the following technique may be used: following analyte identification, construct a standard calibration curve of concentration versus integrated peak area. The calibration curve should span at least one order of magnitude and the working range should bracket the analyte concentration. This method is most practical for repetitive, target compound analyses.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 One Hundred Percent Line Test - Set the GC/FT-IR operating conditions to those employed for the Sensitivity Test (see Section 7.5). Collect 16 scans over the entire detector spectral range. Plot the test and measure the peak-to-peak noise between 1800 and 2000 cm^{-1}. This noise should be $\leq$ 0.15%. Store this plot for future reference.

8.3 Single Beam Test - With the GC/FT-IR at analysis conditions, collect 16 scans in the single beam mode. Plot the co-added file and compare with a subsequent file acquired in the same fashion several minutes later. Note if the spectrometer is at purge equilibrium. Also check the plot for signs of deterioration of the lightpipe potassium bromide windows. Store this plot for future reference.

8.4 Align Test - With the lightpipe and MCT detector at thermal equilibrium, check the intensity of the centerburst versus the signal temperature

calibration curve. Signal intensity deviation from the predicted intensity may mean thermal equilibrium has not yet been achieved, loss of detector coolant, decrease in source output, or a loss in signal throughput resulting from lightpipe deterioration.

8.5 Mirror Alignment - Adjust the interferometer mirrors to attain the most intense signal. Data collection should not be initiated until the interferogram is stable. If necessary, align the mirrors prior to each GC/FT-IR run.

8.6 Lightpipe - The lightpipe and lightpipe windows should be protected from moisture and other corrosive substances at all times. For this purpose, maintain the lightpipe temperature above the maximum GC program temperature but below its thermal degradation limit. When not in use, maintain the lightpipe temperature slightly above ambient. At all times maintain a flow of dry, inert, carrier gas through the lightpipe.

8.7 Beamsplitter - If the spectrometer is thermostatted, maintain the beamsplitter at a temperature slightly above ambient at all times. If the spectrometer is not thermostated, minimize exposure of the beamsplitter to atmospheric water vapor.

9.0 METHOD PERFORMANCE

9.1 Method 8410 has been in use at the U.S. Environmental Protection Agency Environmental Monitoring Systems Laboratory for more than two years. Portions of it have been reviewed by key members of the FT-IR spectroscopic community (9). Side by side comparisons with GC/MS sample analyses indicate similar demands upon analytical personnel for the two techniques. Extracts previously subjected to GC/MS analysis are generally compatible with GC/FT-IR. However, it should be kept in mind that lightpipe windows are typically water soluble. Thus, extracts must be vigorously dried prior to analysis.

10.0 REFERENCES

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TABLE 1.
FUSED SILICA CAPILLARY COLUMN GAS CHROMATOGRAPHIC/FOURIER TRANSFORM INFRARED IDENTIFICATION LIMITS FOR BASE/NEUTRAL EXTRACTABLES

Compound	Identification Limit ng injected[a]	Identification Limit µg/L[b]	νmax, cm^{-1}[c]
Acenaphthene	40(25)	20(12.5)	799
Acenaphthylene	50(50)	25(25)	799
Anthracene	40(50)	20(25)	874
Benzo(a)anthracene	(50)	(25)	745
Benzo(a)pyrene	(100)	(50)	756
Bis(2-chloroethyl) ether	70(10)	35(5)	1115
Bis(2-chloroethoxy)methane	50(10)	25(5)	1084
Bis(2-chloroisopropyl) ether	50(10)	25(5)	1088
Butyl benzyl phthalate	25(10)	12.5(5)	1748
4-Bromophenyl phenyl ether	40(5)	20(2.5)	1238
2-Chloronaphthalene	110	55	851
4-Chloroaniline	40	20	1543
4-Chlorophenyl phenyl ether	20(5)	10(2.5)	1242
Chrysene	(100)	(50)	757
Di-n-butyl phthalate	20(5)	10(2.5)	1748
Dibenzofuran	40	20	1192
Diethyl phthalate	20(5)	10(2.5)	1748
Dimethyl phthalate	20(5)[d]	10(2.5)	1751
Di-n-octyl phthalate	25(10)	12.5(5)	1748
Di-n-propyl phthalate	25(5)	12.5(2.5)	1748
1,2-Dichlorobenzene	50	25	1458
1,3-Dichlorobenzene	50	25	779
1,4-Dichlorobenzene	50	25	1474
2,4-Dinitrotoluene	20	10	1547
2,6-Dinitrotoluene	20	10	1551
Bis-(2-ethylhexyl) phthalate	25(10)	12.5(5)	1748
Fluoranthene	100(50)	50(25)	773
Fluorene	40(50)	20(25)	737
Hexachlorobenzene	40	20	1346
Hexachlorocyclopentadiene	120	60	814
Hexachloroethane	50	25	783
1,3-Hexachlorobutadiene	120	60	853
Isophorone	40	20	1690
2-Methylnaphthalene	110	55	3069
Naphthalene	40(25)	20(12.5)	779
Nitrobenzene	25	12.5	1539
N-Nitrosodimethylamine	20(5)	10(2.5)	1483
N-Nitrosodi-n-propylamine	50(5)	25(2.5)	1485
N-Nitrosodiphenylamine[e]	40	20	1501
2-Nitroaniline	40	20	1564
3-Nitroaniline	40	20	1583
4-Nitroaniline	40	20	1362
Phenanthrene	50(50)	25(25)	729
Pyrene	100(50)	50(25)	820
1,2,4-Trichlorobenzene	50(25)	25(12.5)	750

TABLE 1.
(Continued)

[a] Determined using on-column injection and the conditions of Section 7.3. A medium band HgCdTe detector [3800-700 cm^{-1}; D^* value (λpeak 1000 Hz, 1) 4.5 x 10^{10} cm $Hz^{1/2}W^{-1}$] type with a 0.25 mm^2 focal chip was used. The GC/FT-IR system is a 1976 retrofitted model.

[b] Based on a 2 μL injection of a one liter sample that has been extracted and concentrated to a volume of 1.0 mL.

[c] Most intense IR peak and suggested quantitation peak.

[d] Values in parentheses were determined with a new (1986) GC/FT-IR system. A narrow band HgCdTe detector [3800-750cm^{-1}; D^* value (λpeak 1000 Hz, 1) 4 x 10^{10} cm $Hz^{1/2}W^{-1}$] was used. Chromatographic conditions are those of Section 7.3.

[e] Detected as diphenylamine.

TABLE 2.
FUSED SILICA CAPILLARY COLUMN GAS CHROMATOGRAPHIC/FOURIER TRANSFORM INFRARED ON-LINE AUTOMATED IDENTIFICATION LIMITS FOR ACIDIC EXTRACTABLES

Compound	Identification Limit		
	ng injected[a]	µg/L[b]	νmax, cm^{-1}[c]
Benzoic acid	70	35	1751
2-Chlorophenol	50	25	1485
4-Chlorophenol[d]	100	50	1500
4-Chloro-3-methylphenol	25	12.5	1177
2-Methylphenol	50	25	748
4-Methylphenol	50	25	1177
2,4-Dichlorophenol	50	25	1481
2,4-Dinitrophenol	60	30	1346
4,6-Dinitro-2-methylphenol	60	30	1346
2-Nitrophenol[d]	40	20	1335
4-Nitrophenol	50	25	1350
Pentachlorophenol	50	25	1381
Phenol	70	35	1184
2,4,6-Trichlorophenol	120	60	1470
2,4,5-Trichlorophenol	120	60	1458

[a] Operating conditions are the same as those cited in Section 7.3.

[b] Based on a 2 µL injection of a one liter sample that has been extracted and concentrated to a volume of 1.0 mL.

[c] Most intense IR peak and suggested quantitation peak.

[d] Subject to interference from co-eluting compounds.

TABLE 3.
GAS-PHASE GROUP FREQUENCIES

Functionality	Class	Number of Compounds	Frequency Range, vcm^{-1}
Ether	Aryl, Alkyl	14	1215-1275
	Benzyl, Alkyl	3	1103-1117
	Diaryl	5	1238-1250
	Dialkyl	12	1084-1130
	Alkyl, Vinyl	3	1204-1207
			1128-1142
Ester	Unsubstituted Aliphatic	29	1748-1761
	Aromatic	11	1703-1759
	Monosubstituted Acetate	34	1753-1788
Nitro	Aliphatic	5	1566-1594
			1548-1589
			1377-1408
			1327-1381
	Aromatic	18	1535-1566
			1335-1358
Nitrile	Aliphatic	9	2240-2265
	Aromatic	9	2234-2245
Ketone	Aliphatic (acyclic)	13	1726-1732
	(α,ß unsaturated)	2	1638-1699
	Aromatic	16	1701-1722
Amide	Substituted Acetamides	8	1710-1724
Alkyne	Aliphatic	8	3323-3329
Acid	Aliphatic	24	3574-3580
		22	1770-1782
	Dimerized-Aliphatic	2	3586-3595
	Aromatic	10	3574-3586
		10	1757-1774
Phenol	1,4-Disubstituted	15	3645-3657
		15	1233-1269
		15	1171-1190
	1,3-Disubstituted	10	3643-3655
		10	1256-1315
		10	1157-1198
	1,2-Disubstituted	6	3582-3595
			1255-1274

TABLE 3.
(Continued)

Functionality	Class	Number of Compounds	Frequency Range, νcm^{-1}
Alcohol	Primary Aliphatic	20	3630-3680
		11	1206-1270
		16	1026-1094
	Secondary Aliphatic	17	3604-3665
		10	1231-1270
	Tertiary Aliphatic	10	3640-3670
		6	1213-1245
Amine	Primary Aromatic	15	3480-3532
	Secondary Aromatic	5	3387-3480
	Aliphatic	10	760- 785
Alkane		14	2930-2970
			2851-2884
			1450-1475
			1355-1389
Aldehyde	Aromatic	12	1703-1749
		12	2820-2866
		12	2720-2760
	Aliphatic	6	1742-1744
		6	2802-2877
		6	2698-2712
Benzene	Monosubstituted	7	1707-1737
		24	1582-1630
		24	1470-1510
		11	831- 893
		23	735- 790
		25	675- 698

TABLE 4. FUSED SILICA CAPILLARY COLUMN GC/FT-IR QUANTITATION RESULTS

Compound	Concentration Range, and Identification Limit, ng[a]	Maximum Absorbance[b] Correlation Coefficient[d]	Integrated Absorbance[c] Correlation Coefficient[d]
Acenaphthene	25-250	0.9995	0.9985
Acenaphthylene	25-250	0.9959	0.9985
Anthracene	50-250	0.9969	0.9971
Benzo(a)anthracene	50-250	0.9918	0.9921
Benzoic acid	50-250	0.9864	0.9892
Benzo(a)pyrene	100-250	0.9966	0.9074
Bis(2-chloroethoxy)methane	25-250	0.9992	0.9991
Bis(2-chloroethyl) ether	25-250	0.9955	0.9992
Bis(2-chloroisopropyl) ether	50-250	0.9981	0.9998
4-Bromophenyl phenyl ether	25-250	0.9995	0.9996
Butyl benzyl phthalate	25-250	0.9999	0.9994
4-Chloroaniline	25-250	0.9991	0.9965
4-Chloro-3-methylphenol	25-250	0.9975	0.9946
2-Chloronaphthalene	100-250	0.9897	0.9988
2-Chlorophenol	25-250	0.9976	0.9965
4-Chlorophenol[e]			
4-Chlorophenyl phenyl ether	25-250	0.9999	0.9997
Chrysene	100-250	0.9985	0.9984
Dibenzofuran	25-250	0.9697	0.8579
Di-n-butyl phthalate	25-250	0.9998	0.9996
1,2-Dichlorobenzene	25-250	0.9937	0.9947
1,3-Dichlorobenzene	25-250	0.9985	0.9950
1,4-Dichlorobenzene	25-250	0.9994	0.9994
2,4-Dichlorophenol	25-250	0.9964	0.9969
Dimethyl phthalate	25-250	0.9998	0.9996
Dimethyl phthalate	25-250	0.9998	0.9997
Dinitro-2-methylphenol	50-250	0.9936	0.9967
2,4-Dinitrophenol	50-250	0.9920	0.9916
2,4-Dinitrotoluene	25-250	0.9966	0.9928
2,6-Dinitrotoluene	25-250	0.9947	0.9966
Di-n-octyl phthalate	25-250	0.9983	0.9991
Bis(2-ethylhexyl) phthalate	25-250	0.9991	0.9993
Fluoranthene	25-250	0.9983	0.9966
Fluorene	25-250	0.9987	0.9989
Hexachlorobenzene	50-250	0.9981	0.9995
1,3-Hexachlorobutadiene	50-250	0.9960	0.9979
Hexachlorocyclopentadiene	100-250	0.9862	0.9845
Hexachloroethane	25-250	0.9986	0.9992
Isophorone	25-250	0.9984	0.9990
2-Methylnaphthalene	50-250	0.9981	0.9950

(continued)

TABLE 4. (Continued)

Compound	Concentration Range, and Identification Limit, ng[a]	Maximum Absorbance[b] Correlation Coefficient[d]	Integrated Absorbance[c] Correlation Coefficient[d]
2-Methylphenol	25-250	0.9972	0.9964
4-Methylphenol	25-250	0.9972	0.9959
Naphthalene	25-250	0.9956	0.9954
2-Nitroaniline	25-250	0.9996	0.9994
3-Nitroaniline	25-250	0.9985	0.9990
4-Nitroaniline	25-250	0.9936	0.9992
Nitrobenzene	25-250	0.9997	0.9979
2-Nitrophenol[e]			
4-Nitrophenol	50-250	0.9951	0.9953
N-Nitrosodimethylamine	25-250	0.9982	0.9993
N-Nitrosodiphenylamine	25-250	0.9994	0.9971
N-Nitrosodi-n-propylamine	25-250	0.9991	0.9995
Pentachlorophenol	50-250	0.9859	0.9883
Phenanthrene	25-250	0.9941	0.9989
Phenol	25-250	0.9978	0.9966
Pyrene	50-250	0.9971	0.9977
1,2,4-Trichlorobenzene	50-250	0.9969	0.991
2,4,5-Trichlorophenol	25-250	0.9952	0.9966
2,4,6-Trichlorophenol	25-250	0.9969	0.9965

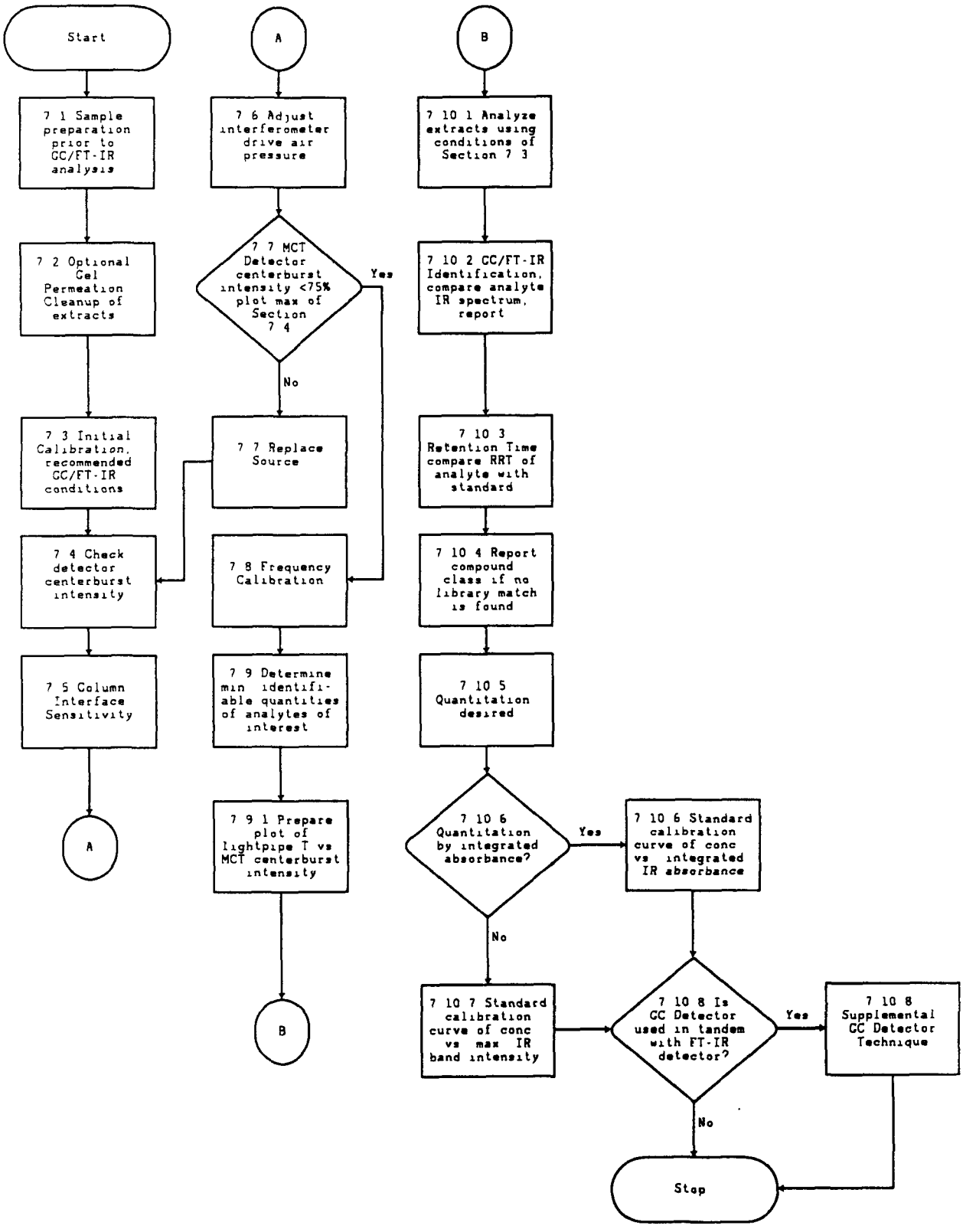
[a] Lower end of range is at or near the identification limit.

[b] FT-IR scan with highest absorbance plotted against concentration.

[c] Integrated absorbance of combined FT-IR scans which occur at or above the chromatogram peak half-height.

[d] Regression analysis carried out at four concentration levels. Each level analyzed in duplicate chromatographic conditions are stated in Section 7.3.

[e] Subject to interference from co-eluting compounds.


Start
7 1 Sample preparation prior to GC/FT-IR analysis
7 2 Optional Gel Permeation Cleanup of extracts
7 3 Initial Calibration, recommended GC/FT-IR conditions
7 4 Check detector centerburst intensity
7 5 Column Interface Sensitivity
A
A
7 6 Adjust interferometer drive air pressure
7 7 MCT Detector centerburst intensity <75% plot max of Section 7 4
Yes
No
7 7 Replace Source
7 8 Frequency Calibration
7 9 Determine min identifiable quantities of analytes of interest
7 9 1 Prepare plot of lightpipe T vs MCT centerburst intensity
B
B
7 10 1 Analyze extracts using conditions of Section 7 3
7 10 2 GC/FT-IR Identification, compare analyte IR spectrum, report
7 10 3 Retention Time compare RRT of analyte with standard
7 10 4 Report compound class if no library match is found
7 10 5 Quantitation desired
7 10 6 Quantitation by integrated absorbance?
Yes
7 10 6 Standard calibration curve of conc vs integrated IR absorbance
No
7 10 7 Standard calibration curve of conc vs max IR band intensity
7 10 8 Is GC Detector used in tandem with FT-IR detector?
Yes
7 10 8 Supplemental GC Detector Technique
No
Stop

METHOD 8275

THERMAL CHROMATOGRAPHY/MASS SPECTROMETRY (TC/MS) FOR SCREENING SEMIVOLATILE ORGANIC COMPOUNDS

1.0 SCOPE AND APPLICATION

1.1 Method 8275 is a screening technique that may be used for the qualitative identification of semivolatile organic compounds in extracts prepared from nonaqueous solid wastes and soils. Direct injection of a sample may be used in limited applications. The following analytes can be qualitatively determined by this method:

Compound Name	CAS No.[a]
2-Chlorophenol	95-57-8
4-Methylphenol	106-44-5
2,4-Dichlorophenol	120-83-2
Naphthalene	91-20-3
4-Chloro-3-methylphenol	59-50-7
1-Chloronaphthalene	90-13-1
2,4-Dinitrotoluene	121-14-2
Fluorene	86-73-7
Diphenylamine	122-39-4
Hexachlorobenzene	118-74-1
Dibenzothiophene	132-65-0
Phenanthrene	85-01-8
Carbazole	86-74-8
Aldrin	309-00-2
Pyrene	129-00-0
Benzo(k)fluoranthene	207-08-9
Benzo(a)pyrene	50-32-8

[a] Chemical Abstract Services Registry Number.

1.2 Method 8275 can be used to qualitatively identify most neutral, acidic, and basic organic compounds that can be thermally desorbed from a sample, and are capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone.

1.3 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 A portion of the sample (0.010-0.100 g) is weighed into a sample crucible. The crucible is placed in a pyrocell and heated. The compounds desorbed from the sample are detected using a flame ionization detector (FID). The FID response is used to calculate the optimal amount of sample needed for mass spectrometry. A second sample is desorbed and the compounds are condensed on the head of a fused silica capillary column. The column is heated using a temperature program, and the effluent from the column is introduced into the mass spectrometer.

3.0 INTERFERENCES

3.1 Contamination by carryover can occur whenever low-level samples are analyzed after high-level samples. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of an empty (clean) crucible to check for cross contamination.

4.0 APPARATUS AND MATERIALS

4.1 Thermal Chromatograph (TC) System

4.1.1 Thermal chromatograph™, Ruska Laboratories, or equivalent.

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 Flame Ionization detector (FID).

4.2 Mass Spectrometer (MS) system

4.2.1 Mass Spectrometer - Capable of scanning from 35 to 500 amu every one second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode.

4.2.2 TC/MS interface - Any GC-to-MS interface producing acceptable calibration data in the concentration range of interest may be used.

4.2.3 Data System - A computer must be interfaced to the mass spectrometer. The data 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 (or group of masses) and that can plot such ion abundances versus time or scan number. This type of plot is defined as a reconstructed ion chromatogram (RIC). Software must also be available that allows for integration of the abundances in, and RIC between, specified time or scan-number limits.

4.3 Tools and equipment

4.3.1 Fused quartz spatula.

4.3.2 Fused quartz incinerator ladle.

4.3.3 Metal forceps for sample crucible.

4.3.4 Sample crucible storage dishes.

4.3.5 Porous fused quartz sample crucibles with lids.

4.3.6 Sample crucible cleaning incinerator.

4.3.7 Cooling rack.

4.3.8 Microbalance, 1 g capacity, 0.000001 g sensitivity, Mettler Model M-3 or equivalent.

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

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

5.2 Solvents

5.2.1 Methanol, CH_3OH - Pesticide grade or equivalent.

5.2.2 Acetone, CH_3COCH_3 - Pesticide grade or equivalent.

5.2.3 Toluene, $C_6H_5CH_3$ - Pesticide grade or equivalent.

5.2.4 Methylene chloride, CH_2Cl_2 - Pesticide grade or equivalent.

5.2.5 Carbon disulfide, CS_2 - Pesticide grade or equivalent.

5.2.6 Hexane, C_6H_{14} - Pesticide grade or equivalent.

5.2.7 Other suitable solvents - Pesticide grade or equivalent.

5.3 Stock Standard solutions - Standard solutions may be prepared from pure standard materials or purchased as certified solutions.

5.3.1 Prepare stock standard solutions by weighing about 0.01 g of pure material. Dissolve the material in pesticide quality acetone, or other suitable solvent, and dilute to 10 mL in a volumetric flask. Larger volumes may be used at the convenience of the analyst.

5.3.2 Transfer the stock standard solutions into glass vials with Teflon lined screw-caps or crimp tops. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially prior to use in preparation of calibration standards.

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 are met. Dissolve about 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 20/80 (V/V) carbon disulfide/methylene chloride. Most of the compounds are also soluble in small volumes of methanol, acetone, or toluene, except for perylene-d_{12}. Prior to each analysis, evaporate about 10 μL of the internal standard onto the lid of the crucible. Store internal standard solutions at 4°C or less before, and between, use.

5.5 Calibration standards - Prepare calibration standards within the working range of the TC/MS system. Each standard should contain each analyte or interest (e.g. some or all of the compounds listed in Section 1.1 may be included). Each aliquot of calibration standard should be spiked with internal standards prior to analysis. Stock solutions 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.

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 Crucible Preparation

7.1.1 Turn on the incinerator and let it heat for at least 10 minutes. The bore of the incinerator should be glowing red.

7.1.2 Load the sample crucible and lid into the incinerator ladle and insert into the incinerator bore. Leave in the incinerator for 5 minutes, then remove and place on the cooling rack.

7.1.3 Allow the crucibles and lids to cool for five minutes before placing them in the storage dishes.

CAUTION: Do not touch the crucibles with your fingers. This can result in a serious burn, as well as contamination of

the crucible. Always handle the sample crucibles and lids with forceps and tools specified.

7.1.4 All sample crucibles and lids required for the number of analyses planned should be cleaned and placed in the storage dishes ready for use.

7.2 Sample Preparation and Loading

7.2.1 The analyst should take care in selecting a sample for analysis, since the sample size is generally limited to 0.100 g or less. This implies that the sample should be mixed as thoroughly as possible before taking an aliquot. Because the sample size is limited, the analyst may wish to analyze several aliquots for determination.

7.2.2 The sample should be mixed or ground such that a 0.010 to 0,100 g aliquot can be removed. Remove one sample crucible from the storage dish and place it on the microbalance. Establish the tare weight. Remove the sample crucible from the balance with the forceps and place it on a clean surface.

7.2.3 Load an amount of sample into the sample crucible using the fused quartz spatula. Place the assembly on the microbalance and determine the weight of the sample. For severely contaminated samples, less than 0.010 g will suffice, while 0.050-0.100 g is needed for low concentrations of contaminants. Place the crucible lid on the crucible; the sample is now ready for analysis.

7.3 FID Analysis

7.3.1 Load the sample into the TC. Hold the sample at 30°C for 2 minutes followed by linear temperature programmed heating to 260°C at 30°C/minute. Follow the temperature program with an isothermal heating period of 10 minutes at 260°C, followed by cooling back to 30°C. The total analysis cycle time is 24.2 minutes

7.3.2 Monitor the FID response in real time during analysis, and note the highest response in millivolts (mV). Use this information to determine the proper weight of sample needed for combined thermal extraction/gas chromatography/mass spectrometry.

7.4 Thermal Extraction/GC/MS

7.4.1 Prepare a calibration curve using a clean crucible and lid by spiking the compounds of interest at five concentrations into the crucible and applying the internal standards to the crucible lid. Analyze these standards and establish response factors at different concentrations.

7.4.2 Weigh out the amount of fresh sample that will provide approximately 1000 to 3000 mv response. For example, if 0.010 g of sample gives an FID response of 500 mv, then 0.020 to 0.060 g (0.040 g ± 50 %) should be used. If 0.100 g gives 8000 mv, then 0.025 g ± 50 % should be used.

7.4.3 After weighing out the sample into the crucible, deposit the internal standards (10 μL) onto the lid of the crucible. Load the crucible into the pyrocell, using the same temperature program in Section 7.3.1. Hold the capillary at 5°C during this time to focus the released semi-volatiles (the intermediate trap is held at 330°C to pass all compounds onto the column). Maintain the splitter zone at 310°C, and the GC/MS transfer line at 285°C. After the isothermal heating period is complete, temperature program the column from 5°C to 285°C at 10°C/minute and hold at 285°C for 5 minutes. Acquire data during the entire run time.

7.4.4 If the response for any quantitation ion exceeds the initial calibration curve range of the TC/MS system, a smaller sample should be analyzed.

7.5 Data Interpretation

7.5.1 Qualitative Analysis

7.5.1.1 The qualitative identification of compounds determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met.

7.5.1.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.5.1.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

7.5.1.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.5.1.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.5.1.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributing by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.5.1.2 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 non-target 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 $\pm$ 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be within 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. Data system library reduction programs can sometimes create these discrepancies.

Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual

comparison of sample with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

8.0 QUALITY CONTROL

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

9.0 METHOD PERFORMANCE

9.1 Table 1 presents method performance data, generated using spiked soil samples. Method performance data in an aqueous matrix are not available.

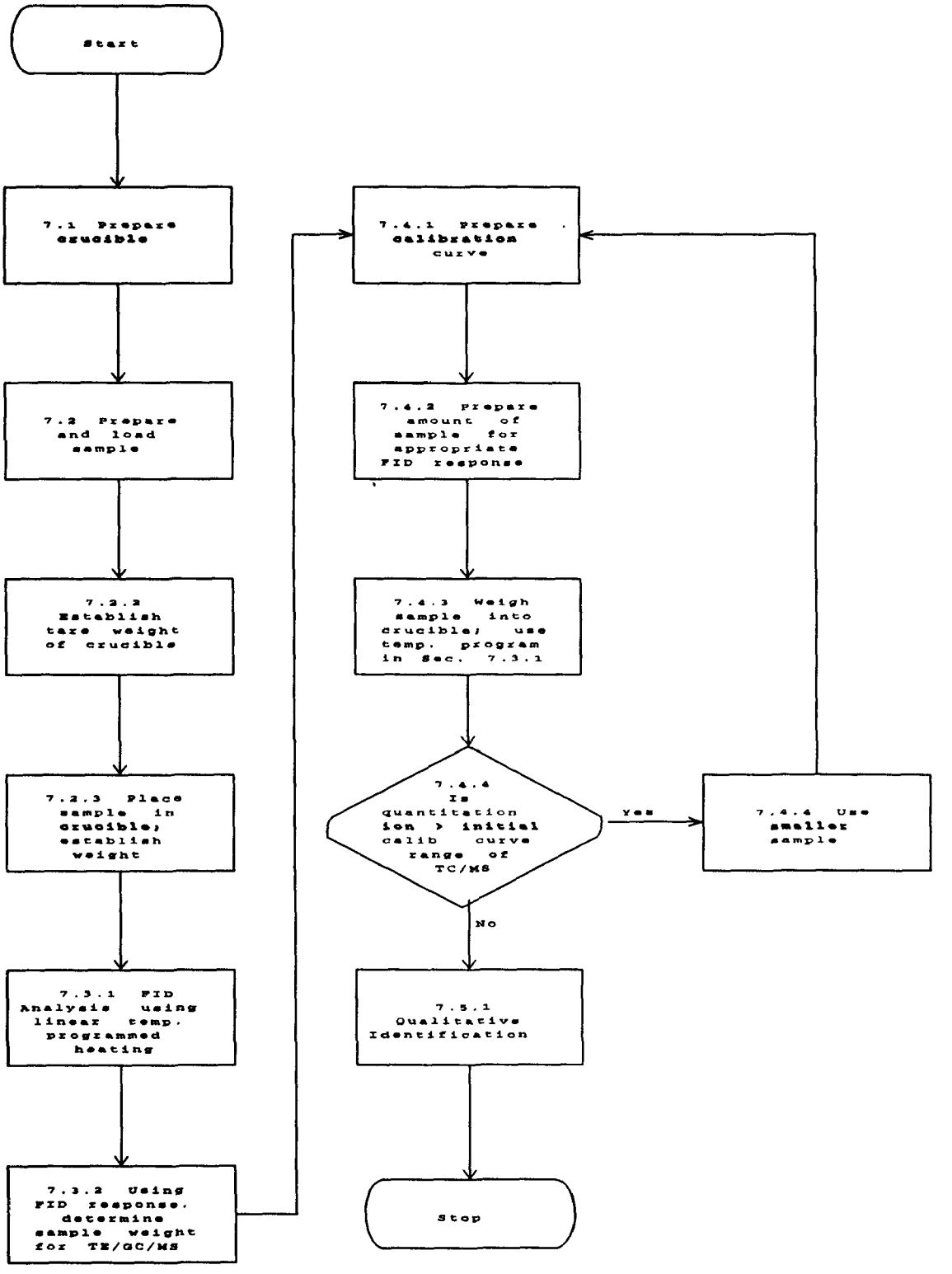
10.0 REFERENCES

1. Zumberge, J.E., C. Sutton, R.D. Worden, T. Junk, T.R. Irvin, C.B. Henry, V. Shirley, and E.B. Overton, "Determination of Semi-Volatile Organic Pollutants in Soils by Thermal Chromatography-Mass Spectrometry (TC/MS): an Assessment for Field Analysis," in preparation.

TABLE 1
METHOD PERFORMANCE, SOIL MATRIX

Analyte	Average % Recovery[a]			Mean Recovery
	Clay	Silt	Subsoil	
2-Chlorophenol	30	22	2	18
4-Methylphenol	10	77	7	31
2,4-Dichlorophenol	23	20	26	23
Naphthalene	77	120	63	87
4-Chloro-3-methyl-phenol	9	12	9	10
1-Chloronaphthalene	96	103	70	90
2,4-Dinitrotoluene	7	10	10	9
Fluorene	9	25	19	18
Diphenylamine	5	6	6	6
Hexachlorobenzene	68	64	80	71
Dibenzothiophene	20	35	50	35
Phenanthrene	11	31	40	24
Carbazole	4	8	9	7
Aldrin	3	19	15	12
Pyrene	7	19	20	15
Benzo(k)fluoranthene	4	9	11	8
Benzo(a)pyrene	4	8	11	8

[a] Percent theoretical recovery based upon linearity of injections deposited on the crucible lid (slope and y-intercept). Average of 9 replicates (~10 mg soil spiked with 50 ppm of analyte); 3 different instruments at 3 different laboratories.


Start
7.1 Prepare crucible
7.2 Prepare and load sample
7.2.2 Establish tare weight of crucible
7.2.3 Place sample in crucible; establish weight
7.3.1 FID Analysis using linear temp. programmed heating
7.3.2 Using FID response, determine sample weight for TE/GC/MS
7.4.1 Prepare calibration curve
7.4.2 Prepare amount of sample for appropriate FID response
7.4.3 Weigh sample into crucible; use temp. program in Sec. 7.3.1
7.4.4 Is quantitation ion > initial calib curve range of TC/MS
Yes
7.4.4 Use smaller sample
No
7.5.1 Qualitative Identification
Stop

METHOD 5050

BOMB COMBUSTION METHOD FOR SOLID WASTE

1.0 SCOPE AND APPLICATION

1.1 This method describes the sample preparation steps necessary to determine total chlorine in solid waste and virgin and used oils, fuels and related materials, including: crankcase, hydraulic, diesel, lubricating and fuel oils, and kerosene by bomb oxidation and titration or ion chromatography. Depending on the analytical finish chosen, other halogens (bromine and fluorine) and other elements (sulfur and nitrogen) may also be determined.

1.2 The applicable range of this method varies depending on the analytical finish chosen. In general, levels as low as 500 μg/g chlorine in the original oil sample can be determined. The upper range can be extended to percentage levels by dilution of the combustate.

1.3 This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. Specific safety statements are given in Section 3.0.

2.0 SUMMARY OF METHOD

2.1 The sample is oxidized by combustion in a bomb containing oxygen under pressure. The liberated halogen compounds are absorbed in a sodium carbonate/sodium bicarbonate solution. Approximately 30 to 40 minutes are required to prepare a sample by this method. Samples with a high water content (> 25%) may not combust efficiently and may require the addition of a mineral oil to facilitate combustion. Complete combustion is still not guaranteed for such samples.

2.2 The bomb combustate solution can then be analyzed for the following elements as their anion species by one or more of the following methods:

Method	Title
9252	Chloride (Titrimetric, Mercuric Nitrate)
9253	Chloride (Titrimetric, Silver Nitrate)
9056	Anion Chromatography Method (Chloride, Sulfate, Nitrate, Phosphate, Fluoride, Bromide)

NOTE: Strict adherence to all of the provisions prescribed hereinafter ensures against explosive rupture of the bomb, or a blowout, provided the bomb is of proper design and construction and in good mechanical condition. It is desirable, however, that the bomb be enclosed in a shield of steel plate at least 1/2 in. (12.7 mm) thick, or equivalent protection be provided against unforeseeable contingencies.

3.0 INTERFERENCES

3.1 Samples with very high water content (> 25%) may not combust efficiently and may require the addition of a mineral oil to facilitate combustion.

3.2 To determine total nitrogen in samples, the bombs must first be purged of ambient air. Otherwise, nitrogen results will be biased high.

4.0 APPARATUS AND MATERIALS

4.1 Bomb, having a capacity of not less than 300 mL, so constructed that it will not leak during the test, and that quantitative recovery of the liquids from the bomb may be readily achieved. The inner surface of the bomb may be made of stainless steel or any other material that will not be affected by the combustion process or products. Materials used in the bomb assembly, such as the head gasket and lead-wire insulation, shall be resistant to heat and chemical action and shall not undergo any reaction that will affect the chlorine content of the sample in the bomb.

4.2 Sample cup, platinum or stainless steel, 24 mm in outside diameter at the bottom, 27 mm in outside diameter at the top, 12 mm in height outside, and weighing 10 to 11 g.

4.3 Firing wire, platinum or stainless steel, approximately No. 26 B & S gage.

4.4 Ignition circuit, capable of supplying sufficient current to ignite the nylon thread or cotton wicking without melting the wire.

NOTE: The switch in the ignition circuit shall be of the type that remains open, except when held in closed position by the operator.

4.5 Nylon sewing thread, or Cotton Wicking, white.

4.6 Funnel, to fit a 100-mL volumetric flask.

4.7 Class A volumetric flasks, 100-mL, one per sample.

4.8 Syringe, 5- or 10-mL disposable plastic.

4.9 Apparatus for specific analysis methods are given in the methods.

4.10 Analytical balance: capable of weighing to 0.0001 g.

5.0 REAGENTS

5.1 Purity of reagents. 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 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Oxygen. Free of combustible material and halogen compounds, available at a pressure of 40 atm.

WARNING: Oxygen vigorously accelerates combustion (see Appendix A1.1)

5.4 Sodium bicarbonate/sodium carbonate solution. Dissolve 2.5200 g $NaHCO_3$ and 2.5440 g Na_2CO_3 in reagent water and dilute to 1 L.

5.5 White oil. Refined.

5.6 Reagents and materials for specific analysis methods are given in the methods.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine.

6.2 Ensure that the portion of the sample used for the test is representative of the sample.

6.3 To minimize losses of volatile halogenated solvents that may be present in the sample, keep the field and laboratory samples as free of headspace as possible.

6.4 Because used oils may contain toxic and/or carcinogenic substances appropriate field and laboratory safety procedures should be followed.

7.0 PROCEDURE

7.1 Sample Preparation

7.1.1 Preparation of bomb and sample. Cut a piece of firing wire approximately 100 mm in length and attach the free ends to the terminals. Arrange the wire so that it will be just above and not touching the sample cup. Loop a cotton thread around the wire so that the ends will extend into the sampling cup. Pipet 10 mL of the $NaHCO_3/Na_2CO_3$ solution into the bomb, wetting the sides. Take an aliquot of the oil sample of approximately 0.5 g using a 5- or 10-mL disposable plastic syringe, and place in the sample cup. The actual sample weight is determined by the difference

between the weight of the empty and filled syringe. Do not use more than 1 g of sample.

NOTE: After repeated use of the bomb for chlorine determination, a film may be noticed on the inner surface. This dullness should be removed by periodic polishing of the bomb. A satisfactory method for doing this is to rotate the bomb in a lathe at about 300 rpm and polish the inside surface with Grit No. 2/0 or equivalent paper[1] coated with a light machine oil to prevent cutting, and then with a paste of grit-free chromic oxide[2] and water. This procedure will remove all but very deep pits and put a high polish on the surface. Before using the bomb, it should be washed with soap and water to remove oil or paste left from the polishing operation. Bombs with porous or pitted surfaces should never be used because of the tendency to retain chlorine from sample to sample.

NOTE: If the sample is not readily combustible, other nonvolatile, chlorine-free combustible diluents such as white oil may be employed. However, the combined weight of sample and nonvolatile diluent shall not exceed 1 g. Some solid additives are relatively insoluble but may be satisfactorily burned when covered with a layer of white oil.

NOTE: The practice of alternately running samples high and low in chlorine content should be avoided whenever possible. It is difficult to rinse the last traces of chlorine from the walls of the bomb, and the tendency for residual chlorine to carry over from sample to sample has been observed in a number of laboratories. When a sample high in chlorine has preceded one low in chlorine content, the test on the low-chlorine sample should be repeated, and one or both of the low values thus obtained should be considered suspect if they do not agree within the limits of repeatability of this method.

NOTE: Do not use more than 1 g total of sample and white oil or other chlorine-free combustible material. Use of excess amounts of these materials could cause a buildup of dangerously high pressure and possible rupture of the bomb.

7.1.2 Addition of oxygen. Place the sample cup in position and arrange the thread so that the end dips into the sample. Assemble the bomb and tighten the cover securely. Admit oxygen slowly (to avoid blowing the oil from the cup) until a pressure is reached as indicated in Table 1.

NOTE: Do not add oxygen or ignite the sample if the bomb has been jarred, dropped, or tiled.

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[1]Emery Polishing Paper grit No. 2/0 may be purchased from the Behr-Manning Co., Troy, NY.

[2]Chromic oxide may be purchased from J.T. Baker & Co., Phillipsburg, NJ.

7.1.3 Combustion. Immerse the bomb in a cold water bath. Connect the terminals to the open electrical circuit. Close the circuit to ignite the sample. Remove the bomb from the bath after immersion for at least 10 minutes. Release the pressure at a slow, uniform rate such that the operation requires at least 1 min. Open the bomb and examine the contents. If traces of unburned oil or sooty deposits are found, discard the determination, and thoroughly clean the bomb before using it again.

7.1.4 Collection of halogen solution. Using reagent water and a funnel, thoroughly rinse the interior of the bomb, the sample cup, the terminals, and the inner surface of the bomb cover into a 100-mL volumetric flask. Dilute to the mark with reagent water.

7.1.5 Cleaning procedure for bomb and sample cup. Remove any residual fuse wire from the terminals and the cup. Using hot water, rinse the interior of the bomb, the sample cup, the terminals, and the inner surface of the bomb cover. (If any residue remains, first scrub the bomb with Alconox solution). Copiously rinse the bomb, cover, and cup with reagent water.

7.2 Sample Analysis. Analyze the combustate for chlorine or other halogens using the methods listed in Step 2.2. It may be necessary to dilute the samples so that the concentration will fall within the range of standards.

7.3 Calculations. Calculate the concentrations of each element detected in the sample according to the following equation:

$$C_o = \frac{C_{com} \times V_{com} \times DF}{W_o} \qquad (1)$$

where:

C_o = concentration of element in the sample, μg/g
C_{com} = concentration of element in the combustate, μg/mL
V_{com} = total volume of combustate, mL
DF = dilution factor
W_o = weight of sample combusted, g.

Report the concentration of each element detected in the sample in micrograms per gram.

Example: A 0.5-g oil sample was combusted, yielding 10 mL of combustate. The combustate was diluted to 100 mL total volume and analyzed for chloride, which was measured to be 5 μg/mL. The concentration of chlorine in the original sample is then calculated as shown below:

$$C_o = \frac{\frac{5\ \mu g}{mL} \times (10\ mL) \times (10)}{0.5\ g} \qquad (2)$$

$$C_o = \frac{1{,}000\ \mu g}{g} \qquad (3)$$

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 One sample in ten should be bombed twice. The results should agree to within 10%, expressed as the relative percent difference of the results.

8.3 Analyze matrix spike and matrix spike duplicates - spike samples with the elements of interest at a level commensurate with the levels being determined. The spiked compounds should be similar to those expected in the sample. Any sample suspected of containing > 25% water should also be spiked with organic chlorine.

8.4 For higher levels (e.g., percent levels), spiking may be inappropriate. For these cases, samples of known composition should be combusted. The results should agree to within 10% of the expected result.

8.5 Quality control for the analytical method(s) of choice should be followed.

9.0 PERFORMANCE

See analytical methods referenced in Step 2.2.

10.0 REFERENCES

1. ASTM Method D 808-81, Standard Test Method for Chlorine in New and Used Petroleum Products (Bomb Method). 1988 Annual Book of ASTM Standards. Volume 05.01 Petroleum Products and Lubricants.

2. Gaskill, A.; Estes, E. D.; Hardison, D. L.; and Myers, L. E. Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels. Prepared for U.S. Environmental Protection Agency, Office of Solid Waste. EPA Contract No. 68-01-7075, WA 80. July 1988.

TABLE 1.
GAGE PRESSURES

Capacity of bomb, mL	Minimum gage pressure[a], atm	Maximum gage pressure[a], atm
300 to 350	38	40
350 to 400	35	37
400 to 450	30	32
450 to 500	27	29

[a]The minimum pressures are specified to provide sufficient oxygen for complete combustion, and the maximum pressures represent a safety requirement. Refer to manufacturers' specifications for appropriate gage pressure, which may be lower than those listed here.

APPENDIX

A1. PRECAUTIONARY STATEMENTS

A1.1 Oxygen

Warning--Oxygen vigorously accelerates combustion.

Keep oil and grease away. Do not use oil or grease on regulators, gages, or control equipment.

Use only with equipment conditioned for oxygen service by careful cleaning to remove oil, grease, and other combustibles.

Keep combustibles away from oxygen and eliminate ignition sources.

Keep surfaces clean to prevent ignition or explosion, or both, on contact with oxygen.

Always use a pressure regulator. Release regulator tension before opening cylinder valve.

All equipment and containers used must be suitable and recommended for oxygen service.

Never attempt to transfer oxygen from cylinder in which it is received to any other cylinder. Do not mix gases in cylinders.

Do not drop cylinder. Make sure cylinder is secured at all times.

Keep cylinder valve closed when not in use.

Stand away from outlet when opening cylinder valve.

For technical use only. Do not use for inhalation purposes.

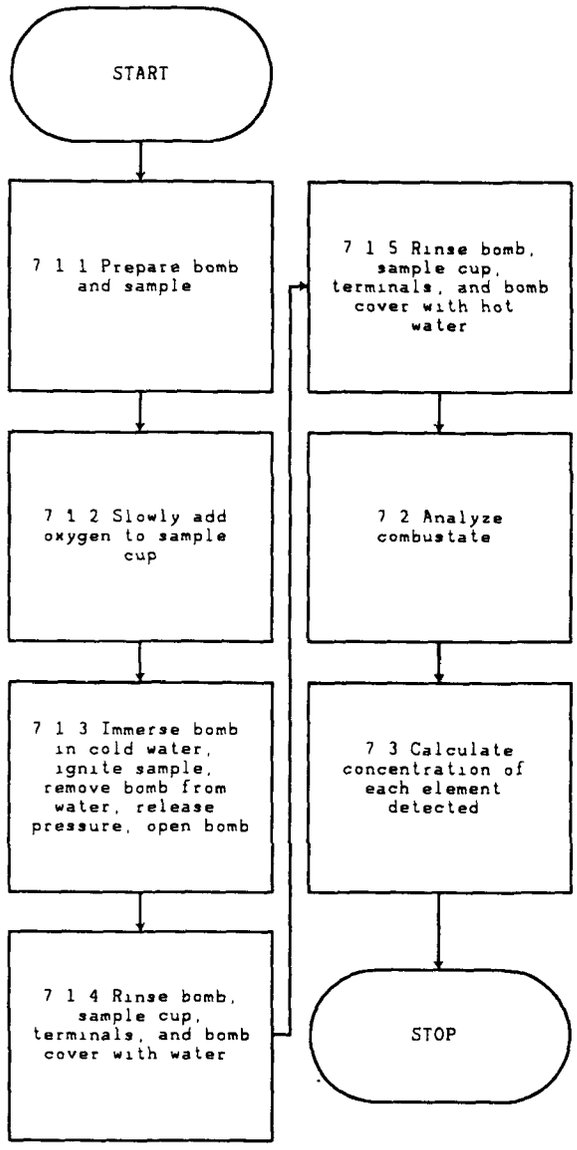
Keep cylinder out of sun and away from heat.

Keep cylinders from corrosive environment.

Do not use cylinder without label.

Do not use dented or damaged cylinders.

See Compressed Gas Association booklets G-4 and G4.1 for details of safe practice in the use of oxygen.


START
7 1 1 Prepare bomb and sample
7 1 2 Slowly add oxygen to sample cup
7 1 3 Immerse bomb in cold water, ignite sample, remove bomb from water, release pressure, open bomb
7 1 4 Rinse bomb, sample cup, terminals, and bomb cover with water
7 1 5 Rinse bomb, sample cup, terminals, and bomb cover with hot water
7 2 Analyze combustate
7 3 Calculate concentration of each element detected
STOP

METHOD 9010

TOTAL AND AMENABLE CYANIDE

1.0 SCOPE AND APPLICATION

1.1 Method 9010 is used to determine the concentration of inorganic cyanide (CAS Registry Number 57-12-5) in wastes or leachate. The method detects inorganic cyanides that are present as either soluble salts or complexes. It is used to determine values for both total cyanide and cyanide amenable to chlorination. The "reactive" cyanide content of a waste, that is, the cyanide content that could generate toxic fumes when exposed to mild acidic conditions, is not determined by Method 9010 (refer to Chapter Seven, Step 7.3.3.2). Method 9010 is not intended to determine if a waste is hazardous by the characteristic of reactivity.

1.2 The titration procedure using silver nitrate with p-dimethylamino-benzal-rhodanine indicator is used for measuring concentrations of cyanide exceeding 0.1 mg/L (0.025 mg/250 mL of absorbing liquid).

1.3 The colorimetric procedure is used for concentrations below 1 mg/L of cyanide and is sensitive to about 0.02 mg/L.

2.0 SUMMARY OF METHOD

2.1 The cyanide, as hydrocyanic acid (HCN), is released from samples containing cyanide by means of a reflux-distillation operation under acidic conditions and absorbed in a scrubber containing sodium hydroxide solution. The cyanide in the absorbing solution is then determined colorimetrically or titrametrically.

2.2 In the colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCl) by reaction of cyanide with chloramine-T at a pH less than 8. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent. The absorbance is read at 578 nm for the complex formed with pyridine-barbituric acid reagent and CNCl. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

2.3 The titration measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

3.0 INTERFERENCES

3.1 Interferences are eliminated or reduced by using the distillation procedure. Chlorine and sulfide are interferences in Method 9010.

3.2 Oxidizing agents such as chlorine decompose most cyanides. Chlorine interferences can be removed by adding an excess of sodium arsenite to the waste prior to preservation and storage of the sample to reduce the chlorine to chloride which does not interfere.

3.3 Sulfide interference can be removed by adding an excess of bismuth nitrate to the waste (to precipitate the sulfide) before distillation. Samples that contain hydrogen sulfide, metal sulfides, or other compounds that may produce hydrogen sulfide during the distillation should be treated by the addition of bismuth nitrate.

3.4 High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation, nitrate and nitrite will form nitrous acid, which will react with some organic compounds to form oximes. These compounds once formed will decompose under test conditions to generate HCN. The possibility of interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid just before distillation. Nitrate and nitrite are interferences when present at levels higher than 10 mg/L and in conjunction with certain organic compounds.

3.5 Thiocyanate is reported to be an interference when present at very high levels. Levels of 10 mg/L were not found to interfere.

3.6 Fatty acids, detergents, surfactants, and other compounds may cause foaming during the distillation when they are present in large concentrations and will make the endpoint of the titration difficult to detect. They may be extracted at pH 6-7.

4.0 APPARATUS AND MATERIALS

4.1 Reflux distillation apparatus such as shown in Figure 1 or Figure 2. The boiling flask should be of one liter size with inlet tube and provision for condenser. The gas absorber may be a 270-mL Fisher-Milligan scrubber (Fisher, Part No. 07-513 or equivalent). The reflux apparatus may be a Wheaton 377160 distillation unit or equivalent.

4.2 Spectrophotometer - Suitable for measurements at 578 nm with a 1.0 cm cell or larger.

4.3 Hot plate stirrer/heating mantle.

4.4 pH meter.

4.5 Amber light.

4.6 Vacuum source.

4.7 Refrigerator.

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 ASTM Type II Water (ASTM D1193-77 (1983)). All water used in this method will be Type II unless otherwise specified.

5.3 Reagents for sample collection, preservation, and handling

5.3.1 Sodium arsenite (0.1N), $NaAsO_2$. Dissolve 3.2 g $NaAsO_2$ in 250 mL water.

5.3.2 Ascorbic acid, $C_6H_8O_6$.

5.3.3 Sodium hydroxide solution (50%), NaOH. Commercially available.

5.3.4 Acetic acid (1.6M) CH_3COOH. Dilute one part of concentrated acetic acid with 9 parts of water.

5.3.5 2,2,4-Trimethylpentane, C_8H_{18}.

5.3.6 Hexane, C_6H_{14}.

5.3.7 Chloroform, $CHCl_3$.

5.4 Reagents for cyanides amenable to chlorination

5.4.1 Calcium hypochlorite solution (0.35M), $Ca(OCl)_2$. Combine 5 g of calcium hypochlorite and 100 mL of water. Shake before using.

5.4.2 Sodium hydroxide solution (1.25N), NaOH. Dissolve 50 g of NaOH in 1 liter of water.

5.4.3 Sodium arsenite (0.1N). See Step 5.3.1.

5.5 Reagents for distillation

5.5.1 Sodium hydroxide (1.25N). See Step 5.4.2.

5.5.2 Bismuth nitrate (0.062M), $Bi(NO)_3 \cdot 5H_2O$. Dissolve 30 g $Bi(NO)_3 \cdot 5H_2O$ in 100 mL of water. While stirring, add 250 mL of glacial acetic acid, CH_3COOH. Stir until dissolved and dilute to 1 liter with water.

5.5.3 Sulfamic acid (0.4N), H_2NSO_3H. Dissolve 40 g H_2NSO_3H in 1 liter of water.

5.5.4 Sulfuric acid (18N), H_2SO_4. Slowly and carefully add 500 mL of concentrated H_2SO_4 to 500 mL of water.

5.5.5 Magnesium chloride solution (2.5M), $MgCl_2 \cdot 6H_2O$. Dissolve 510 g of $MgCl_2 \cdot 6H_2O$ in 1 liter of water.

5.6 Reagents for colorimetric determination

5.6.1 Sodium hydroxide solution (0.25N), NaOH. Dissolve 10 g NaOH in 1 liter of water.

5.6.2 Sodium phosphate monobasic (1M), $NaH_2PO_4 \cdot H_2O$. Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in 1 liter of water. Refrigerate this solution.

5.6.3 Chloramine-T solution (0.44%), $C_7H_7ClNNaO_2S$. Dissolve 1.0 g of white, water soluble chloramine-T in 100 mL of water and refrigerate until ready to use.

5.6.4 Pyridine-Barbituric acid reagent, $C_5H_5N \cdot C_4H_4N_2O_3$. Place 15 g of barbituric acid in a 250-mL volumetric flask and add just enough water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of concentrated hydrochloric acid (HCl), mix, and cool to room temperature. Dilute to 250 mL with water. This reagent is stable for approximately six months if stored in a cool, dark place.

5.6.5 Stock potassium cyanide solution (1 mL = 1000 ug CN), KCN. Dissolve 2.51 g of KCN and 2 g KOH in 900 mL of water. Standardize with 0.0192N silver nitrate, $AgNO_3$. Dilute to appropriate concentration to achieve 1 mL = 1000 ug of CN.

NOTE: Detailed procedure for $AgNO_3$ standardization is described in "Standard Methods for the Examination of Water and Wastewater", 16th Edition, (1985), Methods 412C and 407A.

5.6.6 Intermediate standard potassium cyanide solution, (1 mL = 100 ug CN), KCN. Dilute 100 mL of stock potassium cyanide solution (1 mL = 1000 ug CN) to 1000 mL with water.

5.6.7 Working standard potassium cyanide solution (1 mL = 10 ug CN), KCN. Prepare fresh daily by diluting 100 mL of intermediate standard potassium cyanide solution and 10 mL of 1N NaOH to 1 liter with water.

5.7 Reagents for titration procedure

5.7.1 Rhodanine indicator - Dissolve 20 mg of p-dimethylamino-benzal-rhodanine, $C_{12}H_{12}N_2OS_2$, in 100 mL of acetone.

5.7.2 Standard silver nitrate solution (0.0192N), $AgNO_3$. Prepare by crushing approximately 5 g $AgNO_3$ and drying to constant weight at 40°C. Weigh out 3.2647 g of dried $AgNO_3$. Dissolve in 1 liter of water.

NOTE: Detailed procedure for $AgNO_3$ standardization is described in "Standard Methods for the Examination of Water and Wastewater", 16th Edition, (1985), Methods 412C and 407A.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine.

6.2 Samples should be collected in plastic or glass containers. All containers must be thoroughly cleaned and rinsed.

6.3 Oxidizing agents such as chlorine decompose most cyanides. To determine whether oxidizing agents are present, test a drop of the sample with potassium iodide-starch test paper. A blue color indicates the need for treatment. Add 0.1N sodium arsenite solution a few mL at a time until a drop of sample produces no color on the indicator paper. Add an additional 5 mL of sodium arsenite solution for each liter of sample. Ascorbic acid can be used as an alternative although it is not as effective as arsenite. Add a few crystals of ascorbic acid at a time until a drop of sample produces no color on the indicator paper. Then add an additional 0.06 g of ascorbic acid for each liter of sample volume.

6.4 Aqueous samples must be preserved by adding 50% sodium hydroxide until the pH is greater than or equal to 12 at the time of collection.

6.5 Samples should be chilled to 4°C.

6.6 When properly preserved, cyanide samples can be stored for up to 14 days prior to analysis.

6.7 Solid and oily wastes may be extracted prior to analysis by the method in Appendix A. It uses a dilute NaOH solution (pH = 12) as the extractant. This yields extractable cyanide.

6.8 If fatty acids, detergents, and surfactants are a problem, they may be extracted using the following procedure. Acidify the sample with acetic acid (1.6M) to pH 6.0 to 7.0.

CAUTION: The initial reaction product of alkaline chlorination is the very toxic gas cyanogen chloride; therefore, it is necessary that this reaction be performed in a hood.

Extract with isooctane, hexane, or chloroform (preference in order named) with solvent volume equal to 20% of the sample volume. One extraction is usually adequate to reduce the compounds below the interference level. Avoid multiple extractions or a long contact time at low pH in order to keep the loss of HCN at a minimum. When the extraction is completed, immediately raise the pH of the sample to above 12 with 50% NaOH solution.

CAUTION: This procedure can produce lethal HCN gas.

7.0 PROCEDURE

7.1 Pretreatment for cyanides amenable to chlorination

7.1.1 This test must be performed under amber light. $K_3[Fe\text{-}(CN)_6]$ may decompose under UV light and hence will test positive for cyanide amenable to chlorination if exposed to fluorescent lighting or sunlight. Two identical sample aliquots are required to determine cyanides amenable to chlorination.

7.1.2 To one 500 mL sample or to a sample diluted to 500 mL, add calcium hypochlorite solution dropwise while agitating and maintaining the pH between 11 and 12 with 1.25N sodium hydroxide until an excess of

chlorine is present as indicated by KI-starch paper turning blue. The sample will be subjected to alkaline chlorination by this step.

CAUTION: The initial reaction product of alkaline chlorination is the very toxic gas cyanogen chloride; therefore, it is necessary that this reaction be performed in a hood.

7.1.3 Test for excess chlorine with KI-starch paper and maintain this excess for one hour with continuous agitation. A distinct blue color on the test paper indicates a sufficient chlorine level. If necessary, add additional calcium hypochlorite solution.

7.1.4 After one hour, add 1 mL portions of 0.1N sodium arsenite until KI-starch paper shows no residual chlorine. Add 5 mL of excess sodium arsenite to ensure the presence of excess reducing agent.

7.1.5 Test for total cyanide as described below in both the chlorinated and the unchlorinated samples. The difference of total cyanide in the chlorinated and unchlorinated samples is the cyanide amenable to chlorination.

7.2 Distillation Procedure

7.2.1 Place 500 mL of sample, or sample diluted to 500 mL in the one liter boiling flask. Pipet 50 mL of 1.25N sodium hydroxide into the gas absorber. If the apparatus in Figure 1 is used, add water until the spiral is covered. Connect the boiling flask, condenser, gas absorber and vacuum trap.

7.2.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately two bubbles of air per second enter the boiling flask through the air inlet tube.

7.2.3 If samples are known to contain sulfide, add 50 mL of 0.062M bismuth nitrate solution through the air inlet tube. Mix for three minutes. Use lead acetate paper to check the sample for the presence of sulfide. A positive test is indicated by a black color on the paper.

7.2.4 If samples are known or suspected to contain nitrate or nitrite, add 50 mL of 0.4N sulfamic acid solution through the air inlet tube. Mix for three minutes.

7.2.5 Slowly add 50 mL of 18N sulfuric acid through the air inlet tube. Rinse the tube with water and allow the airflow to mix the flask contents for three minutes. Add 20 mL of 2.5M magnesium chloride through the air inlet and wash the inlet tube with a stream of water.

7.2.6 Heat the solution to boiling. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, and closing the vacuum source, disconnect the gas absorber.

7.2.7 Transfer the solution from the absorber into a 250-mL volumetric flask. Rinse the absorber and add the rinse water to the volumetric flask. Dilute to volume with water.

7.2.8 If the manual spectrophotometric determination will be performed, proceed to Step 7.3.1. If the titration procedure will be performed, proceed to Step 7.7.

7.3 Manual spectrophotometric determination

7.3.1 Pipet 50 mL of the absorber solution into a 100-mL volumetric flask. If the sample is later found to be beyond the linear range of the colorimetric determination and redistillation of a smaller sample is not feasible, a smaller aliquot may be taken. If less than 50 mL is taken, dilute to 50 mL with 0.25N sodium hydroxide solution.

NOTE: Temperature of reagents and spiking solution can affect the response factor of the colorimetric determination. The reagents stored in the refrigerator should be warmed to ambient temperature before use. Samples should not be left in a warm instrument to develop color, but instead they should be aliquoted to a cuvette immediately prior to reading the absorbance.

7.3.2 Add 15 mL of 1M sodium phosphate solution and mix. Add 2 mL of chloramine-T and mix. Some distillates may contain compounds that have chlorine demand. One minute after the addition of chloramine-T, test for excess chlorine with KI-starch paper. If the test is negative, add 0.5 mL chloramine-T. After one minute recheck with KI-starch paper. Continue to add chloramine-T in 0.5 mL increments until an excess is maintained. After 1 to 2 minutes, add 5 mL of pyridine-barbituric acid solution and mix.

7.3.3 Dilute to 100 mL with water and mix again. Allow 8 minutes for color development and then read the absorbance at 578 nm in a 1-cm cell within 15 minutes. The sodium hydroxide concentration will be 0.125N.

7.4 Standard curve for samples without sulfide

7.4.1 Prepare a series of standards by pipetting suitable volumes of working standard potassium cyanide solution into 250-mL volumetric flasks. To each flask, add 50 mL of 1.25N sodium hydroxide and dilute to 250 mL with water. Prepare using the following table. The sodium hydroxide concentration will be 0.25N.

mL of Working Standard Solution (1 mL = 10 ug CN)	Concentration (ug CN/L)
0	Blank
1.0	40
2.0	80
5.0	200
10.0	400
15.0	600
20.0	800

7.4.2 After the standard solutions have been prepared according to the table above, pipet 50 mL of each standard solution into a 100-mL volumetric flask and proceed to Steps 7.3.2 and 7.3.3 to obtain absorbance values for the standard curve. The final concentrations for the standard curve will be one half of the amounts in the above table (ranging from 20 to 400 ug/L).

7.4.3 It is recommended that at least two standards (a high and a low) be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. If distilled standards do not agree within $\pm$ 10% of the undistilled standards, the analyst should find the cause of the apparent error before proceeding.

7.4.4 Prepare a standard curve by plotting absorbance of standard versus the cyanide concentration.

7.4.5 To check the efficiency of the sample distillation, add cyanide from the working standard to 500 mL of sample to ensure a level of 40 ug/L. Proceed with the analysis as in Step 7.2.1.

7.5 Standard curve for samples with sulfide

7.5.1 It is imperative that all standards be distilled in the same manner as the samples using the method of standard additions. Standards distilled by this method will give a linear curve, at low concentrations, but as the concentration increases, the recovery decreases. It is recommended that at least five standards be distilled.

7.5.2 Prepare a series of standards similar in concentration to those mentioned in Step 7.4.1 and analyze as in Step 7.2.1. Prepare a standard curve by plotting absorbance of standard versus the cyanide concentration.

7.6 Calculation - If the colorimetric procedure is used, calculate the cyanide, in ug/L, in the original sample as follows.

$$CN\ (ug/L) = \frac{A \times B \times C}{D \times E}$$

where:

A = ug/L CN read from standard curve.
B = mL of original sample for distillation (500 recommended).
C = mL of sample after distillation (250).
D = mL used for colorimetric analysis (50 recommended).
E = mL of sample after preparation of colorimetric analysis (100).

7.7 Titration Procedure

7.7.1 Transfer the gas absorber solution or a suitable aliquot from the 250-mL volumetric flask to a 500-mL Erlenmeyer flask. Add 10-12 drops of the rhodanine indicator.

7.7.2 Titrate with standard 0.0192N silver nitrate to the first change in color from yellow to brownish-pink. Titrate a water blank using the same amount of sodium hydroxide and indicator as in the sample.

7.7.3 The analyst should be familiar with the endpoint of the titration and the amount of indicator to be used before actually titrating the samples. A 5-mL buret may be conveniently used to obtain a precise titration.

7.7.4 Calculation - If the titrimetric procedure is used, calculate concentration of CN in mg/L in the original sample as follows:

$$CN\ (mg/L) = \frac{(A - B)\ 1000}{D} \times \frac{C}{E}$$

where:

A = mL of $AgNO_3$ for titration of sample.
B = mL of $AgNO_3$ for titration of blank.
C = mL of sample after distillation (250).
D = mL of original sample for distillation (500 recommended).
E = mL of sample taken for titration (250 recommended).

The above equation assumes that the standard silver nitrate concentration is exactly 0.0192N which is equivalent to one mL of silver nitrate to one mg of cyanide.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one reagent blank per analytical batch or once in every 20 samples to determine if contamination or any memory effects are occurring.

8.3 Analyze check standards with every analytical batch of samples. If the standards are not within 15% of the expected value, then the samples must be reanalyzed.

8.4 Run one replicate sample for every 10 samples. A replicate sample is a sample brought through the entire sample preparation process. The CV of the replicates should be 15% or less. If this criterion is not met, the samples should be reanalyzed.

8.5 The method of standard additions shall be used for the analysis of all samples that suffer from matrix interferences such as samples which contain sulfides.

9.0 METHOD PERFORMANCE

9.1 The titration procedure using silver nitrate is used for measuring concentrations of cyanide exceeding 0.1 mg/L. The colorimetric procedure is used for concentrations below 1 mg/L of cyanide and is sensitive to about 0.02 mg/L.

9.2 EPA Method 335.2 (sample distillation with titration) reports that in a single laboratory using mixed industrial and domestic waste samples at concentrations of 0.06 to 0.62 mg/L CN, the standard deviations for precision were $\pm$ 0.005 to $\pm$ 0.094, respectively. In a single laboratory using mixed industrial and domestic waste samples at concentrations of 0.28 and 0.62 mg/L CN, recoveries (accuracy) were 85% and 102%, respectively.

9.3 In two additional studies using surface water, ground water, and landfill leachate samples, the titration procedure was further evaluated. The concentration range used in these studies was 0.5 to 10 mg/L cyanide. The detection limit was found to be 0.2 mg/L for both total and amenable cyanide determinations. The precision (CV) was 6.9 and 2.6 for total cyanide determinations and 18.6 and 9.1 for amenable cyanide determinations. The mean recoveries were 94% and 98.9% for total cyanide, and 86.7% and 97.4% for amenable cyanide.

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FIGURE 1.
APPARATUS FOR CYANIDE DISTILLATION

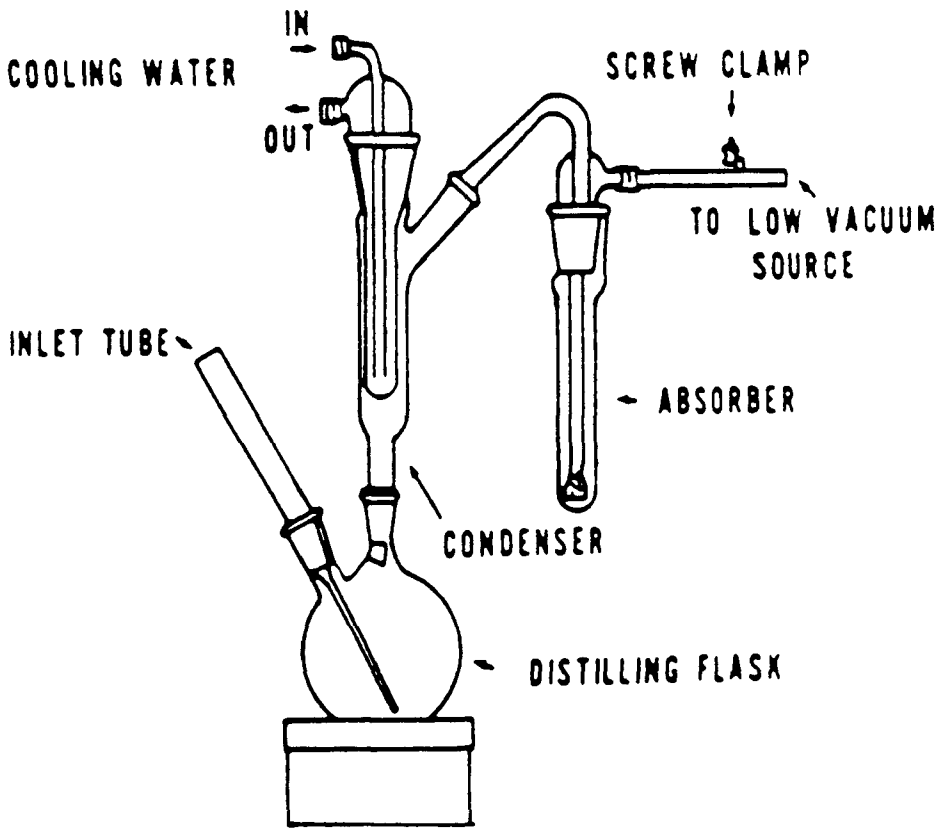
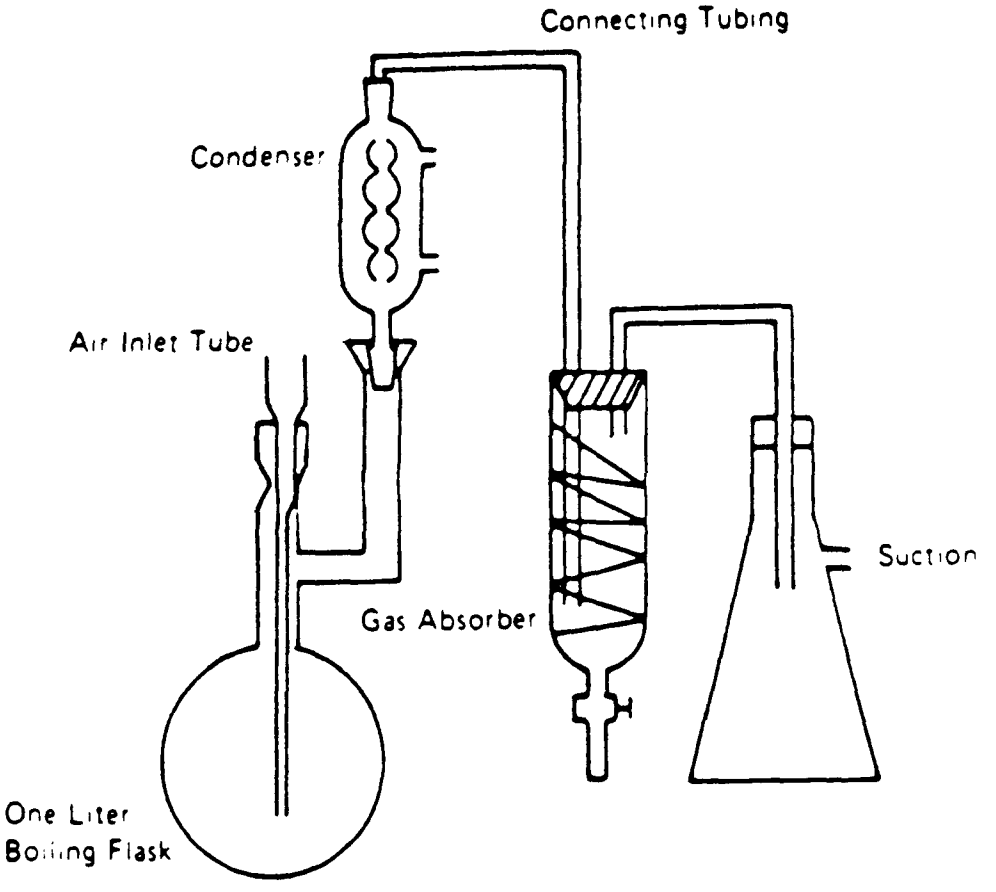
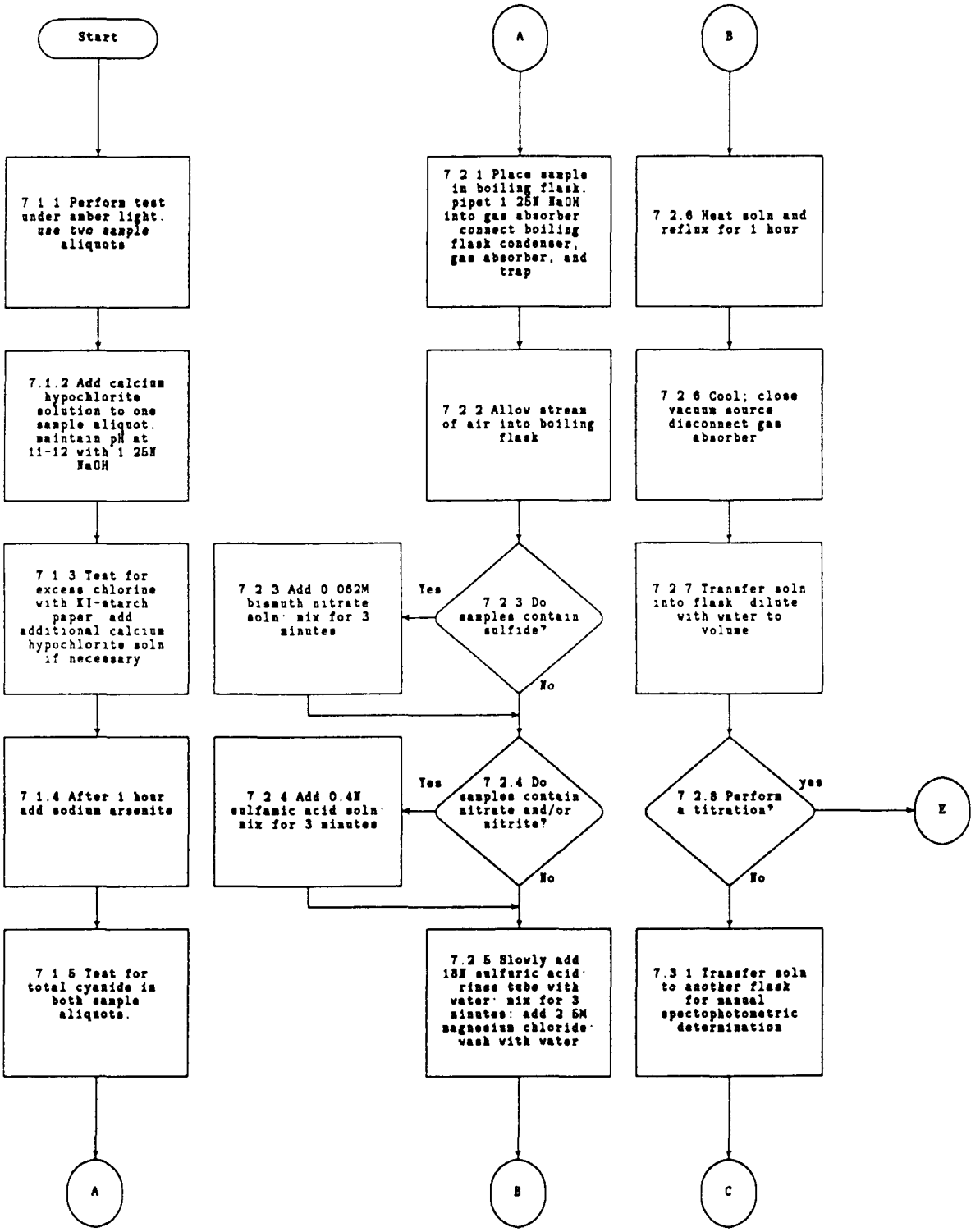
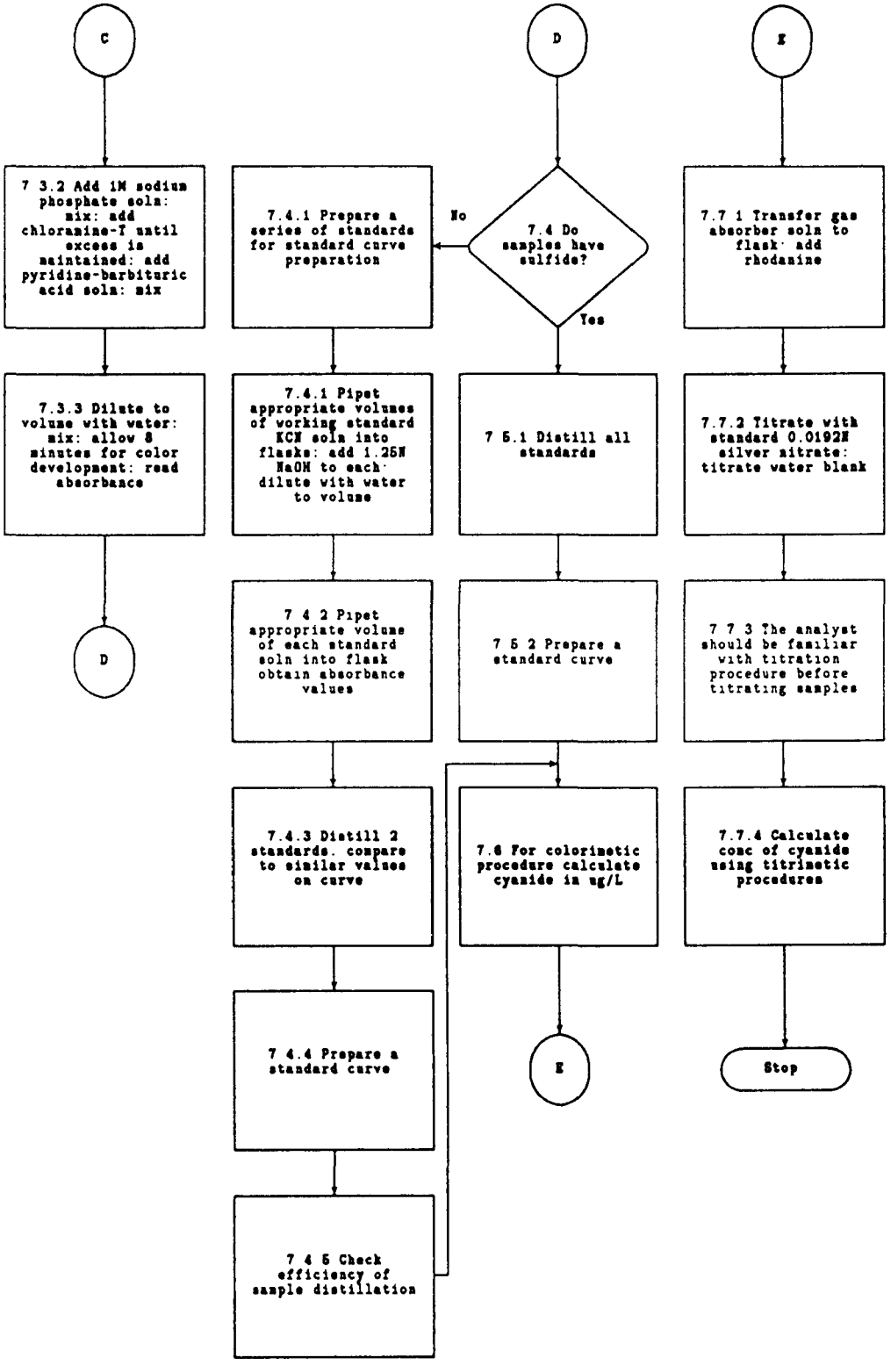


FIGURE 2.
APPARATUS FOR CYANIDE DISTILLATION



METHOD 9010
TOTAL AND AMENABLE CYANIDE




C
D
E
7 3.2 Add 1M sodium phosphate soln: mix: add chloramine-T until excess is maintained: add pyridine-barbituric acid soln: mix
7.4.1 Prepare a series of standards for standard curve preparation
No
7.4 Do samples have sulfide?
Yes
7.7 1 Transfer gas absorber soln to flask· add rhodanine
7.3.3 Dilute to volume with water: mix: allow 8 minutes for color development: read absorbance
7.4.1 Pipet appropriate volumes of working standard KCN soln into flasks: add 1.25N NaOH to each· dilute with water to volume
7 5.1 Distill all standards
7.7.2 Titrate with standard 0.0192N silver nitrate: titrate water blank
D
7 4 2 Pipet appropriate volume of each standard soln into flask obtain absorbance values
7 5 2 Prepare a standard curve
7 7 3 The analyst should be familiar with titration procedure before titrating samples
7.4.3 Distill 2 standards. compare to similar values on curve
7.6 For colorimetic procedure calculate cyanide in ug/L
7.7.4 Calculate conc of cyanide using titrimetic procedures
7 4.4 Prepare a standard curve
E
Stop
7 4 5 Check efficiency of sample distillation

APPENDIX 9010A

CYANIDE EXTRACTION PROCEDURE FOR SOLIDS AND OILS

1.0 SCOPE AND APPLICATION

1.1 The extraction procedure described in this appendix is designed for the extraction of soluble cyanides from solid and oil wastes. The method is applicable to oil, solid, and multiphasic samples. This method is not applicable to samples containing insoluble cyanide compounds.

2.0 SUMMARY OF METHOD

2.1 If the waste sample contains so much solid, or solids of such a size as to interfere with agitation and homogenization of the sample mixture in the distillation flask, or so much oil or grease as to interfere with the formation of a homogeneous emulsion, the sample must be extracted with water at pH 10 or greater, and the extract analyzed by Method 9010. Samples that contain free water must be filtered and separated into an aqueous component and a combined oil and solid component. The nonaqueous component may then be extracted, and an aliquot of the extract combined with an aliquot of the filtrate in proportion to the composition of the sample. Alternatively, the components may be analyzed separately, and cyanide levels reported for each component. However, if the sample solids are known to contain sufficient levels of cyanide (about 50 ug/g) as to be well above the limit of detection, the extraction step may be deleted and the solids analyzed directly by Method 9010. This can be accomplished by diluting a small aliquot of the waste solid (1-5 g) in 500 mL water in the distillation flask and suspending the slurry during distillation with a magnetic stir-bar.

3.0 INTERFERENCES

3.1 Potential interferences that may be encountered during analysis are discussed in Method 9010.

4.0 APPARATUS AND MATERIALS

4.1 Extractor - Any suitable device that sufficiently agitates a sealed container of one liter volume or greater. For the purpose of this analysis, agitation is sufficient when:

1. All sample surfaces are continuously brought into contact with extraction fluid, and

2. The agitation prevents stratification of the sample and fluid.

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 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Sodium hydroxide (50% w/v), NaOH. Commercially available.

5.4 n-Hexane, C_6H_{14}.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a plan that addresses the considerations discussed in Chapter 4 of this manual. See Section 6.0 of Method 9010 for additional guidance.

7.0 PROCEDURE

7.1 If the waste does not contain any free aqueous phase, go to Step 7.5. If the sample is a homogeneous fluid or slurry that does not separate or settle in the distillation flask when using a Teflon coated magnetic stirring bar but mixes so that the solids are entirely suspended, then the sample may be analyzed by Method 9010 without an extraction step.

7.2 Assemble Buchner funnel apparatus. Unroll glass filtering fiber and fold the fiber over itself several times to make a pad about 1 cm thick when lightly compressed. Cut the pad to fit the Buchner funnel. Weigh the pad, then place it in the funnel. Turn the aspirator on and wet the pad with a known amount of water.

7.3 Transfer the sample to the Buchner funnel in small aliquots, first decanting the fluid. Rinse the sample container with known amounts of water and add the rinses to the Buchner funnel. When no free water remains in the funnel, slowly open the stopcock to allow air to enter the vacuum flask. A small amount of sediment may have passed through the glass fiber pad. This will not interfere with the analysis.

7.4 Transfer the solid and the glass fiber pad to a tared weighing dish. Since most greases and oils will not pass through the fiber pad, solids, oils, and greases will be extracted together. If the filtrate includes an oil phase, transfer the filtrate to a separatory funnel. Collect and measure the volume of the aqueous phase. Transfer the oil phase to the weighing dish with the solid.

7.5 Weigh the dish containing solid, oil (if any), and filter pad. Subtract the weight of the dry filter pad. Calculate the net volume of water present in the original sample by subtracting the total volume of rinses used from the measured volume of the filtrate.

7.6 Place the following in a 1-liter wide-mouthed bottle:

500 mL water
5 mL 50% w/v NaOH
50 mL n-Hexane (if a heavy grease is present)

If the weight of the solids (Step 7.5) is greater than 25 g, weigh out a representative aliquot of 25 g and add it to the bottle; otherwise add all of the solids. Cap the bottle.

7.7 The pH of the extract must be maintained above 10 throughout the extraction step and subsequent filtration. Since some samples may release acid, the pH must be monitored as follows. Shake the extraction bottle and after one minute, check the pH. If the pH is below 12, add 50% NaOH in 5 mL increments until it is at least 12. Recap the bottle, and repeat the procedure until the pH does not drop.

7.8 Place the bottle or bottles in the tumbler, making sure there is enough foam insulation to cushion the bottle. Turn the tumbler on and allow the extraction to run for about 16 hours.

7.9 Prepare a Buchner funnel apparatus as in Step 7.1 with a glass fiber pad filter.

7.10 Decant the extract to the Buchner funnel. Full recovery of the extract is not necessary.

7.11 If the extract contains an oil phase, separate the aqueous phase using a separatory funnel. Neither the separation nor the filtration are critical, but are necessary to be able to measure the volume of the aliquot of the aqueous extract analyzed. Small amounts of suspended solids and oil emulsions will not interfere.

7.12 At this point, an aliquot of the filtrate of the original sample may be combined with an aliquot of the extract in a proportion representative of the sample. Alternatively, they may be analyzed separately and concentrations given for each phase. This is described by the following equation:

$$\frac{\text{Liquid Sample Aliquot (mL)}}{\text{Extract Aliquot (mL)}} = \frac{\text{Solid Extracted (g)}}{\text{Total Solid (g)}} \times \frac{\text{Total Sample Filtrate (mL)}}{\text{Total Extraction Fluid (mL)}}$$

Where the Total Solids are from Step 7.5, weight of solids and oil phase, dry weight of filter and tared dish subtracted.

The Total Sample Filtrate includes volume of all rinses added to the filtrate.

The Total Extraction Fluid is 500 mL water plus volume of NaOH solution. Does not include hexane, which is subsequently removed.

Alternatively, the aliquots may be analyzed separately, concentrations for each phase reported separately, and the amounts of each phase present in the sample reported separately.

8.0 QUALITY CONTROL

8.1 Refer to Method 9010.

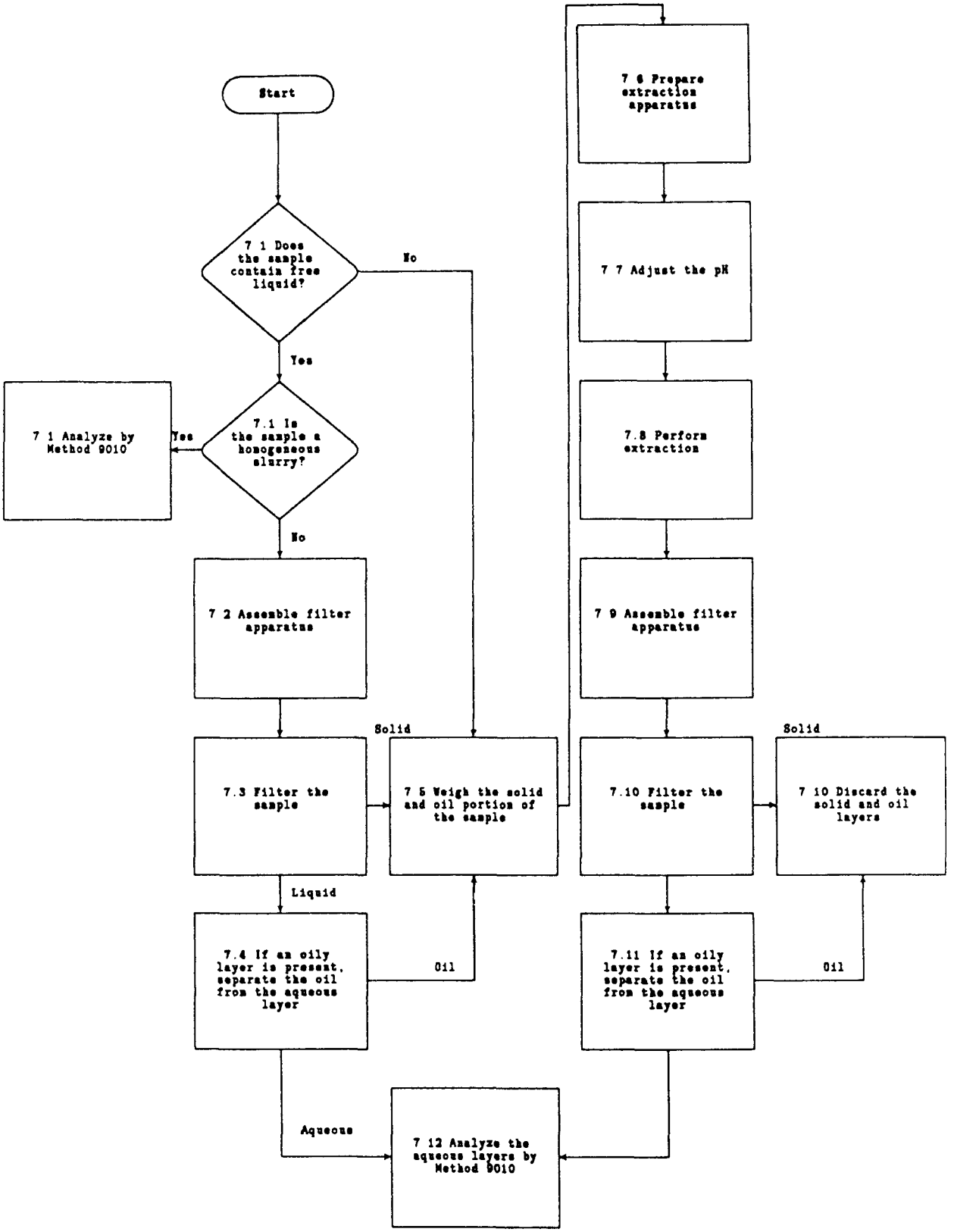
9.0 METHOD PERFORMANCE

9.1 In a single laboratory study, recoveries of 60 to 90% are reported for solids and 88 to 92% for oils. The reported CVs are less than 13.

10.0 REFERENCES

Refer to Method 9010.

APPENDIX 9010A
CYANIDE EXTRACTION PROCEDURE FOR SOLIDS AND OILS



METHOD 9020B

TOTAL ORGANIC HALIDES (TOX)

1.0 SCOPE AND APPLICATION

1.1 Method 9020 determines Total Organic Halides (TOX) as chloride in drinking water and ground waters. The method uses carbon adsorption with a microcoulometric-titration detector.

1.2 Method 9020 detects all organic halides containing chlorine, bromine, and iodine that are adsorbed by granular activated carbon under the conditions of the method. Fluorine-containing species are not determined by this method.

1.3 Method 9020 is applicable to samples whose inorganic-halide concentration does not exceed the organic-halide concentration by more than 20,000 times.

1.4 Method 9020 does not measure TOX of compounds adsorbed to undissolved solids.

1.5 Method 9020 is restricted to use by, or under the supervision of, analysts experienced in the operation of a pyrolysis/microcoulometer and in the interpretation of the results.

1.6 This method is provided as a recommended procedure. It may be used as a reference for comparing the suitability of other methods thought to be appropriate for measurement of TOX (i.e., by comparison of sensitivity, accuracy, and precision of data). There are three instruments that can be used to carry out this method. They are the TOX-10 available from Cosa Instruments, and the DX-20 and DX-20A available from Xertex-Dohrmann Instruments.

2.0 SUMMARY OF METHOD

2.1 A sample of water that has been protected against the loss of volatiles by the elimination of headspace in the sampling container, and that is free of undissolved solids, is passed through a column containing 40 mg of activated carbon. The column is washed to remove any trapped inorganic halides and is then combusted to convert the adsorbed organohalides to HX, which is trapped and titrated electrolytically using a microcoulometric detector.

3.0 INTERFERENCES

3.1 Method interferences may be caused by contaminants, reagents, glassware, and other sample-processing hardware. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running method blanks.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by treating with chromate cleaning solution. This should be followed by detergent washing in hot water. Rinse with tap water and distilled water and drain dry; glassware which is

not volumetric should, in addition, be heated in a muffle furnace at 400°C for 15 to 30 min. (Volumetric ware should not be heated in a muffle furnace.) Glassware should be sealed and stored in a clean environment after drying and cooling to prevent any accumulation of dust or other contaminants.

3.1.2 The use of high-purity reagents and gases helps to minimize interference problems.

3.2 Purity of the activated carbon must be verified before use. Only carbon samples that register less than 1,000 ng Cl^-/40 mg should be used. The stock of activated carbon should be stored in its granular form in a glass container with a Teflon seal. Exposure to the air must be minimized, especially during and after milling and sieving the activated carbon. No more than a 2-wk supply should be prepared in advance. Protect carbon at all times from all sources of halogenated organic vapors. Store prepared carbon and packed columns in glass containers with Teflon seals.

3.3 Particulate matter will prevent the passage of the sample through the adsorption column. Particulates must, therefore, be eliminated from the sample. This must be done as gently as possible, with the least possible sample manipulation, in order to minimize the loss of volatiles. It should also be noted that the measured TOX will be biased by the exclusion of TOX from compounds adsorbed onto the particulates. The following techniques may be used to remove particulates; however, data users must be informed of the techniques used and their possible effects on the data. These techniques are listed in order of preference:

3.3.1 Allow the particulates to settle in the sample container and decant the supernatant liquid into the adsorption system.

3.3.2 Centrifuge sample and decant the supernatant liquid into the adsorption system.

3.3.3 Measure Purgeable Organic Halides (POX) of sample (see SW-846 Method 9021) and Non-Purgeable Organic Halides (NPOX, that is, TOX of sample that has been purged of volatiles) separately, where the NPOX sample is centrifuged or filtered.

4.0 APPARATUS AND MATERIALS

4.1 Adsorption system (a schematic diagram of the adsorption system is shown in Figure 1):

4.1.1 Adsorption module: Pressurized sample and nitrate-wash reservoirs. (There are three instruments known to EPA at this time that can be used to carry out this method. They are the TOX-10, available from Cosa Instruments, and the DX-20 and DX-20A, available from Xertex-Dohrmann Instruments.)

4.1.2 Adsorption columns: Pyrex, 5-cm-long x 6-mm-O.D. x 2-mm-I.D.

4.1.3 Granular activated carbon (GAC): Filtrasorb-400, Calgon-APC or equivalent, ground or milled, and screened to a 100/200 mesh range. Upon combustion of 40 mg of GAC, the apparent halide background should be 1,000 ng Cl^- equivalent or less.

4.1.4 Cerafelt (available from Johns-Manville) or equivalent: Form this material into plugs to fit the adsorption module and to hold 40 mg of GAC in the adsorption columns.

CAUTION: Do not touch this material with your fingers. Oily residue will contaminate carbon.

4.1.5 Column holders.

4.1.6 Class A volumetric flasks: 100-mL and 50-mL.

4.2 Analytical system:

4.2.1 Microcoulometric-titration system: Containing the following components (a flowchart of the analytical system is shown in Figure 2):

4.2.1.1 Boat sampler: Muffled at 800°C for at least 2-4 min and cleaned of any residue by vacuuming after each run.

4.2.1.2 Pyrolysis furnace.

4.2.1.3 Microcoulometer with integrator.

4.2.1.4 Titration cell.

4.2.2 Strip-chart recorder.

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 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Sodium sulfite (0.1 M), Na_2SO_3: Dissolve 12.6 g ACS reagent grade Na_2SO_3 in reagent water and dilute to 1 L.

5.4 Concentrated nitric acid (HNO_3).

5.5 Nitrate-wash solution (5,000 mg NO_3^-/L), KNO_3: Prepare a nitrate-wash solution by transferring approximately 8.2 g of potassium nitrate (KNO_3) into a 1-liter Class A volumetric flask and diluting to volume with reagent water.

5.6 Carbon dioxide (CO_2): Gas, 99.9% purity.

5.7 Oxygen (O_2): 99.9% purity.

5.8 Nitrogen (N_2): Prepurified.

5.9 Acetic acid in water (70%), $C_2H_4O_2$: Dilute 7 volumes of glacial acetic acid with 3 volumes of reagent water.

5.10 Trichlorophenol solution, stock (1 μL = 10 μg Cl^-): Prepare a stock solution by accurately weighing accurately 1.856 g of trichlorophenol into a 100-mL Class A volumetric flask. Dilute to volume with methanol.

5.11 Trichlorophenol solution, calibration (1 μL = 500 ng Cl^-), $C_6H_3Cl_3O$: Dilute 5 mL of the trichlorophenol stock solution to 100 mL with methanol.

5.12 Trichlorophenol standard, instrument calibration: First, nitrate-wash a single column packed with 40 mg of activated carbon, as instructed for sample analysis, and then inject the column with 10 μL of the calibration solution.

5.13 Trichlorophenol standard, adsorption efficiency (100 μg Cl^-/liter): Prepare an adsorption-efficiency standard by injecting 10 μL of stock solution into 1 liter of reagent water.

5.14 Blank standard: The methanol used to prepare the calibration standard should be used as the blank standard.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine.

6.2 All samples should be collected in bottles with Teflon septa (e.g., Pierce #12722 or equivalent) and be protected from light. If this is not possible, use amber glass 250-mL bottles fitted with Teflon-lined caps. Foil may be substituted for Teflon if the sample is not corrosive. Samples must be preserved by acidification to pH <2 with sulfuric acid, stored at 4°C, and protected against loss of volatiles by eliminating headspace in the container. Samples should be analyzed within 28 days. The container must be washed and muffled at 400°C before use, to minimize contamination.

6.3 All glassware must be dried prior to use according to the method discussed in Step 3.1.1.

7.0 PROCEDURE

7.1 Sample preparation:

7.1.1 Special care should be taken in handling the sample in order to minimize the loss of volatile organohalides. The adsorption procedure should be performed simultaneously on duplicates.

7.1.2 Reduce residual chlorine by adding sulfite (5 mg sodium sulfite crystals per liter of sample). Sulfite should be added at the time of sampling if the analysis is meant to determine the TOX concentration at the time of sampling. It should be recognized that TOX may increase on storage of the sample. Samples should be stored at 4°C without headspace.

7.2 Calibration:

7.2.1 Check the adsorption efficiency of each newly prepared batch of carbon by analyzing 100 mL of the adsorption efficiency standard, in duplicate, along with duplicates of the blank standard. The net recovery should be within 5% of the standard value.

7.2.2 Nitrate-wash blanks (method blanks): Establish the repeatability of the method background each day by first analyzing several nitrate-wash blanks. Monitor this background by spacing nitrate-wash blanks between each group of eight pyrolysis determinations. The nitrate-wash blank values are obtained on single columns packed with 40 mg of activated carbon. Wash with the nitrate solution, as instructed for sample analysis, and then pyrolyze the carbon.

7.2.3 Pyrolyze duplicate instrument-calibration standards and the blank standard each day before beginning sample analysis. The net response to the calibration standard should be within 3% of the calibration-standard value. Repeat analysis of the instrument-calibration standard after each group of eight pyrolysis determinations and before resuming sample analysis, and after cleaning or reconditioning the titration cell or pyrolysis system.

7.3 Adsorption procedure:

7.3.1 Connect two columns in series, each containing 40 mg of 100/200-mesh activated carbon.

7.3.2 Fill the sample reservoir and pass a metered amount of sample through the activated-carbon columns at a rate of approximately 3 mL/min.

NOTE: 100 mL of sample is the preferred volume for concentrations of TOX between 5 and 500 µg/L, 50 mL for 501 to 1000 µg/L, and 25 mL for 1001 to 2000 µg/L. If the anticipated TOX is greater than 2000 µg/L, dilute the sample so that 100 mL will contain between 1 and 50 µg TOX.

7.3.3 Wash the columns-in-series with 2 mL of the 5,000-mg/L nitrate solution at a rate of approximately 2 mL/min to displace inorganic chloride ions.

7.4 Pyrolysis procedure:

7.4.1 The contents of each column are pyrolyzed separately. After being rinsed with the nitrate solution, the columns should be

protected from the atmosphere and other sources of contamination until ready for further analysis.

7.4.2 Pyrolysis of the sample is accomplished in two stages. The volatile components are pyrolyzed in a CO_2-rich atmosphere at a low temperature to ensure the conversion of brominated trihalomethanes to a titratable species. The less volatile components are then pyrolyzed at a high temperature in an O_2-rich atmosphere.

7.4.3 Transfer the contents of each column to the quartz boat for individual analysis.

7.4.4 Adjust gas flow according to manufacturer's directions.

7.4.5 Position the sample for 2 min in the 200°C zone of the pyrolysis tube.

7.4.6 After 2 min, advance the boat into the 800°C zone (center) of the pyrolysis furnace. This second and final stage of pyrolysis may require from 6 to 10 min to complete.

7.5 Detection: The effluent gases are directly analyzed in the micro-coulometric-titration cell. Carefully follow manual instructions for optimizing cell performance.

7.6 Breakthrough: The unpredictable nature of the background bias makes it especially difficult to recognize the extent of breakthrough of organohalides from one column to another. All second-column measurements for a properly operating system should not exceed 10% of the two-column total measurement. If the 10% figure is exceeded, one of three events could have happened: (1) the first column was overloaded and a legitimate measure of breakthrough was obtained, in which case taking a smaller sample may be necessary; (2) channeling or some other failure occurred, in which case the sample may need to be rerun; or (3) a high random bias occurred, and the result should be rejected and the sample rerun. Because it may not be possible to determine which event occurred, a sample analysis should be repeated often enough to gain confidence in results. As a general rule, any analysis that is rejected should be repeated whenever a sample is available. In the event that repeated analyses show that the second column consistently exceeds the 10% figure and the total is too low for the first column to be saturated and the inorganic Cl is less than 20,000 times the organic chlorine value, then the result should be reported, but the data user should be informed of the problem. If the second-column measurement is equal to or less than the nitrate-wash blank value, the second-column value should be disregarded.

7.7 Calculations: TOX as Cl^- is calculated using the following formula:

$$\frac{(C_1 - C_3) + (C_2 - C_3)}{V} = \mu g/L \text{ Total Organic Halide}$$

where:

C_1 = μg Cl^- on the first column in series;

C_2 = μg Cl^- on the second column in series;

C_3 = predetermined, daily, average, method-blank value (nitrate-wash blank for a 40-mg carbon column); and

V = the sample volume in liters.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control guidelines.

8.2 This method requires all samples be run in duplicate.

8.3 Employ a minimum of two blanks to establish the repeatability of the method background, and monitor the background by spacing method blanks between each group of eight analytical determinations.

8.4 After calibration, verify calibration with an independently prepared check standard.

8.5 A matrix spike is run in between every 10 samples and is brought through the entire sample preparation and analytical process.

9.0 METHOD PERFORMANCE

9.1 Under conditions of duplicate analysis, the method detection limit is 10 μg/L.

9.2 Analyses of distilled water, uncontaminated ground water, and ground water from RCRA waste management facilities spiked with volatile chlorinated organics generally gave recoveries between 75-100% over the concentration range 10-500 μg/L. Relative standard deviations were generally 20% at concentrations greater than 25 μg/L. These data are shown in Tables 1 and 2.

10.0 REFERENCES

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2. Stevens, A.A., R.C. Dressman, R.K. Sorrell, and H.J. Brass, Organic Halogen Measurements: Current Uses and Future Prospects, Journal of the American Water Works Association, pp. 146-154, April 1985.

3. Tate, C., B. Chow, et al., EPA Method Study 32, Method 450.1, Total Organic Halides (TOX), EPA/600/S4-85/080, NTIS: PB 86 136538/AS.

TABLE 1. METHOD PERFORMANCE DATA[a]

Spiked Compound	Matrix[b]	TOX Concentration (μg/L)	Percent Recovery
Bromobenzene	D.W.	443	95
Bromodichloromethane	D.W	160	98
Bromoform	D.W.	160	110
Bromoform	D.W.	238	100
Bromoform	G.W.	10	140
Bromoform	G.W.	31	93
Bromoform	G.W.	100	120
Chloroform	D.W.	98	89
Chloroform	D.W.	112	94
Chloroform	G.W.	10	79
Chloroform	G.W.	30	76
Chloroform	G.W.	100	81
Dibromodichloromethane	D.W.	155	86
Dibromodichloromethane	D.W.	374	73
Tetrachloroethylene	G.W.	10	79
Tetrachloroethylene	G.W.	30	75
Tetrachloroethylene	G.W.	101	78
trans-Dichloroethylene	G.W.	10	84
trans-Dichloroethylene	G.W.	30	63
trans-Dichloroethylene	G.W.	98	60

[a]Results from Reference 2.

[b]G.W. = Ground Water.
D.W. = Distilled Water.

TABLE 2. METHOD PERFORMANCE DATA[a]

Sample Matrix	Unspiked TOX (μg/L)	Spike Level	Percent Recovery
Ground Water	68, 69	100	98, 99
Ground Water	5, 12	100	110, 110
Ground Water	5, 10	100	95, 105
Ground Water	54, 37	100	111, 106
Ground Water	17, 15	100	98, 89
Ground Water	11, 21	100	97, 89

[a]Results from Reference 3.

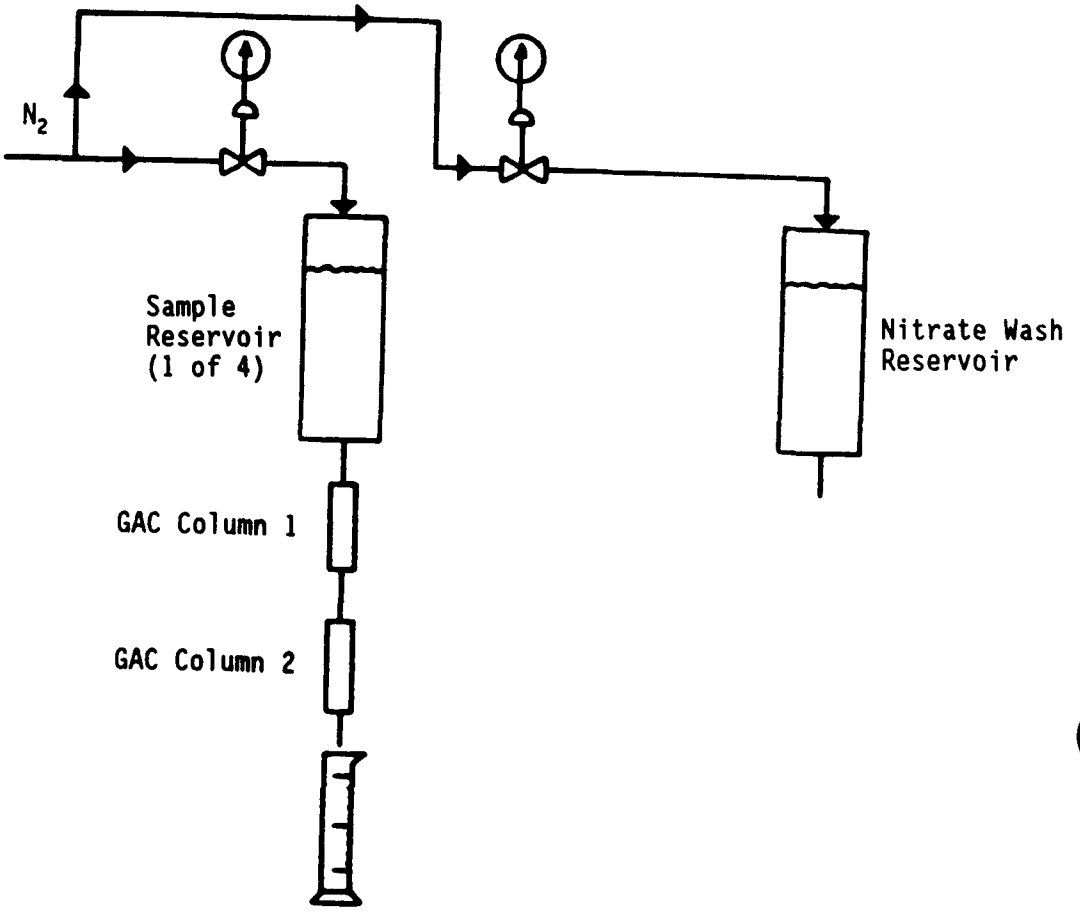


Figure 1. Schematic Diagram of Adsorption System

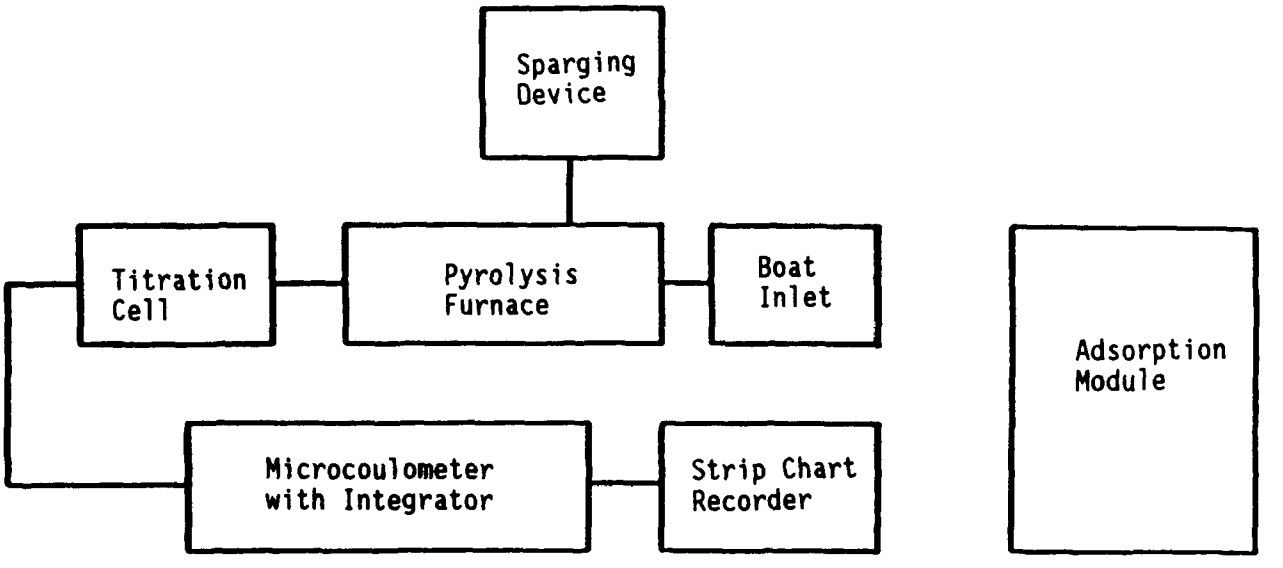
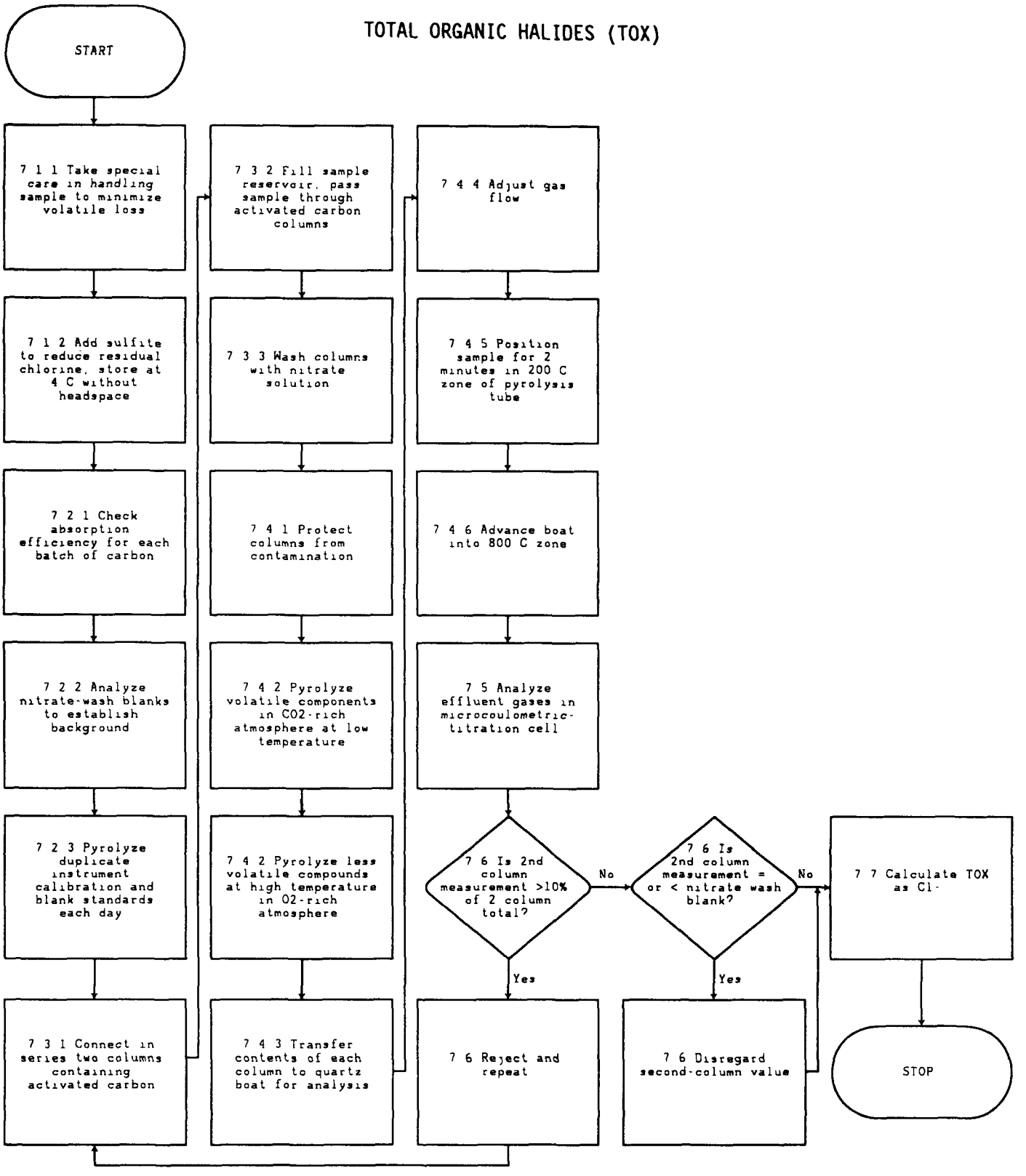


Figure 2. Flowchart of Analytical System

TOTAL ORGANIC HALIDES (TOX)



METHOD 9021

PURGEABLE ORGANIC HALIDES (POX)

1.0 SCOPE AND APPLICATION

1.1 Method 9021 determines organically bound halides (chloride, bromide, and iodide) purged from a sample of drinking water or ground water. They are reported as chloride. This method is a quick screening procedure requiring about 10 minutes. The method uses a sparging device, a pyrolysis furnace, and a microcoulometric-titration detector.

1.2 Method 9021 detects purgeable organically bound chlorine, bromine, and iodine. Fluorine containing species are not determined by this method. Method 9021 measures POX concentrations ranging from 5 to 1,000 ug/L.

1.3 This method provides a recommended procedure. It may be used as a reference for comparing the suitability of other methods thought to be appropriate for measurement of POX (i.e. by comparison of sensitivity, accuracy, and precision of data).

1.4 Method 9021 is restricted to use by, or under the supervision of, analysts experienced in the operation of a pyrolysis/microcoulometer and in the interpretation of the results.

2.0 SUMMARY OF METHOD

2.1 A sample of water, protected against the loss of volatiles by the elimination of headspace in the sampling container, is transferred to a purging vessel. The volatile organic halides are purged into a pyrolysis furnace using a stream of CO_2 and the hydrogen halide (HX) pyrolysis product is trapped and titrated electrolytically using a microcoulometric detector.

3.0 INTERFERENCES

3.1 Contaminants, reagents, glassware, and other sample processing hardware may cause interferences. Method blanks must be routinely run to demonstrate freedom from interferences under the conditions of the analysis.

3.1.1 Glassware must be scrupulously clean. Clean all glassware as soon as possible after use by treating with chromate cleaning solution. This should be followed by detergent washing in hot water. Rinse with tap water and ASTM Type II water and dry at 105°C for 1 hour or until dry. Glassware which is not volumetric should, in addition, be heated in a muffle furnace at 300°C for 15 to 30 minutes (volumetric ware should not be heated in a muffle furnace). Glassware should be sealed and stored in a clean environment after drying and cooling to prevent any accumulation of dust or other contaminants.

3.1.2 Use high purity reagents and gases to minimize interference problems.

3.1.3 Avoid using non-PTFE (polytetrafluoroethylene) plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purge gas stream.

3.2 Samples can be contaminated by diffusion of volatile organics (methylene chloride) through the septum seal into the sample during shipment and especially during storage. A trip blank prepared from water and carried through the sampling and handling protocol serves as a check on such contamination. A trip blank should be run with each analytical batch.

3.3 Contamination by carryover occurs whenever high level and low level samples are sequentially analyzed. To reduce carryover, the purging device and sample syringe must be rinsed with water between sample analyses. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of water to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high organohalide levels, wash out the purging device with a detergent solution, rinse it with water, and then dry it in a 105°C oven between analyses.

3.4 All operations should be carried out in an area where halogenated solvents, such as methylene chloride, are not being used.

3.5 Residual free chlorine interferes in the method. Free chlorine must be destroyed by adding sodium sulfite when the sample is collected.

4.0 APPARATUS AND MATERIALS

4.1 Sampling equipment (for discrete sampling)

4.1.1 Vial - 25-mL capacity or larger, equipped with a screw-cap with hole in center (Pierce #13075 or equivalent).

4.1.2 Septum - Teflon lined silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and ASTM Type II water, and dry at 105°C for 1 hour before use.

4.2 Analytical system

4.2.1 Microcoulometric-titration system containing the following components (a schematic diagram of the microcoulometric-titration system is shown in Figure 1).

4.2.1.1 Purging device.

4.2.1.2 Pyrolysis furnace.

4.2.1.3 Titration cell.

4.2.2 Strip chart recorder (optional) - The recorder is recommended to make sure the peak in down to baselines before stopping integration.

4.2.3 Microsyringes - 10-uL and 25-uL with 0.006 in i.d. needle (Hamilton 702N or equivalent).

4.2.4 Syringe valve - 2 way, with Luer ends.

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 ASTM Type II water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Sodium sulfide, Na_2S. Granular, anhydrous.

5.4 Acetic acid in water (70%), CH_3COOH. Dilute 7 volumes of glacial acetic acid with 3 volumes of water.

5.5 Sodium chloride calibration standard (1 ug Cl^-/uL). Dissolve 1.648 g NaCl in water and dilute to 1 liter.

5.6 Carbon dioxide.

5.7 Methanol, CH_3OH. Store away from other solvents.

5.8 Chloroform, $CHCl_3$.

5.9 Chloroform (stock) solution (1 uL = 11.2 ug of $CHCl_3$ or 10 ug Cl^-). Prepare a stock solution by delivering accurately 760 uL (1120 mg) of chloroform into a 100-mL volumetric flask containing approximately 90 mL of methanol. Dilute to volume with methanol (10,000 mg of chlorine/L).

5.10 Chloroform (calibration) solution (1 uL = 0.1 ug Cl^-). Dilute 1 mL of the chloroform stock solution to 100 mL with methanol (100 mg of chlorine/L).

5.11 Chloroform Quality Control (QC) reference sample (100 ug/L). Prepare an aqueous standard by injecting 100 uL of the chloroform calibration standard (100 mg of Cl^-/L) into a volumetric flask containing 100 mL of water. Mix and store in a bottle with zero headspace. Analyze within two hours after preparation.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All samples should be collected in bottles with Teflon lined silicone septa (e.g. Pierce #12722 or equivalent) and be protected from light. If this is not possible, use amber glass 250-mL bottles fitted with Teflon lined caps.

6.3 All glassware must be cleaned prior to use according to the process described in Step 3.1.1.

6.4 Special care should be taken in handling the sample in order to minimize the loss of volatile organohalides. This is accomplished through elimination of headspace and by minimizing the number of transfers.

6.5 Reduce residual chlorine, if present, by adding sodium sulfite (5 mg of sodium sulfite crystals per liter of sample). Sodium sulfite should be added to empty sample bottles at the time of sampling. Shake vigorously for 1 minute after bottle has been filled with sample and properly sealed. Samples should be stored at 4°C without headspace. POX may increase during storage of the sample.

6.6 All samples must be analyzed within 14 days of collection.

7.0 PROCEDURE

7.1 Calibration.

7.1.1 Assemble the sparging/pyrolysis/microcoulometric-titration apparatus shown in Figure 1 in accordance with the manufacturer's specifications. Typically a CO_2 flow of 150 mL/min and a sparger temperature of 45 $\pm$ 5°C are employed. The pyrolysis furnace should be set at 800 $\pm$ 10°C. Attach the titration cell to the pyrolysis tube outlet and fill with electrolyte (70% acetic acid). Flow rate and temperature changes will affect the compounds that are purged and change the percent recovery of marginal compounds. Therefore, these parameters should not be varied. Adjust gas flow rate according to manufacturer's directions.

7.1.2 Turn on the instrument and allow the gas flow and temperatures to stabilize. When the background current of the titration cell has stabilized the instrument is ready for use.

7.1.3 Calibrate the microcoulometric-titration system for Cl^- equivalents by injecting various amounts (1 to 80 uL) of the sodium chloride calibration standard directly into the titration cell and integrating the response using the POX integration mode. If desired, the analog output of the titration cell can be displayed on a strip chart recorder. The range of sodium chloride amounts should cover the range of expected sample concentrations and should always be less than 80 ug of Cl^-. The integrated response should read within 2% or 0.05 ug of the quantity injected (whichever is larger) over the range 1-80 ug Cl^-. If this calibration requirement is not met, then the instrument sensitivity parameters should be adjusted according to the manufacturer's specifications to achieve an accurate response.

7.1.4 Check the performance of the analytical system daily by analyzing three 5-mL aliquots of a freshly prepared 100 ug/mL chloroform

check standard. The mean of these three analyses should be between 0.4-0.55 ug of Cl^- and the percent relative standard deviation should be 5% or less. If these criteria are not met, the system should be checked as described in the instrument maintenance manual in order to isolate the problem. Low chloroform recovery can often be traced to a vitrified inlet tube. The tube should be replaced weekly.

7.1.5 Determine a reagent blank daily by running an analysis with the purge vessel empty. The reagent blank should be 0.00 ± 0.05 ug of Cl^-. Analyze a calibration blank sample daily. The calibration blank should be within 0.02 ug of Cl^- of the reagent blank.

7.2 Sample analysis

7.2.1 Select a chloroform spike concentration representative of the expected levels in the samples. Using the chloroform stock solution, prepare a spiking solution in methanol which is 500 times more concentrated than the selected spike concentration. Add 10 uL of the spiking solution to 5-mL aliquots of the samples chosen for spiking (refer to Section 8.0, Quality Control, for guidance in selecting the appropriate number of samples to be spiked).

7.2.2 Allow sample to come to ambient temperature prior to drawing it into the syringe. Remove the plunger from a 5-mL or 10-mL syringe and attach a closed syringe valve. If maximum sensitivity is desired and the sample does not foam excessively, a 10-mL sample aliquot may be analyzed. Otherwise 5-mL aliquots should be used. Open the sample bottle (or standard) and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5 mL. Since this process of taking an aliquot destroys the validity of the sample for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data (e.g. accidental spill), or for duplicate anlaysis.

7.2.3 Attach the syringe valve assembly to the syringe valve on the purging device. Place the pyrolysis/microcoulometer system in the POX integration mode to activate the integration system. Immediately open the syringe valves and inject the sample into the purging chamber.

7.2.4 Close both valves and purge the sample for 10 minutes.

7.2.5 After integration is complete, open the syringe valves and withdraw the purged sample. Flush the syringe and purging device with water prior to analyzing other samples.

7.2.6 If the integrated response exceeds the working range of the instrument, prepare a dilution of the sample from the aliquot in the second syringe with water and reanalyze. The water must meet the criteria of Step 7.1.5. It may be necessary to heat and purge dilution waters.

7.3 Pyrolysis procedure

7.3.1 Pyrolysis of the purged organic component of the sample is accomplished by pyrolyzing in a CO_2-rich atmosphere at a low temperature to ensure the conversion of brominated trihalomethanes to a titratable species.

7.4 Directly analyze the effluent gases in the microcoulometric-titration cell. Carefully follow instrument manual instructions for optimizing cell performance.

7.5 Calculations - POX as Cl^- is calculated using the following formula:

$$\frac{Q_S}{V} \times 1000 = \text{g/L Purgeable Organic Halide}$$

where:

Q_S = Quantity of POX as ug of Cl^- in the sample aliquot.
V = Volume of sample aliquot in mL.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection for 3 years. This method is restricted to use by or under supervision of experienced analysts. Refer to the appropriate section of Chapter One for additional quality control requirements.

8.2 Analyze a minimum of one reagent blank every 20 samples or per analytical batch, whichever is more frequent, to determine if contamination or any memory effects are occurring.

8.3 In addition to the performance check mentioned in Step 7.1.4, verify calibration with an independently prepared chloroform QC reference sample every 15 samples.

8.4 Analyze matrix spiked samples for every 10 samples or analytical batch, whichever is more frequent. The spiked sample is carried through the whole sample preparation and analytical process.

8.5 Analyze all samples in replicate.

9.0 METHOD PERFORMANCE

9.1 Under conditions of duplicate analysis, the reliable limit of detection is 5 ug/L.

9.2 Analyses of distilled water, uncontaminated ground water, and ground water from RCRA waste management facilities spiked with volatile chlorinated organics generally give recoveries of 44-128% over the concentration range of 29-4500 ug/L. Relative standard deviations are generally less than 20% at concentrations greater than 25 ug/L. These data are shown in Tables 1 and 2.

10.0 REFERENCES

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7. Dohrmann. Rosemount Analytical Division. Santa Clara, CA 95052-8007.

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TABLE 1.
PRECISION AND ACCURACY DATA FOR SELECTED PURGEABLE ORGANIC HALIDES
(Reference 5)

Compound	Dose[1] (ug/L as Cl^-)	Average Percent Recovery	Standard Deviation	MDL[2] (ug/L)	Number of Replicates
Chloroform	11	100	14	4.5	7
Trichloroethene	10	60	11	2.2	7
Tetrachloroethene	10	50	20	3.2	7
Chlorobenzene	8	38	20	2.0[3]	7

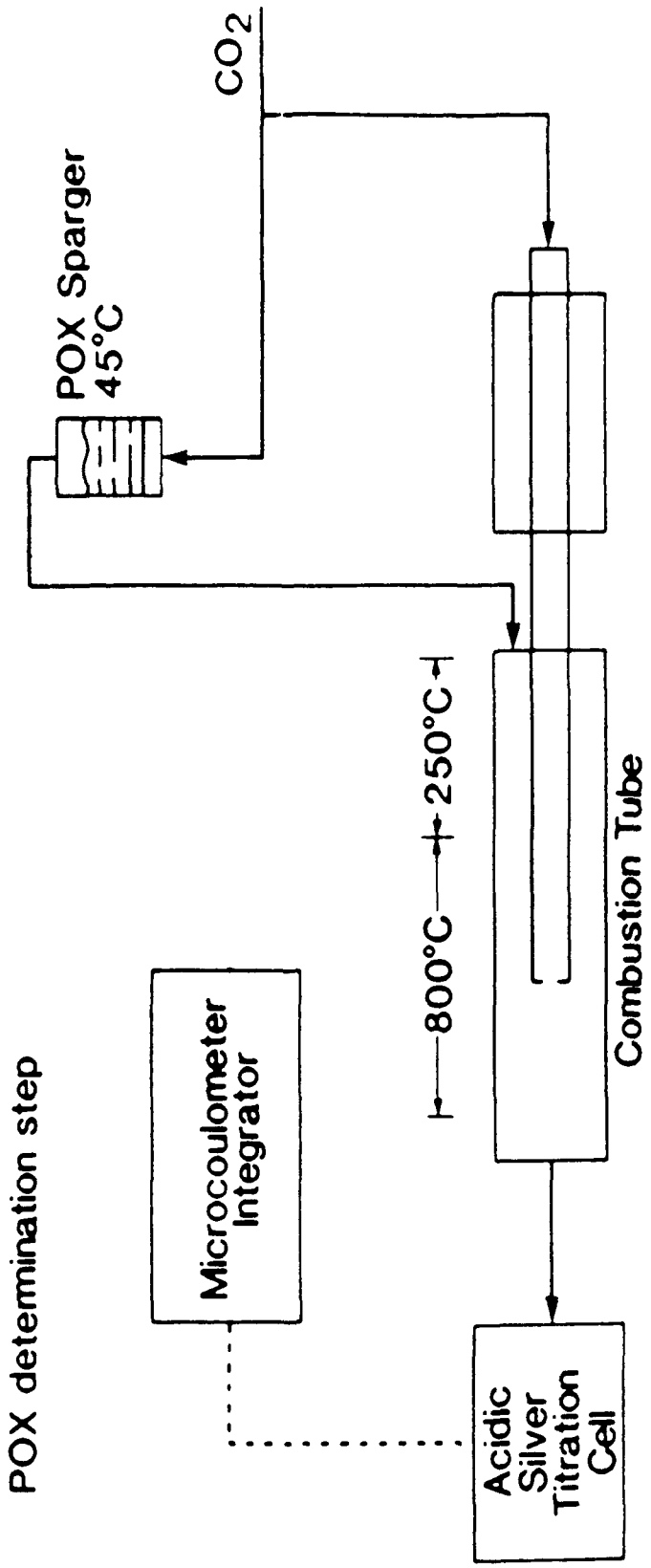
1 Ten milliliter aliquot of spiked reagent water analyzed.
2 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.
3 Practical MDL probably greater (approximately 5 to 6 ug/L) due to low recovery.

TABLE 2.
PRECISION AND ACCURACY DATA FOR VARIOUS WATER SAMPLES
(Reference 5)

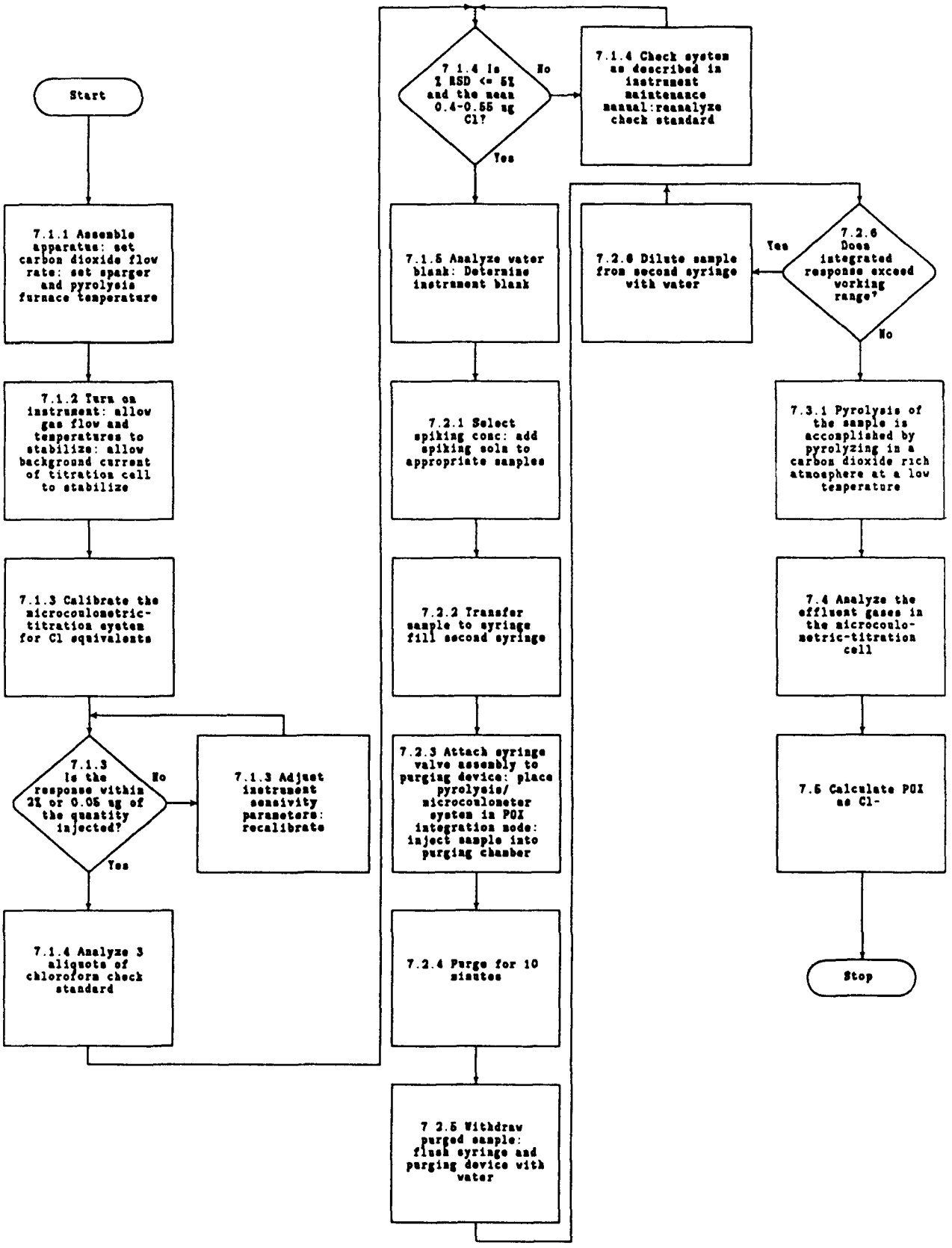
Sample[1]	Spike Component	Background Level ($\mu g/L$ as Cl^-)	Spike Level ($\mu g/L$ as Cl^-)	Average Percent Recovery	Standard Deviation	Number of Replicates
POTW Sewage	Chloroform	88	29	128	5	3
Chlorinated Hydrocarbon Plant Wastewater	Chloroform	114	460	77	7	3
Chlorinated Hydrocarbon Plant Wastewater	Chloroform	32	1500	50	4	3
Chlorinated Hydrocarbon Plant Wastewater	Chloroform	171	4500	87	12	3
Solid Waste Leachate	1,1-Dichloro-ethane	171	800	44	2	3
Industrial[2] Wastewater	Methylene chloride	510	120	65	12	3

1 Five milliliter sample aliquots analyzed.
2 Diluted 200:1 prior to analysis. Values for this sample are in mg/L for original sample.

FIGURE 1.
MICROCOULOMETRIC - TITRATION SYSTEM



METHOD 9021
PURGEABLE ORGANIC HALIDES (POX)



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METHOD 9030

ACID-SOLUBLE AND ACID-INSOLUBLE SULFIDES

1.0 SCOPE AND APPLICATION

1.1 The distillation procedure described in this method is designed for the determination of sulfides in aqueous and solid waste materials and effluents.

1.2 This method provides only a semi-quantitative determination of sulfide compounds considered "acid-insoluble" (e.g. CuS and SnS_2) in solid samples. Recovery has been shown to be 20 to 40% for CuS, one of the most stable and insoluble compounds, and 40 to 60% for SnS_2 which is slightly more soluble.

1.3 This method is not applicable to oil or multiphasic samples or samples not amenable to the distillation procedure. These samples can be analyzed by Method 9031.

1.4 Method 9030 is suitable for measuring sulfide concentrations in samples which contain between 0.2 and 50 mg/kg of sulfide.

1.5 This method is not applicable for reactive sulfide. Refer to Chapter Seven, Step 7.3.4.1 for the determination of reactive sulfide.

1.6 This method measures total sulfide which is usually defined as the acid-soluble fraction of a waste. If, however, one has previous knowledge of the waste and is concerned about both soluble sulfides such as H_2S, and metal sulfides, such as CuS and SnS_2, then total sulfide is defined as the combination of both acid-soluble and acid-insoluble fractions. For wastes where only metal sulfides are suspected to be present, only the acid-insoluble fraction needs to be performed.

2.0 SUMMARY OF METHOD

2.1 For acid-soluble sulfide samples, separation of sulfide from the sample matrix is accomplished by the addition of sulfuric acid to the sample. The sample is heated to 70°C and the hydrogen sulfide (H_2S) which is formed is distilled under acidic conditions and carried by a nitrogen stream into zinc acetate gas scrubbing bottles where it is precipitated as zinc sulfide.

2.2 For acid-insoluble sulfide samples, separation of sulfide from the sample matrix is accomplished by suspending the sample in concentrated hydrochloric acid by vigorous agitation. Tin(II) chloride is present to prevent oxidation of sulfide to sulfur by the metal ion (as in copper(II)), by the matrix, or by dissolved oxygen in the reagents. The prepared sample is distilled under acidic conditions at 100°C under a stream of nitrogen. Hydrogen sulfide gas is released from the sample and collected in gas scrubbing bottles containing zinc(II) and a strong acetate buffer. Zinc sulfide precipitates.

2.3 The sulfide in the zinc sulfide precipitate is oxidized to sulfur with a known excess amount of iodine. Then the excess iodine is determined by titration with a standard solution of phenyl arsine oxide (PAO) or sodium thiosulfate until the blue iodine starch complex disappears. As the use of standard sulfide solutions is not possible because of oxidative degradation, quantitation is based on the PAO or sodium thiosulfate.

3.0 INTERFERENCES

3.1 Aqueous samples must be taken with a minimum of aeration to avoid volatilization of sulfide or reaction with oxygen, which oxidizes sulfide to sulfur compounds that are not detected.

3.2 Reduced sulfur compounds, such as sulfite and hydrosulfite, decompose in acid, and may form sulfur dioxide. This gas may be carried over to the zinc acetate gas scrubbing bottles and subsequently react with the iodine solution yielding false high values. The addition of formaldehyde into the zinc acetate gas scrubbing bottles removes this interference. Any sulfur dioxide entering the scrubber will form an addition compound with the formaldehyde which is unreactive towards the iodine in the acidified mixture. This method shows no sensitivity to sulfite or hydrosulfite at concentrations up to 10 mg/kg of the interferent.

3.3 Interferences for acid-insoluble sulfides have not been fully investigated. However, sodium sulfite and sodium thiosulfate are known to interfere in the procedure for soluble sulfides. Sulfur also interferes because it may be reduced to sulfide by tin(II) chloride in this procedure.

3.4 The iodometric method suffers interference from reducing substances that react with iodine, including thiosulfate, sulfite, and various organic compounds.

3.5 The insoluble method should not be used for the determination of soluble sulfides because it can reduce sulfer to sulfide, thus creating a positive interference.

4.0 APPARATUS AND MATERIALS

4.1 Distillation apparatus as shown in Figure 1

4.1.1 Three neck flask - 500-mL, 24/40 standard taper joints.

4.1.2 Dropping funnel - 100-mL, 24/40 outlet joint.

4.1.3 Purge gas inlet tube - 24/40 joint, with coarse frit.

4.1.4 Purge gas outlet - 24/40 joint reduced to 1/4 in. tube.

4.1.5 Gas scrubbing bottles - 125-mL, with 1/4 in. o.d. inlet and outlet tubes. Impinger tube must be fritted.

4.1.6 Tubing - 1/4 in. o.d. Teflon or polypropylene. Do not use rubber.

NOTE: When analyzing for acid-insoluble sulfides, the distillation apparatus is identical to that used in the distillation procedure for acid-soluble sulfides except that the tubing and unions downstream of the distillation flask must be all Teflon, polypropylene or other material resistant to gaseous HCl. The ground glass joints should be fitted with Teflon sleeves to prevent seizing and to prevent gas leaks. Pinch clamps should also be used on the joints to prevent leaks.

4.2 Hot plate stirrer.

4.3 pH meter.

4.4 Nitrogen regulator.

4.5 Flowmeter.

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 ASTM Type II water (ASTM D-1193-77 (1983)). All water used in this method will be Type II unless otherwise specified.

5.3 Zinc acetate solution for sample preservation (2N), $Zn(CH_3COO)_2 \cdot 2H_2O$. Dissolve 220 g of zinc acetate dihydrate in 500 mL of water.

5.4 Sodium hydroxide (1N), NaOH. Dissolve 40 g of NaOH in water and dilute to 1 liter.

5.5 Formaldehyde (37% solution), CH_2O. This solution is commercially available.

5.6 Zinc acetate for the scrubber

5.6.1 For acid-soluble sulfides: Zinc acetate solution (approximately 0.5M). Dissolve about 110 g zinc acetate dihydrate in 200 mL of water. Add 1 mL hydrochloric acid (concentrated), HCl, to prevent precipitation of zinc hydroxide. Dilute to 1 liter.

5.6.2 For acid-insoluble sulfides: Zinc acetate/sodium acetate buffer. Dissolve 100 g sodium acetate, $NaC_2H_3O_2$, and 11 g zinc acetate dihydrate in 800 mL of water. Add 1 mL concentrated hydrochloric acid and dilute to 1 liter. The resulting pH should be 6.8.

5.7 Acid to acidify the sample

5.7.1 For acid-soluble sulfides: Sulfuric acid (concentrated), H_2SO_4.

5.7.2 For acid-insoluble sulfides: Hydrochloric acid (9.8N), HCl. Place 200 mL of water in a 1-liter beaker. Slowly add concentrated HCl to bring the total volume to 1 liter.

5.8 Starch solution - Use either an aqueous solution or soluble starch powder mixtures. Prepare an aqueous solution as follows. Dissolve 2 g soluble starch and 2 g salicylic acid, $C_7H_6O_3$, as a preservative, in 100 mL hot water.

5.9 Nitrogen.

5.10 Iodine solution (approximately 0.025N)

5.10.1 Dissolve 25 g potassium iodide, KI, in 700 mL of water in a 1-liter volumetric flask. Add 3.2 g iodine, I_2. Allow to dissolve. Dilute to 1 liter and standardize as follows. Dissolve approximately 2 g KI in 150 mL of water. Pipet exactly 20 mL of the iodine solution to be titrated and dilute to 300 mL with water. Titrate with 0.025N standardized phenylarsine oxide or 0.025N sodium thiosulfate until the amber color fades to yellow. Add starch indicator solution. Continue titration drop by drop until the blue color disappears.

5.10.2 Run in replicate.

5.10.3 Calculate the normality as follows.

$$\text{Normality } (I_2) = \frac{\text{mL of titrant x normality of titrant}}{\text{sample size in mL}}$$

5.11 Sodium sulfide nonahydrate, $Na_2S \cdot 9H_2O$. For the preparation of standard solutions to be used for calibration curves. Standards must be prepared at pH > 9 or < 11. Protect standard from exposure to oxygen by preparing it without headspace. These standards are unstable and should be prepared daily.

5.12 Tin(II) chloride, $SnCl_2$, granular.

5.13 Titrant.

5.13.1 Standard phenylarsine oxide solution (PAO) (0.025N), C_6H_5AsO. This solution is commercially available.

Caution: PAO is toxic.

5.13.2 Standard sodium thiosulfate solution (0.025N), $Na_2S_2O_3 \cdot 5H_2O$. Dissolve 6.205 $\pm$ 0.005 g $Na_2S_2O_3 \cdot 5H_2O$ in 500 mL water. Add 9 mL 1N NaOH and dilute to 1 liter.

5.14 Sodium hydroxide (6N), NaOH. Dissolve 240 g of sodium hydroxide in 1 liter of water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All aqueous samples and effluents must be preserved with zinc acetate and sodium hydroxide. Use four drops of 2N zinc acetate solution per 100 mL of sample. Adjust the pH to greater than 9 with 6N sodium hydroxide solution. Fill the sample bottle completely and stopper with a minimum of aeration. The treated sample is relatively stable and can be held for up to seven days. If high concentrations of sulfide are expected to be in the sample, continue adding zinc acetate until all the sulfide has precipitated. For solid samples, fill the surface of the solid with 2N zinc acetate until moistened. Samples must be cooled to 4°C and stored headspace free.

6.3 Sample Preparation

6.3.1 For an efficient distillation, the mixture in the distillation flask must be of such a consistency that the motion of the stirring bar is sufficient to keep the solids from settling. The mixture must be free of solid objects that could disrupt the stirring bar. Prepare the sample using one of the procedures in this section then proceed with the distillation step (Section 7.0).

6.3.2 If the sample is aqueous, shake the sample container to suspend any solids, then quickly decant the appropriate volume (up to 250 mL) of the sample to a graduated cylinder, weigh the cylinder, transfer to the distillation flask and reweigh the cylinder to the nearest milligram. Be sure that a representative aliquot is used, or use the entire sample.

6.3.3 If the sample is aqueous but contains soft clumps of solid, it may be possible to break the clumps and homogenize the sample by placing the sample container on a jar mill and tumble or roll the sample for a few hours. The slurry may then be aliquotted and weighed as above to the nearest milligram then diluted with water up to a total volume of 250 mL to produce a mixture that is completely suspended by the stirring bar.

6.3.4 If the sample is primarily aqueous, but contains a large proportion of solid, the sample may be roughly separated by phase and the amount of each phase measured and weighed to the nearest milligram into the distillation flask in proportion to their abundance in the sample. Water may be added up to a total volume of 250 mL. As a guideline, no more than 25 g dry weight or 50 g of sludge can be adequately suspended in the apparatus.

6.3.5 If the sample contains solid objects that can not be reduced in size by tumbling, the solids must be broken manually. Clay-like solids should be cut with a spatula or scalpel in a crystallizing dish. If the

solids can be reduced to a size that they can be suspended by the stirring bar, the solid and liquid can be proportionately weighed.

6.3.6 Non-porous harder objects, for example stones or pieces of metal, may be weighed and discarded. The percent weight of non-porous objects should be reported and should be used in the calculation of sulfide concentration if it has a significant effect on the reported result.

7.0 PROCEDURE

For acid-soluble sulfide samples, go to 7.1
For acid-insoluble sulfide samples, go to 7.2

7.1 Acid-Soluble Sulfide

7.1.1 In a preliminary experiment, determine the approximate amount of sulfuric acid required to adjust a measured amount of the sample to pH less than or equal to 1. The sample size should be chosen so that it contains between 0.2 and 50 mg of sulfide. Place a known amount of sample or sample slurry in a beaker. Add water until the total volume is 200 mL. Stir the mixture and determine the pH. Slowly add sulfuric acid until the pH is less than or equal to 1.

CAUTION: Toxic hydrogen sulfide may be generated from the acidified sample. This operation must be performed in the hood and the sample left in the hood until the sample has been made alkaline or the sulfide has been destroyed. From the amount of sulfuric acid required to acidify the sample and the mass or volume of the sample acidified, calculate the amount of acid required to acidify the sample to be placed in the distillation flask.

7.1.2 Prepare the gas evolution apparatus as shown in Figure 1 in a fume hood.

7.1.2.1 Prepare a hot water bath at 70°C by filling a crystallizing dish or other suitable container with water and place it on a hot plate stirrer. Place a thermometer in the bath and monitor the temperature to maintain the bath at 70°C.

7.1.2.2 Assemble the three neck 500-mL flask, fritted gas inlet tube, and exhaust tube. Use Teflon sleeves to seal the ground glass joints. Place a Teflon coated stirring bar into the flask.

7.1.2.3 Place into each gas scrubbing bottle 10 $\pm$ 0.5 mL of the 0.5M zinc acetate solution, 5.0 $\pm$ 0.1 mL of 37% formaldehyde and 100 $\pm$ 5.0 mL water.

7.1.2.4 Connect the gas evolution flask and gas scrubbing bottles as shown in Figure 1. Secure all fittings and joints.

7.1.3 Carefully place an accurately weighed sample which contains 0.2 to 50 mg of sulfide into the flask. If necessary, dilute to approximately 200 mL with water.

7.1.4 Place the dropping funnel onto the flask making sure its stopcock is closed. Add the volume of sulfuric acid calculated in Step 7.1.1 plus an additional 50 mL into the dropping funnel. The bottom stopcock must be closed.

7.1.5 Attach the nitrogen inlet to the top of the dropping funnel gas shut-off valve. Turn on the nitrogen purge gas and adjust the flow through the sample flask to 25 mL/min. The nitrogen in the gas scrubbing bottles should bubble at about five bubbles per second. Nitrogen pressure should be limited to approximately 10 psi to prevent excess stress on the glass system and fittings. Verify that there are no leaks in the system. Open the nitrogen shut-off valve leading to the dropping funnel. Observe that the gas flow into the sample vessel will stop for a short period while the pressure throughout the system equalizes. If the gas flow through the sample flask does not return within a minute, check for leaks around the dropping funnel. Once flow has stabilized, turn on magnetic stirrer. Purge system for 15 minutes with nitrogen to remove oxygen.

7.1.6 Heat sample to 70°C. Open dropping funnel to a position that will allow a flow of sulfuric acid of approximately 5 mL/min. Monitor the system until most of the sulfuric acid within the dropping funnel has entered the sample flask. Solids which absorb water and swell will restrict fluid motion and, therefore, lower recovery will be obtained. Such samples should be limited to 25 g dry weight.

7.1.7 Purge, stir, and maintain a temperature of 70°C for a total of 90 minutes from start to finish. Shut off nitrogen supply. Turn off heat.

7.1.8 Proceed to Step 7.3 for the analysis of the zinc sulfide by titration.

7.2 Acid-Insoluble Sulfide

7.2.1 As the concentration of HCl during distillation must be within a narrow range for successful distillation of H_2S, the water content must be controlled. It is imperative that the final concentration of HCl in the distillation flask be about 6.5N and that the sample is mostly suspended in the fluid by the action of the stirring bar. This is achieved by adding 50 mL of water, including water in the sample, 100 mL of 9.8N HCl, and the sample to the distillation flask. Solids which absorb water and swell will restrict fluid motion and, therefore, lower recovery will be obtained. Such samples should be limited to 25 g dry weight.

7.2.2 If the matrix is a dry solid, weigh a portion of the sample such that it contains 0.2 to 50 mg of sulfide. The solid should be crushed to reduce particle size to 1 mm or less. Add 50 mL of water.

7.2.3 If the matrix is aqueous, then a maximum of 50 g of the sample may be used. No additional water may be added. As none of the target compounds are volatile, drying the sample may be preferable to enhance the sensitivity by concentrating the sample. If less than 50 g of the sample is required to achieve the 0.2 to 50 mg of sulfide range for the test, then add water to a total volume of 50 mL.

7.2.4 If the matrix is a moist solid, the water content of the sample must be determined (Karl Fischer titration, loss on drying, or other suitable means) and the water in the sample included in the total 50 mL of water needed for the correct HCl concentration. For example, if a 20 g sample weight is needed to achieve the desired sulfide level of 0.2 to 50 mg and the sample is 50% water then 40 mL rather than 50 mL of water is added along with the sample and 100 mL of 9.8N HCl to the distillation flask.

7.2.5 Weigh the sample and 5 g $SnCl_2$ into the distillation flask. Use up to 50 mL of water, as calculated above, to rinse any glassware.

7.2.6 Assemble the distillation apparatus as in Figure 1. Place 100 $\pm$ 2.0 mL of zinc acetate/sodium acetate buffer solution and 5.0 $\pm$ 0.1 mL of 37% formaldehyde in each gas scrubbing bottle. Tighten the pinch clamps on the distillation flask joints.

7.2.7 Make sure the stopcock is closed and then add 100 $\pm$ 1.0 mL of 9.8N HCl to the dropping funnel. Connect the nitrogen line to the top of the funnel and turn the nitrogen on to pressurize the dropping funnel headspace.

7.2.8 Set the nitrogen flow at 25 mL/min. The nitrogen in the gas scrubbing bottles should bubble at about five bubbles per second. Purge the oxygen from the system for about 15 minutes.

7.2.9 Turn on the magnetic stirrer. Set the stirring bar to spin as fast as possible. The fluid should form a vortex. If not, the distillation will exhibit poor recovery. Add all of the HCL from the dropping funnel to the flask.

7.2.10 Heat the water bath to the boiling point (100°C). The sample may or may not be boiling. Allow the purged distillation to proceed for 90 minutes at 100°C. Shut off nitrogen supply. Turn off heat.

7.2.11 Proceed to Step 7.3 for the analysis of the zinc sulfide by titration.

7.3 Titration of Distillate

7.3.1 Pipet a known amount of standardized 0.025N iodine solution (See Step 5.10.3) in a 500-mL flask, adding an amount in excess of that needed to oxidize the sulfide. Add enough water to bring the volume to 100 mL. The volume of standardized iodine solution should be about 65 mL for samples with 50 mg of sulfide.

7.3.2 If the distillation for acid-soluble sulfide is being used, add 2 mL of 6N HCl. If the distillation for acid-insoluble sulfides is performed, 10 mL of 6N HCl should be added to the iodine.

7.3.3 Pipet both of the gas scrubbing bottle solutions to the flask, keeping the end of the pipet below the surface of the iodine solution. If at any point in transferring the zinc acetate solution or rinsing the bottles, the amber color of the iodine disappears or fades to yellow, more 0.025N iodine must be added. This additional amount must be added to the amount from Step 7.3.1 for calculations. Record the total volume of standardized 0.025N iodine solution used.

7.3.4 Prepare a rinse solution of a known amount of standardized 0.025N iodine solution, 1 mL of 6N HCl, and water to rinse the remaining white precipitate (zinc sulfide) from the gas scrubbing bottles into the flask. There should be no visible traces of precipitate after rinsing.

7.3.5 Rinse any remaining traces of iodine from the gas scrubbing bottles with water, and transfer the rinses to the flask.

7.3.6 Titrate the solution in the flask with standard 0.025N phenylarsine oxide or 0.025N sodium thiosulfate solution until the amber color fades to yellow. Add enough starch indicator for the solution to turn dark blue and titrate until the blue disappears. Record the volume of titrant used.

$$\frac{(\text{mL of } I_2 \times \text{N of } I_2) - (\text{mL of titrant} \times \text{N of titrant}) \times 16.03}{\text{sample weight (kg)}} = \text{sulfide(mg/kg)}$$

8.0 QUALITY CONTROL

8.1 All quality control data must be maintained and available for reference or inspection for a period of three years. This method is restricted to use by or under supervision of experienced analysts. Refer to the appropriate section of Chapeter One for additional quality control requirements.

8.2 A reagent blank should be run once in twenty analyses or per analytical batch, whichever is more frequent.

8.3 Check standards are prepared from water and a known amount of sodium sulfide. A check standard should be run with each analytical batch of samples, or once in twenty samples. Acceptable recovery will depend on the level and matrix.

8.4 A matrix spiked sample should be run for each analytical batch or every 20 samples, whichever is more frequent, to determine matrix effects. If recovery is low, acid-insoluble sulfides are indicated. A matrix spiked sample is a sample brought through the whole sample preparation and analytical process.

9.0 METHOD PERFORMANCE

9.1 Accuracy - Accuracy for this method was determined by three independent laboratories by measuring percent recoveries of spikes for both clean matrices (water) and actual waste samples. The results are summarized below.

For Acid-Soluble Sulfide

Accuracy of titration step only
Lab A 84-100% recovery
Lab B 110-122% recovery
Accuracy for entire method for clean matrices (H_2O)
Lab C 94-106% recovery
Accuracy of entire method for actual waste samples
Lab C 77-92% recovery

Spiking levels ranged from 0.4 to 8 mg/L

For Acid-Insoluble Sulfide

The percent recovery was not as thoroughly studied for acid-insoluble sulfide as it was for acid-soluble sulfide.

Accuracy of entire method for synthetic waste samples
Lab C 21-81% recovery

Spiking levels ranged from 2.2 to 22 mg/kg

9.2 Precision - For Acid-Soluble Sulfide

Precision of titration step only
Lab A CV% 2.0 to 37
Lab B CV% 1.1 to 3.8
Precision of entire method for clean matrices (H_2O)
Lab C CV% 3.0 to 12
Precision of entire method for actual waste samples
Lab C CV% 0.86 to 45

For Acid-Insoluble Sulfide

Precision of entire method with synthetic wastes
Lab C CV 1.2 to 42

9.3 Detection Limit - The detection limit was determined by analyzing seven replicates at 0.45 and 4.5 mg/L. The detection limit was calculated as the standard deviation times the student's t-value for a one-tailed test with n-1 degrees of freedom at 99% confidence level. The detection limit for a clean matrix (H_2O) was found to be between 0.2 and 0.4 mg/L.

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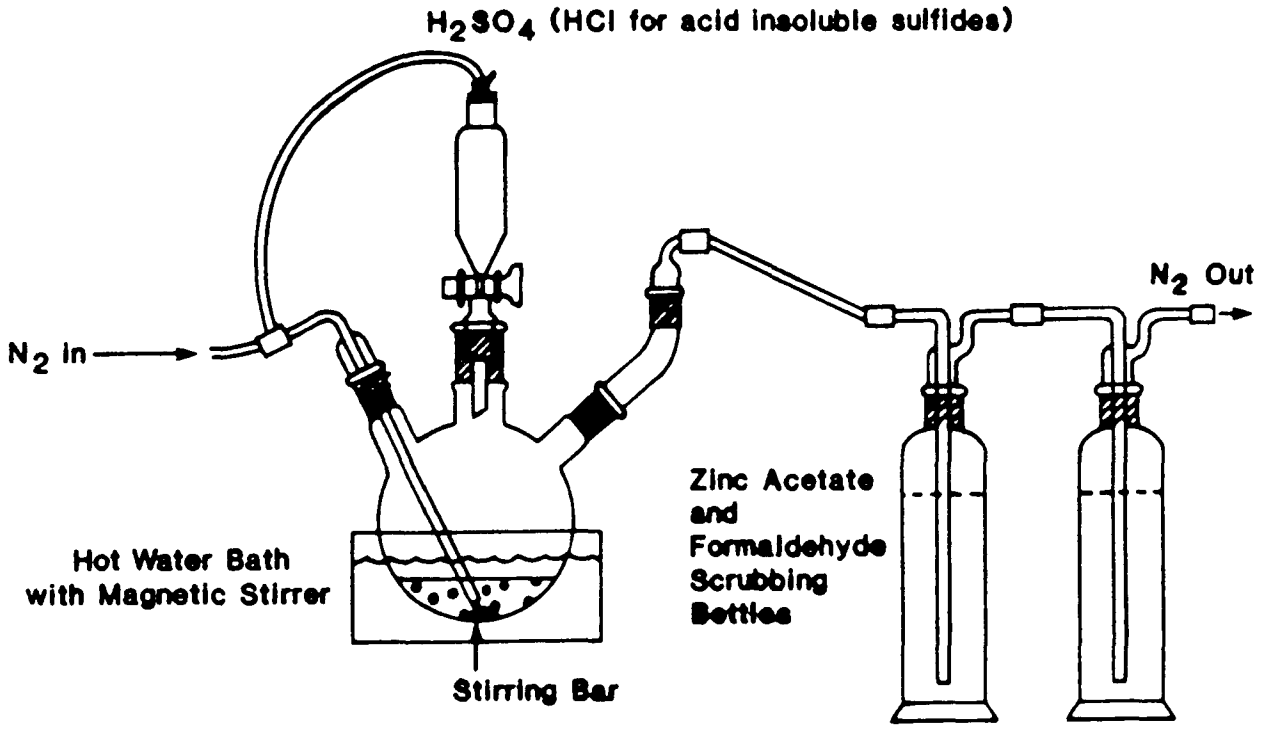
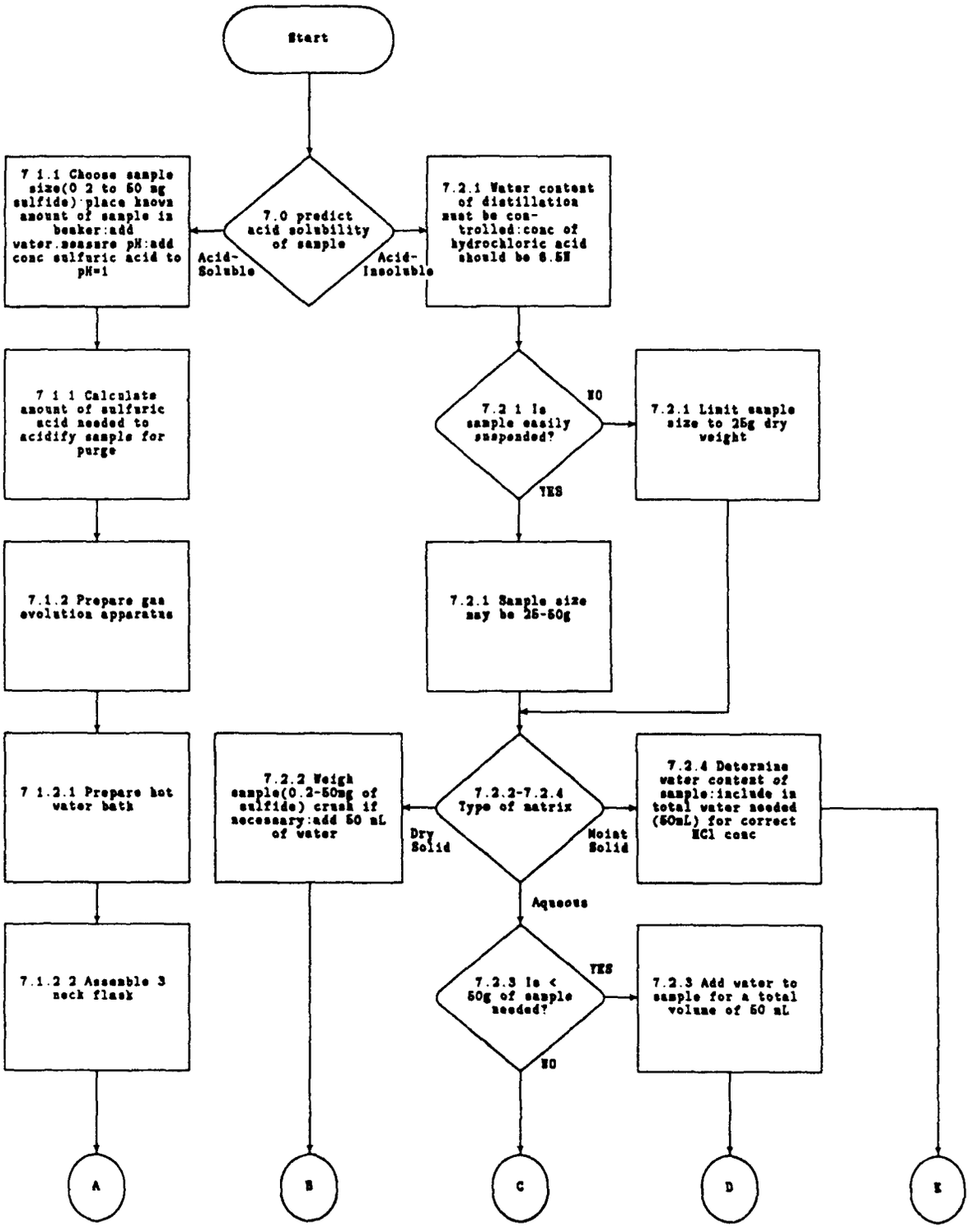
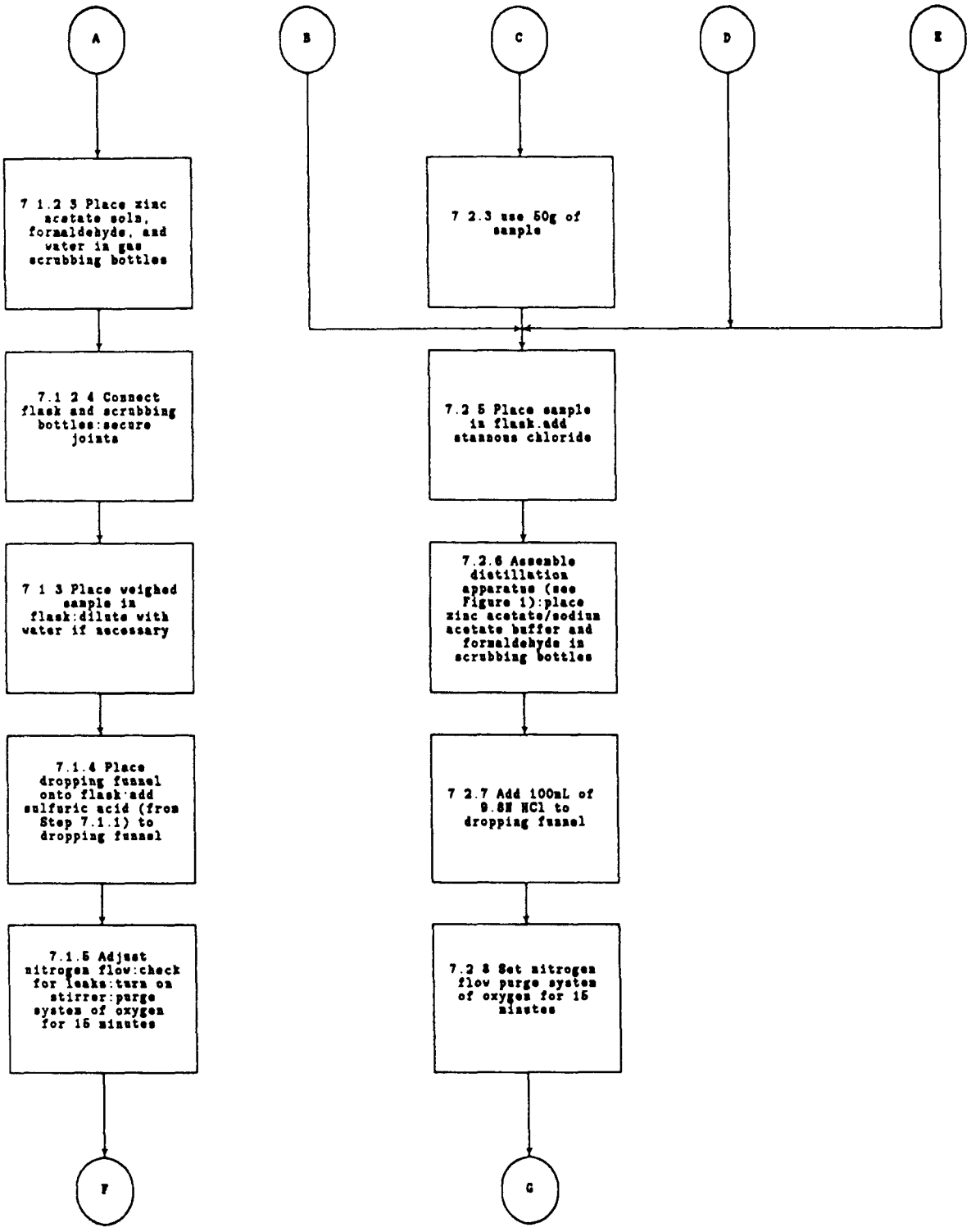
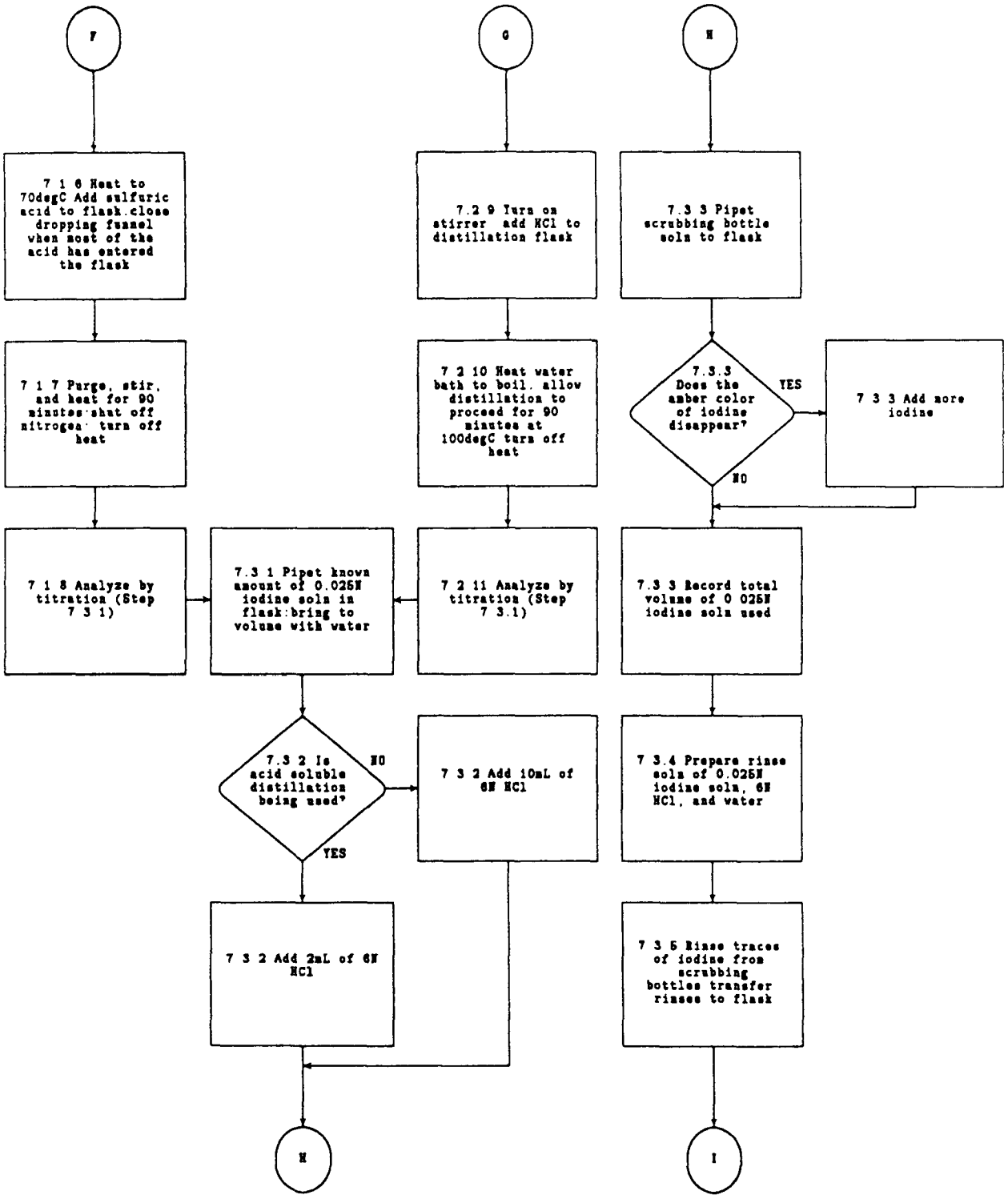
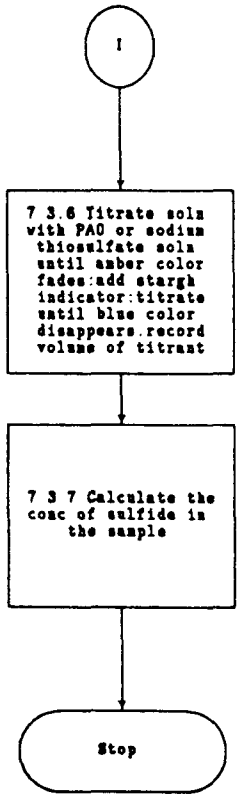
FIGURE 1.
GAS EVOLUTION APPARATUS




Start
7.0 predict acid solubility of sample
Acid-Soluble
Acid-Insoluble
7.1.1 Choose sample size(0.2 to 50 mg sulfide) place known amount of sample in beaker:add water.measure pH:add conc sulfuric acid to pH=1
7.2.1 Water content of distillation must be controlled:conc of hydrochloric acid should be 6.5N
7.1.1 Calculate amount of sulfuric acid needed to acidify sample for purge
7.2.1 Is sample easily suspended?
NO
YES
7.2.1 Limit sample size to 25g dry weight
7.1.2 Prepare gas evolution apparatus
7.2.1 Sample size may be 25-50g
7.1.2.1 Prepare hot water bath
7.2.2 Weigh sample(0.2-50mg of sulfide) crush if necessary:add 50 mL of water
7.2.2-7.2.4 Type of matrix
Dry Solid
Moist Solid
Aqueous
7.2.4 Determine water content of sample:include in total water needed (50mL) for correct HCl conc
7.1.2.2 Assemble 3 neck flask
7.2.3 Is < 50g of sample needed?
YES
NO
7.2.3 Add water to sample for a total volume of 50 mL
A
B
C
D
E


A
B
C
D
E
7 1.2 3 Place zinc acetate soln, formaldehyde, and water in gas scrubbing bottles
7 2.3 use 50g of sample
7.1 2 4 Connect flask and scrubbing bottles:secure joints
7.2 5 Place sample in flask.add stannous chloride
7 1 3 Place weighed sample in flask:dilute with water if necessary
7.2.6 Assemble distillation apparatus (see Figure 1):place zinc acetate/sodium acetate buffer and formaldehyde in scrubbing bottles
7.1.4 Place dropping funnel onto flask:add sulfuric acid (from Step 7.1.1) to dropping funnel
7 2.7 Add 100mL of 9.8N HCl to dropping funnel
7.1.5 Adjust nitrogen flow:check for leaks:turn on stirrer:purge system of oxygen for 15 minutes
7.2 8 Set nitrogen flow purge system of oxygen for 15 minutes
F
G


F
G
H
7 1 6 Heat to 70degC Add sulfuric acid to flask close dropping funnel when most of the acid has entered the flask
7.2 9 Turn on stirrer add HCl to distillation flask
7.3 3 Pipet scrubbing bottle soln to flask
7 1 7 Purge, stir, and heat for 90 minutes shut off nitrogen turn off heat
7 2 10 Heat water bath to boil, allow distillation to proceed for 90 minutes at 100degC turn off heat
7.3.3 Does the amber color of iodine disappear?
YES
NO
7 3 3 Add more iodine
7 1 8 Analyze by titration (Step 7 3 1)
7.3 1 Pipet known amount of 0.025N iodine soln in flask bring to volume with water
7 2 11 Analyze by titration (Step 7 3.1)
7.3 3 Record total volume of 0 025N iodine soln used
7.3 2 Is acid soluble distillation being used?
NO
YES
7 3 2 Add 10mL of 6N HCl
7 3.4 Prepare rinse soln of 0.025N iodine soln, 6N HCl, and water
7 3 2 Add 2mL of 6N HCl
7 3 5 Rinse traces of iodine from scrubbing bottles transfer rinses to flask
H
I


I
7 3.6 Titrate soln with PAO or sodium thiosulfate soln until amber color fades:add stargh indicator:titrate until blue color disappears.record volume of titrant
7 3 7 Calculate the conc of sulfide in the sample
Stop

METHOD 9031

EXTRACTABLE SULFIDES

1.0 SCOPE AND APPLICATION

1.1 The extraction procedure described in this method is designed for the extraction of sulfides from matrices that are not directly amenable to the distillation procedure Method 9030. This method is also not applicable for reactive sulfide. Refer to Chapter Seven, Step 7.3.4.1 for the determination of reactive sulfide. This method is applicable to oil, solid, multiphasic, and all other matrices not amenable to analysis by Method 9030.

1.2 Method 9031 is suitable for measuring sulfide in solid samples at concentrations above 1 mg/kg.

2.0 SUMMARY OF METHOD

2.1 If the sample contains solids that will interfere with agitation and homogenization of the sample mixture, or so much oil or grease as to interfere with the formation of a homogeneous emulsion in the distillation procedure, the sample must be filtered and the solids extracted with water at pH > 9 or < 11. The extract is then combined with the filtrate and analyzed by the distillation procedure. Separation of sulfide from the sample matrix is accomplished by the addition of sulfuric acid to the sample. The sample is heated to 70°C and the hydrogen sulfide (H_2S) which is formed is distilled under acidic conditions and carried by a nitrogen stream into zinc acetate gas scrubbing bottles where it is precipitated as zinc sulfide.

2.2 The sulfide in the zinc sulfide precipitate is oxidized to sulfur with a known amount of excess iodine. Then the excess iodine is determined by titration with a standard solution of phenylarsine oxide (PAO) or sodium thiosulfate until the blue iodine starch complex disappears. The use of standard sulfide solutions is not possible because of their instability to oxidative degradation. Therefore quantitation is based on the PAO or sodium thiosulfate.

3.0 INTERFERENCES

3.1 Samples with aqueous layers must be taken with a minimum of aeration to avoid volatilization of sulfide or reaction with oxygen which oxidizes sulfide to sulfur compounds that are not detected.

3.2 Sulfur compounds such as sulfite and hydrosulfite decompose in acid and may form sulfur dioxide. This gas may be carried over to the zinc acetate gas scrubbing bottles and subsequently react with the iodine solution yielding false high values. The addition of formaldehyde into the zinc acetate gas scrubbing bottles removes this interference. Any sulfur dioxide entering the scrubber will form an addition compound with the formaldehyde which is unreactive towards the iodine in the acidified mixture. This method shows no sensitivity to sulfite or hydrosulfite at concentrations up to 10 mg/kg of the interferent.

3.3 The iodometric method suffers interference from reducing substances that react with iodine including thiosulfate, sulfite, and various organic compounds.

3.4 Interferences have been observed when analyzing samples with high metal content such as electroplating waste and chromium containing tannery waste.

4.0 APPARATUS AND MATERIALS

4.1 Extractor - Any suitable device that sufficiently agitates a sealed container of one liter volume or greater. For the purpose of this analysis, agitation is sufficient when all sample surfaces are continuously brought into contact with extraction fluid, and the agitation prevents stratification of the sample and fluid. Examples of suitable extractors are shown in Figures 2 and 3. The tumble-extractors turn the extraction bottles end-over-end at a rate of about 30 rpm. The apparatus in Figure 2 may be easily fabricated from plywood. The jar compartments must be padded with polyurethane foam to absorb shock. The drive apparatus is a Norton jar mill.

4.2 Buchner funnel apparatus

4.2.1 Buchner funnel - 500-mL capacity, with 1-liter vacuum filtration flask.

4.2.2 Glass wool - Suitable for filtering, 0.8 um diameter such as Corning Pyrex 3950.

4.2.3 Vacuum source - Preferably a water driven aspirator. A valve or stopcock to release vacuum is required.

4.3 Distillation apparatus as shown in Figure 1

4.3.1 Three neck flask - 500-mL, 24/40 standard tapered joints.

4.3.2 Dropping funnel - 100-mL, 24/40 outlet joint.

4.3.3 Purge gas inlet tube - 24/40 joint with course frit.

4.3.4 Purge gas outlet - 24/40 joint reduced to 1/4 inch tube.

4.3.5 Gas scrubbing bottles - 125-mL, with 1/4 in. o.d. inlet and outlet tubes. Impinger tube must not be fritted.

4.3.6 Tubing - 1/4 in. o.d. Teflon or polypropylene. Do not use rubber.

4.4 Hot plate stirrer.

4.5 pH meter.

4.6 Nitrogen regulator.

4.7 Flowmeter.

4.8 Separatory funnels - 500-mL.

4.9 Tumbler - See Figures 2 and 3.

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 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Zinc Acetate (for sample preservation) (2N), $Zn(CH_3COO)_2 \cdot 2H_2O$. Dissolve 220 g of zinc acetate dihydrate in 500 mL of water.

5.4 Sodium Hydroxide (50% w/v in water), NaOH. Commercially available.

5.5 Tin (II) Chloride, $SnCl_2 \cdot 2H_2O$, granular.

5.6 n-Hexane, C_6H_{14}.

5.7 Nitrogen, N_2.

5.8 Sulfuric Acid (concentrated), H_2SO_4.

5.9 Zinc Acetate for the scrubber (approximately 0.5M). Dissolve 110 g zinc acetate dihydrate in 200 mL of water. Add 1 mL concentrated hydrochloric acid, HCl, to prevent precipitation of zinc hydroxide. Dilute to 1 liter.

5.10 Formaldehyde (37% solution), CH_2O. Commercially available.

5.11 Starch solution. Use either an aqueous solution or soluble starch powder mixtures. Prepare an aqueous solution as follows. Dissolve 2 g soluble starch and 2 g salicylic acid, $C_7H_6O_3$, as a preservative, in 100 mL hot water.

5.12 Iodine solution (approximately 0.025N). Dissolve 25 g of potassium iodide, KI, in 700 mL of water in a 1-liter volumetric flask. Add 3.2 g of iodine, I_2. Allow to dissolve. Dilute to 1 liter and standardize as follows. Dissolve approximately 2 g KI in 150 mL of water. Pipet exactly 20 mL of the iodine solution to be titrated and dilute to 300 mL with water. Titrate with 0.025N standard phenylarsine oxide, or 0.025N sodium thiosulfate, $Na_2S_2O_3$, until the amber color fades. Add starch indicator solution until the solution turns deep blue. Continue titration drop by drop until the blue color disappears. Run in replicate. Calculate the normality as follows:

$$\text{Normality } (I_2) = \frac{\text{mL of titrant x normality of titrant}}{\text{Volume of sample (mL)}}$$

5.13 Sodium sulfide nonahydrate $Na_2S \cdot 9H_2O$, for the preparation of standard solutions to be used for calibration curves. Standards must be prepared at pH > 9 or < 11.

5.14 Titrant.

5.14.1 Standard phenylarsine oxide (PAO) solution (0.025N), C_6H_5AsO. This solution is commercially available.

CAUTION: PAO is toxic.

5.14.2 Standard sodium thiosulfate solution (0.025N), $Na_2S_2O_3 \cdot 5H_2O$. Dissolve 6.205 $\pm$ 0.005 g $Na_2S_2O_3 \cdot 5H_2O$ in 500 mL of water. Add 9 mL 1N NaOH and dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All samples must be preserved with zinc acetate and sodium hydroxide. Use four drops of 2N zinc acetate solution per 100 mL of aqueous or multiphasic sample. Adjust the pH to greater than 9.0 with 50% NaOH. Fill the sample bottle completely and stopper with a minimum of aeration. For solid samples, fill the surface of solid with 2N zinc acetate until moistened. Samples must be cooled to 4°C during storage.

7.0 PROCEDURE

7.1 Assemble the Buchner funnel apparatus. Unroll the glass wool and fold the fiber over itself several times to make a pad about 1 cm thick when lightly compressed. Cut the pad to fit the Buchner funnel. Dry and weigh the pad, then place it in the funnel. Turn on the aspirator and wet the pad with a known amount of water.

7.2 Transfer a sample that contains between 1 and 50 mg of sulfide to the Buchner funnel. Rinse the sample container with known amounts of water and add the rinses to the Buchner funnel. When no free water remains in the funnel, slowly open the stopcock to allow air to enter the vacuum flask. A small amount of sediment may have passed through the glass fiber pad. This will not interfere with the analysis.

7.3 Transfer the solid and the glass fiber pad to a dried tared weighing dish. Since most greases and oils will not pass through the fiber pad, solids, oils, and greases will be extracted together. If the filtrate includes an oil phase, transfer the filtrate to a separatory funnel. Collect and measure the volume of the aqueous phase. Transfer the oil phase to the weighing dish with the solid and glass fiber pad.

7.4 Weigh the dish containing solid, oil (if any), and glass fiber pad. Subtract the weight of the dry glass fiber pad. Calculate the volume of water present in the original sample by subtracting the total volume of rinses from the measured volume of the filtrate.

7.5 Place the following in a 1-liter wide-mouth bottle:

500 mL water
5 mL 50% w/v NaOH
1 g $SnCl_2 \cdot 2H_2O$
50 mL n-hexane (if an oil or grease is present).

Cap the bottle with a Teflon or polyethylene lined cap and shake vigorously to saturate the solution with stannous chloride. Direct a stream of nitrogen gas at about 10 mL/min into the bottle for about 1 minute to purge the headspace of oxygen. If the weight of the solids (Step 7.4) is greater than 25 g, weigh out a representative aliquot of 25 g and add it to the bottle while still purging with nitrogen. Otherwise, add all of the solids. Cap the bottle; avoid the influx of air.

7.6 The pH of the extract must be maintained at > 9 or < 11 throughout the extraction step and subsequent filtration. Since some samples may release acid, the pH must be monitored as follows. Shake the extraction bottle and wait 1 minute. Open the bottle under a stream of nitrogen and check the pH. If the pH is below 9, add 50% NaOH in 5 mL increments until it is at least 9. Recap the bottle, and repeat the procedure until the pH does not drop. The bottle must be thoroughly purged of oxygen before each recapping. Oxygen will oxidize sulfide to elemental sulfur or other sulfur containing compounds that will not be detected.

7.7 Place the bottle in the tumbler, making sure there is enough foam insulation to cushion the bottle. Turn the tumbler on and allow the extraction to run for about 18 hours.

7.8 Prepare a Buchner funnel apparatus as in Step 7.1 with a glass fiber pad filter.

7.9 Decant the extract to the Buchner funnel.

7.10 If the extract contains an oil phase, separate the aqueous phase using a separatory funnel. Neither the separation nor the filtration are critical, but are necessary to be able to measure the volume of the aqueous extract analyzed. Small amounts of suspended solids and oil emulsions will not interfere with the extraction.

7.11 At this point, an aliquot of the filtrate of the original sample may be combined with an aliquot of the extract in a proportion representative of the sample. Calculate the proportions as follows:

$$\frac{\text{Aliquot of the Filtrate(mL)}}{\text{Aliquot of the Extract(mL)}} = \frac{\text{Solid Extracted(g)}^a}{\text{Total Solid(g)}^b} \times \frac{\text{Total Sample Filtrate(mL)}^c}{\text{Total Extraction Fluid(mL)}^d}$$

[a]From Step 7.5. Weight of solid sample taken from extraction.

[b]From Step 7.4. Weight of solids and oil phase with the dry weight of filter and tared dish subtracted.

[c]Includes volume of all rinses added to the filtrate (Steps 7.1 and 7.2).

[d]500 mL water plus total volume of NaOH solution. Does not include hexane, which is subsequently removed (Steps 7.5 and 7.6).

Alternatively, the samples may be analyzed separately, concentrations for each phase reported separately, and the amounts of each phase present in the sample reported separately.

7.12 Distillation of Sulfide

7.12.1 In a preliminary experiment, determine the approximate amount of sulfuric acid required to adjust a measured amount of the sample to pH less than or equal to 1. The sample size should be chosen so that it contains between 0.2 and 50 mg of sulfide. Place a known amount of sample or sample slurry in a beaker. Add water until the total volume is 200 mL. Stir the mixture and determine the pH. Slowly add sulfuric acid until the pH is less than or equal to 1.

CAUTION: Toxic hydrogen sulfide may be generated from the acidified sample. This operation must be performed in the hood and the sample left in the hood until the sample has been made alkaline or the sulfide has been destroyed.

From the amount of sulfuric acid required to acidify the sample and the mass or volume of the sample acidified, calculate the amount of acid required to acidify the sample to be placed in the distillation flask.

7.12.2 Prepare the gas evolution apparatus as shown in Figure 1 in a fume hood.

7.12.2.1 Prepare a hot water bath at 70°C by filling a crystallizing dish or other suitable container with water and place it on a hotplate stirrer. Place a thermometer in the bath and monitor the temperature to maintain the bath at 70°C.

7.12.2.2 Assemble the three neck 500-mL flask, fritted gas inlet tube, and exhaust tube. Use Teflon sleeves to seal the ground glass joints. Place a Teflon coated stirring bar into the flask.

7.12.2.3 Place into each gas scrubbing bottle 10 ± 0.5 mL of the 0.5M zinc acetate solution, 5.0 ± 0.1 mL of 37% formaldehyde and 100 ± 5.0 mL water.

7.12.2.4 Connect the gas evolution flask and gas scrubbing bottles as shown in Figure 1. Secure all fittings and joints.

7.12.3 Carefully place an accurately weighed sample which contains 1.0 to 50 mg of sulfide into the flask. If necessary, dilute to approximately 200 mL with water.

7.12.4 Place the dropping funnel onto the flask making sure its stopcock is closed. Add the volume of sulfuric acid calculated in Step 7.1.1 plus an additional 50 mL into the dropping funnel. The bottom stopcock must be closed.

7.12.5 Attach the nitrogen inlet to the top of the dropping funnel gas shut-off valve. Turn on the nitrogen purge gas and adjust the flow through the sample flask to 25 mL/min. The nitrogen in the gas scrubbing bottles should bubble at a rate of about five bubbles per second. Nitrogen pressure should be limited to approximately 10 psi to prevent excess stress on the glass system and fittings. Verify that there are no leaks in the system. Open the nitrogen shut-off valve leading to the dropping funnel. Observe that the gas flow into the sample vessel will stop for a short period while the pressure throughout the system equalizes. If the gas flow through the sample flask does not return within a minute, check for leaks around the dropping funnel. Once flow has stabilized, turn on the magnetic stirrer. Purge the system for 15 minutes with nitrogen to remove oxygen.

7.12.6 Heat sample to 70°C. Open dropping funnel to a position that will allow a flow of sulfuric acid of approximately 5 mL/min. Monitor the system until most of the sulfuric acid contained within the dropping funnel has entered the sample flask. Close the dropping funnel while a small amount of acid remains. Immediately close the gas shut-off valve to the dropping funnel.

7.12.7 Purge, stir, and maintain a temperature of 70°C for a total of 90 minutes from start to finish. Shut off nitrogen supply. Turn off heat.

7.13 Titration of Distillate

7.13.1 Pipet a known amount of standardized 0.025N iodine solution (see Step 5.12) in a 500-mL flask, adding an amount in excess of that needed to oxidize the sulfide. Add enough water to bring the volume to 100 mL. The volume of standardized iodine solution should be about 65 mL for samples with 50 mg of sulfide.

7.13.2 Add 2 mL of 6N HCl to the iodine.

7.13.3 Pipet both of the gas scrubbing bottle solutions into the flask, keeping the end of the pipet below the surface of the iodine solution. If at any point in transferring the zinc acetate solution or rinsing the bottles, the amber color of the iodine disappears or fades to yellow, more 0.025N iodine must be added. This additional amount must be

added to the amount from Step 7.13.1 for calculations. Record the total volume of standardized 0.025N iodine solution used.

7.13.4 Prepare a rinse solution of a known amount of standardized 0.025N iodine solution, 1 mL of 6N HCl, and water to rinse the remaining white precipitate (zinc sulfide) from the gas scrubbing bottles into the flask. There should be no visible traces of precipitate after rinsing.

7.13.5 Rinse any remaining traces of iodine from the gas scrubbing bottles with water, and transfer the rinses to the flask.

7.13.6 Titrate the solution in the flask with standard 0.025N phenylarsine oxide or 0.025N sodium thiosulfate solution until the amber color fades to yellow. Add enough starch indicator for the solution to turn dark blue and titrate until the blue disappears. Record the volume of titrant used.

7.13.7 Calculate the concentration of sulfide in the sample as follows:

$$\frac{[(\text{mL of } I_2 \times \text{N of } I_2)-(\text{mL of titrant} \times \text{N of titrant})](16.03)}{\text{sample weight (kg)}} = \text{sulfide(mg/kg)}$$

8.0 QUALITY CONTROL

8.1 All quality control data must be maintained and available for reference or inspection for a period of three years. This method is restricted to use by or under supervision of experienced analysts. Refer to the appropriate section of Chapter One for additional quality control requirements.

8.2 A reagent blank should be run once every twenty analyses or per analytical batch, whichever is more frequent.

8.3 Check standards are prepared from water and a known amount of sodium sulfide. A check standard should be run with each analytical batch of samples or once every twenty samples. Acceptable recovery will depend on level and matrix.

8.4 A matrix spiked sample should be run for each analytical batch or every twenty samples, whichever is more frequent, to determine matrix effects. If recovery is low, acid-insoluble sulfides are indicated. A matrix spiked sample is a sample brought through the whole sample preparation and analytical process.

8.5 Verify the calibration with an independently prepared QC reference sample every twenty samples or once per analytical batch, whichever is more frequent.

9.0 METHOD PERFORMANCE

9.1 Accuracy - Accuracy for this method was determined by three independent laboratories by measuring percent recoveries of spikes for waste samples. The results are summarized below.

Accuracy for the entire method for four synthetic waste samples
70-104% recovery

9.2 Precision

Precision of entire method for four synthetic waste samples
Percent coefficient of variation 1.0-34

10.0 REFERENCES

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FIGURE 1.
GAS EVOLUTION APPARATUS

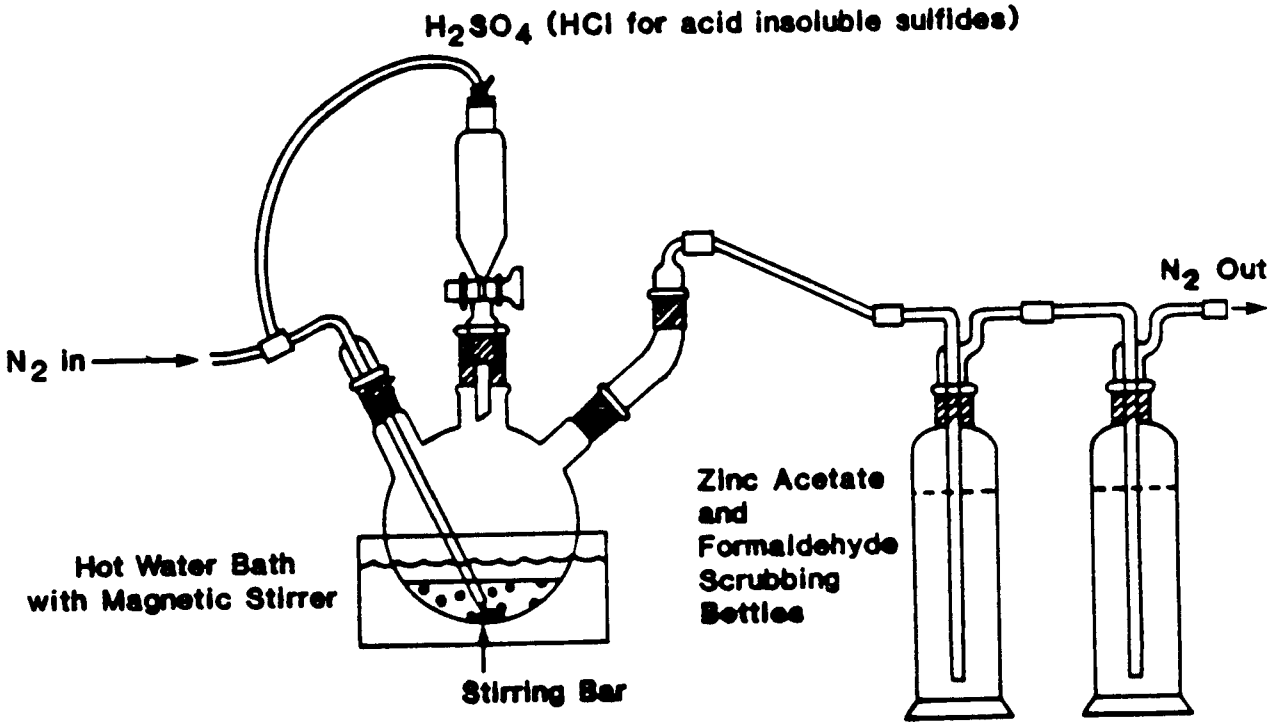


FIGURE 2.
TUMBLER-EXTRACTOR

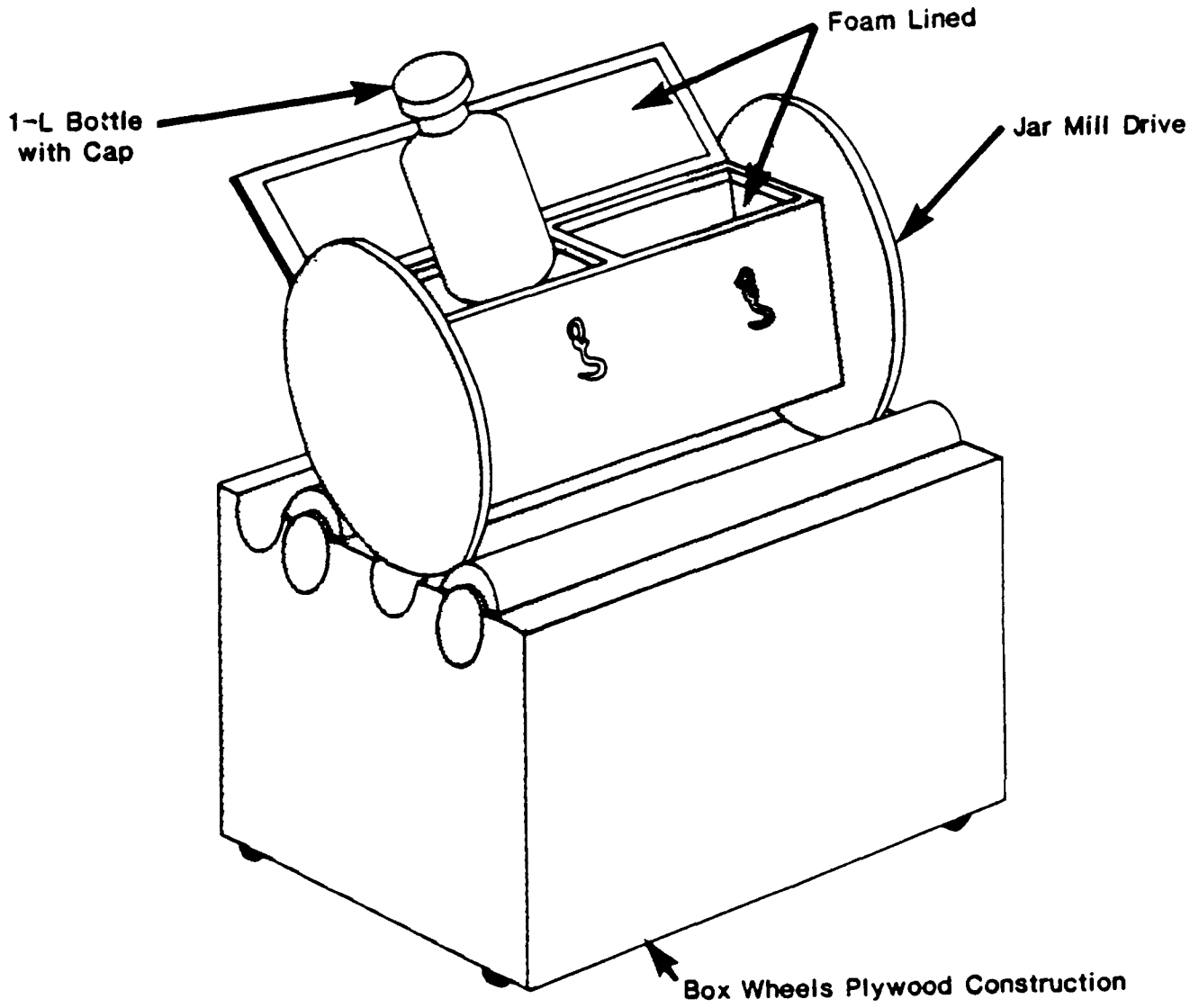
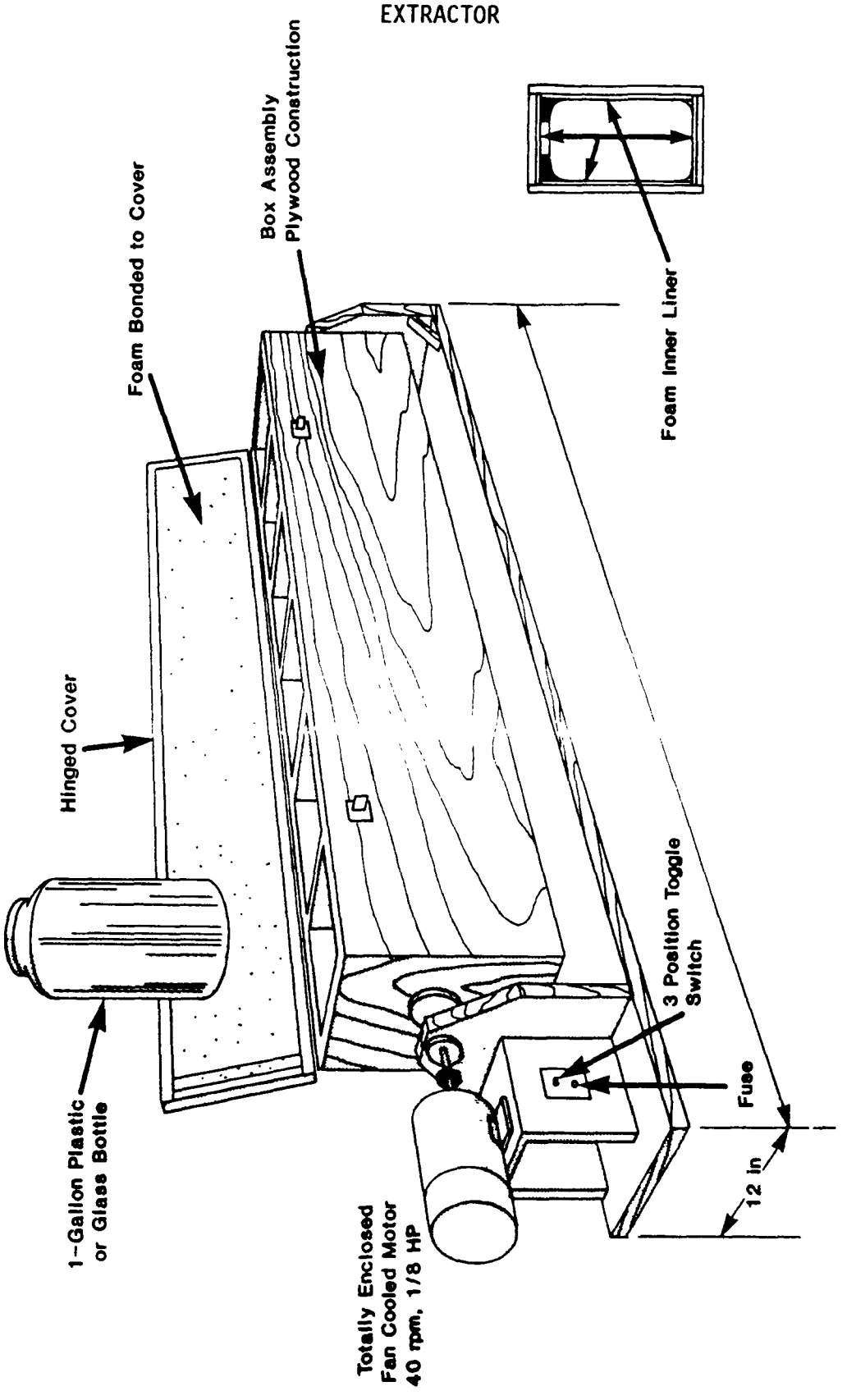
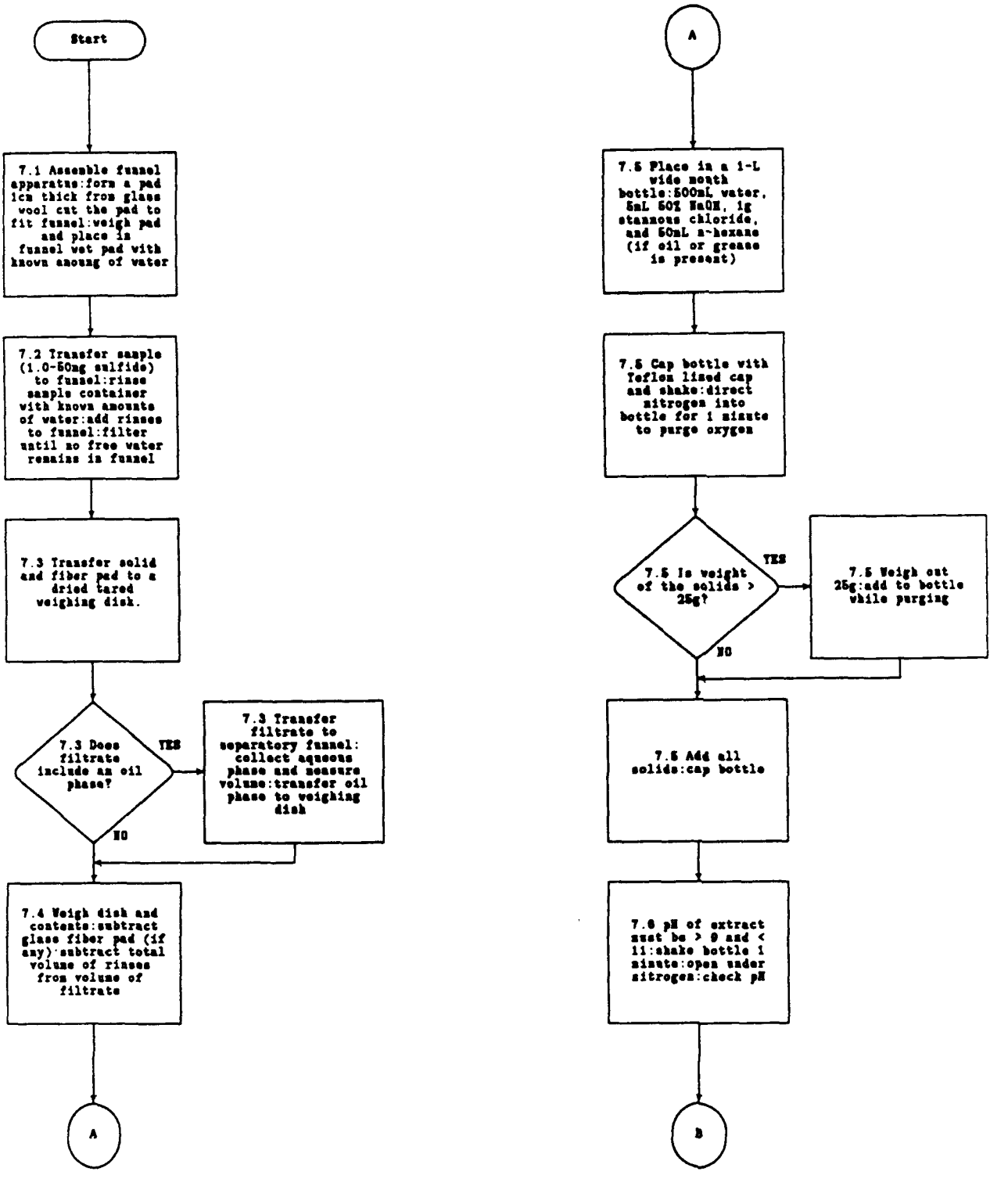
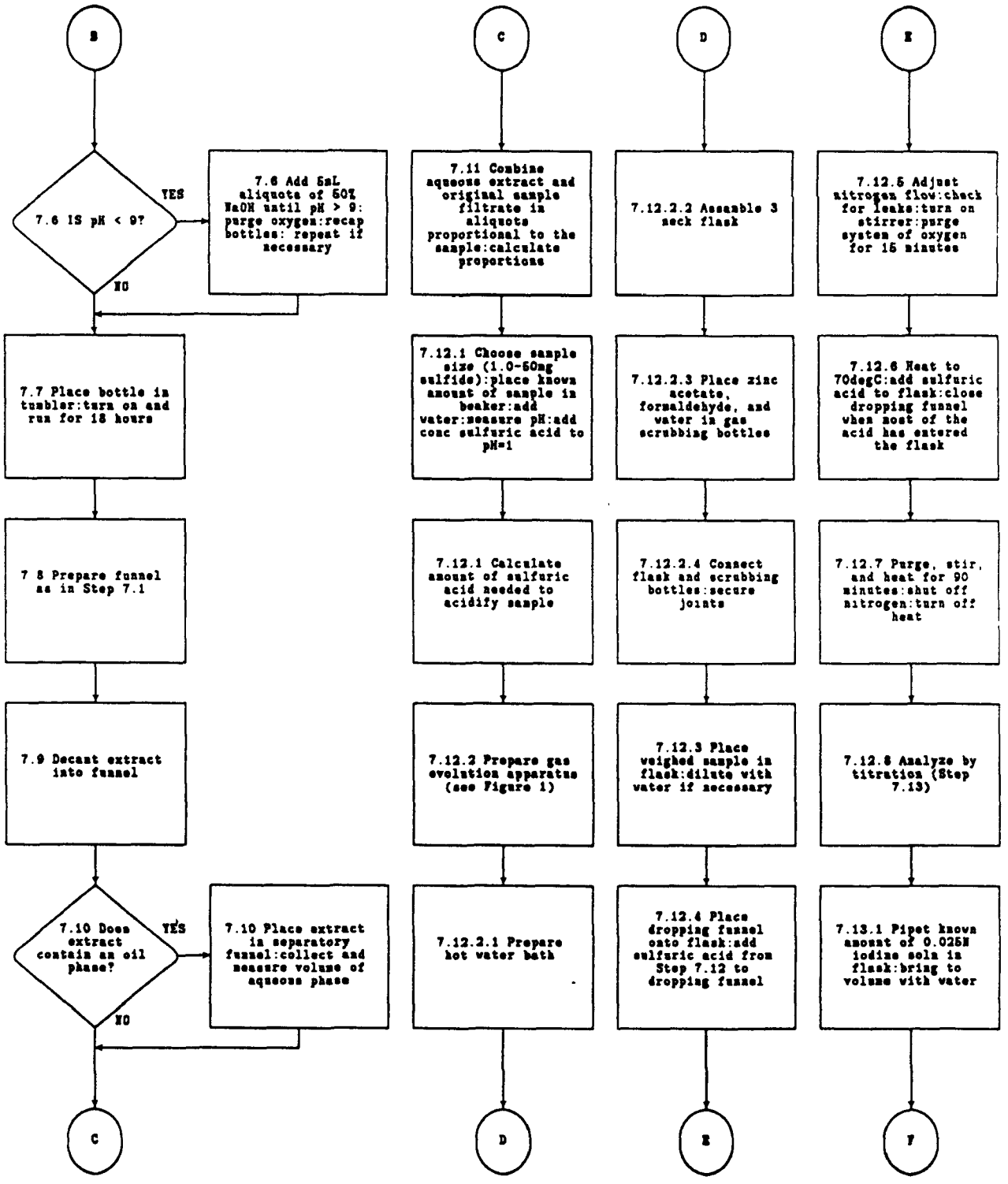
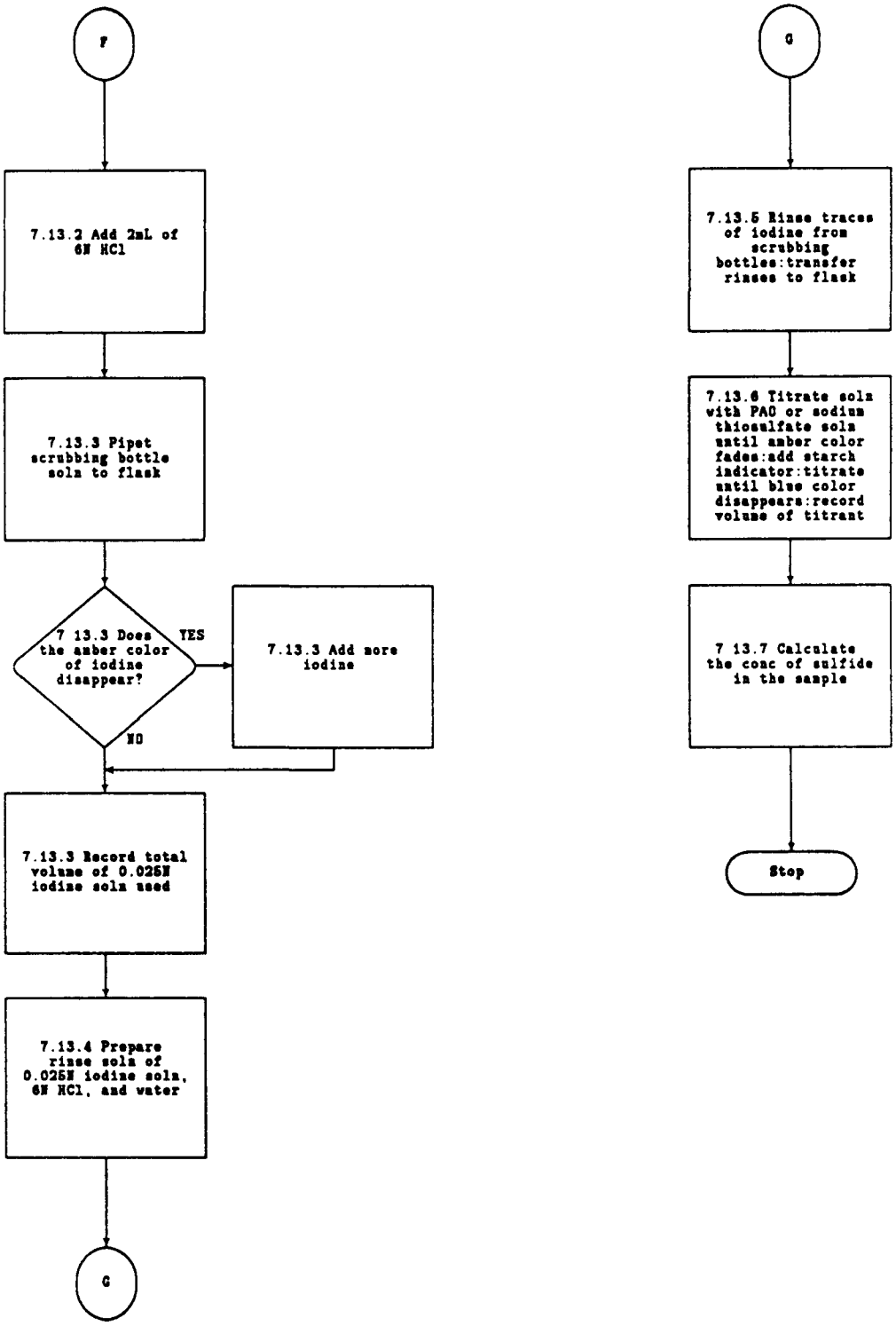


FIGURE 3.
EXTRACTOR




Start
7.1 Assemble funnel apparatus:form a pad 1cm thick from glass wool cut the pad to fit funnel:weigh pad and place in funnel wet pad with known amount of water
7.2 Transfer sample (1.0-50mg sulfide) to funnel:rinse sample container with known amounts of water:add rinses to funnel:filter until no free water remains in funnel
7.3 Transfer solid and fiber pad to a dried tared weighing disk.
7.3 Does filtrate include an oil phase?
YES
7.3 Transfer filtrate to separatory funnel: collect aqueous phase and measure volume:transfer oil phase to weighing dish
NO
7.4 Weigh dish and contents:subtract glass fiber pad (if any):subtract total volume of rinses from volume of filtrate
A
A
7.5 Place in a 1-L wide mouth bottle:500mL water, 5mL 50% NaOH, 1g stannous chloride, and 50mL n-hexane (if oil or grease is present)
7.5 Cap bottle with Teflon lined cap and shake:direct nitrogen into bottle for 1 minute to purge oxygen
7.5 Is weight of the solids > 25g?
YES
7.5 Weigh out 25g:add to bottle while purging
NO
7.6 Add all solids:cap bottle
7.6 pH of extract must be > 9 and < 11:shake bottle 1 minute:open under nitrogen:check pH
B


B
C
D
E
7.6 IS pH < 9?
YES
NO
7.6 Add 5mL aliquots of 50% NaOH until pH > 9: purge oxygen:recap bottles: repeat if necessary
7.7 Place bottle in tumbler:turn on and run for 18 hours
7.8 Prepare funnel as in Step 7.1
7.9 Decant extract into funnel
7.10 Does extract contain an oil phase?
YES
NO
7.10 Place extract in separatory funnel:collect and measure volume of aqueous phase
C
7.11 Combine aqueous extract and original sample filtrate in aliquots proportional to the sample:calculate proportions
7.12.1 Choose sample size (1.0-50mg sulfide):place known amount of sample in beaker:add water:measure pH:add conc sulfuric acid to pH=1
7.12.1 Calculate amount of sulfuric acid needed to acidify sample
7.12.2 Prepare gas evolution apparatus (see Figure 1)
7.12.2.1 Prepare hot water bath
D
7.12.2.2 Assemble 3 neck flask
7.12.2.3 Place zinc acetate, formaldehyde, and water in gas scrubbing bottles
7.12.2.4 Connect flask and scrubbing bottles:secure joints
7.12.3 Place weighed sample in flask:dilute with water if necessary
7.12.4 Place dropping funnel onto flask:add sulfuric acid from Step 7.12 to dropping funnel
E
7.12.5 Adjust nitrogen flow:check for leaks:turn on stirrer:purge system of oxygen for 15 minutes
7.12.6 Heat to 70degC:add sulfuric acid to flask:close dropping funnel when most of the acid has entered the flask
7.12.7 Purge, stir, and heat for 90 minutes:shut off nitrogen:turn off heat
7.12.8 Analyze by titration (Step 7.13)
7.13.1 Pipet known amount of 0.025N iodine soln in flask:bring to volume with water
F


F
7.13.2 Add 2mL of 6N HCl
7.13.3 Pipet scrubbing bottle soln to flask
7 13.3 Does the amber color of iodine disappear?
YES
7.13.3 Add more iodine
NO
7.13.3 Record total volume of 0.025N iodine soln used
7.13.4 Prepare rinse soln of 0.025N iodine soln, 6N HCl, and water
G
G
7.13.5 Rinse traces of iodine from scrubbing bottles:transfer rinses to flask
7.13.6 Titrate soln with PAO or sodium thiosulfate soln until amber color fades:add starch indicator:titrate until blue color disappears:record volume of titrant
7 13.7 Calculate the conc of sulfide in the sample
Stop

METHOD 9056

ANION CHROMATOGRAPHY METHOD

1.0 SCOPE AND APPLICATION

1.1 This method addresses the sequential determination of the anions chloride, fluoride, bromide, nitrate, nitrite, phosphate, and sulfate in the collection solutions from the bomb combustion of solid waste samples, as well as all water samples.

1.2 The minimum detection limit (MDL), the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero, varies for anions as a function of sample size and the conductivity scale used. Generally, minimum detectable concentrations are in the range of 0.05 mg/L for F- and 0.1 mg/L for Br^-, Cl^-, NO_3^-, NO_2^-, PO_4^{3-}, and SO_4^{2-} with a 100-μL sample loop and a 10-umho full-scale setting on the conductivity detector. Similar values may be achieved by using a higher scale setting and an electronic integrator. Idealized detection limits of an order of magnitude lower have been determined in reagent water by using a 1 umho full-scale setting (Table 1).

The upper limit of the method is dependent on total anion concentration and may be determined experimentally. These limits may be extended by appropriate dilution.

2.0 SUMMARY OF METHOD

2.1 A small volume of combustate collection solution or other water sample, typically 2 to 3 mL, is injected into an ion chromatograph to flush and fill a constant volume sample loop. The sample is then injected into a stream of carbonate-bicarbonate eluent of the same strength as the collection solution or water sample.

The sample is pumped through three different ion exchange columns and into a conductivity detector. The first two columns, a precolumn or guard column and a separator column, are packed with low-capacity, strongly basic anion exchanger. Ions are separated into discrete bands based on their affinity for the exchange sites of the resin. The last column is a suppressor column that reduces the background conductivity of the eluent to a low or negligible level and converts the anions in the sample to their corresponding acids. The separated anions in their acid form are measured using an electrical-conductivity cell. Anions are identified based on their retention times compared to known standards. Quantitation is accomplished by measuring the peak height or area and comparing it to a calibration curve generated from known standards.

3.0 INTERFERENCES

3.1 Any species with a retention time similar to that of the desired ion will interfere. Large quantities of ions eluting close to the ion of interest will also result in an interference. Separation can be improved by adjusting the eluent concentration and/or flow rate.

Sample dilution and/or the use of the method of standard additions can also be used.

For example, high levels of organic acids may be present in industrial wastes, which may interfere with inorganic anion analysis. Two common species, formate and acetate, elute between fluoride and chloride.

3.2 Because bromide and nitrate elute very close together, they are potential interferents for each other. It is advisable not to have Br^-/NO_3^- ratios higher than 1:10 or 10:1 if both anions are to be quantified. If nitrate is observed to be an interference with bromide, use of an alternate detector (e.g., electrochemical detector) is recommended.

3.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

3.4 Samples that contain particles larger than 0.45 μm and reagent solutions that contain particles larger than 0.20 μm require filtration to prevent damage to instrument columns and flow systems.

3.5 If a packed bed suppressor column is used, it will be slowly consumed during analysis and, therefore, will need to be regenerated. Use of either an anion fiber suppressor or an anion micromembrane suppressor eliminates the time-consuming regeneration step through the use of a continuous flow of regenerant.

4.0 APPARATUS AND MATERIALS

4.1 Ion chromatograph, capable of delivering 2 to 5 mL of eluent per minute at a pressure of 200 to 700 psi (1.3 to 4.8 MPa). The chromatograph shall be equipped with an injection valve, a 100-μL sample loop, and set up with the following components, as schematically illustrated in Figure 1.

4.1.1 Precolumn, a guard column placed before the separator column to protect the separator column from being fouled by particulates or certain organic constituents (4 x 50 mm, Dionex P/N 030825 [normal run], or P/N 030830 [fast run], or equivalent).

4.1.2 Separator column, a column packed with low-capacity pellicular anion exchange resin that is styrene divinylbenzene-based has been found to be suitable for resolving F^-, Cl^-, NO_2^-, PO_4^{-3}, Br^-, NO_3^-, and SO_4^{-2} (see Figure 2) (4 x 250 mm, Dionex P/N 03827 [normal run], or P/N 030831 [fast run], or equivalent).

4.1.3 Suppressor column, a column that is capable of converting the eluent and separated anions to their respective acid forms (fiber, Dionex P/N 35350, micromembrane, Dionex P/N 38019 or equivalent).

4.1.4 Detector, a low-volume, flowthrough, temperature-compensated, electrical conductivity cell (approximately 6 μL volume, Dionex, or equivalent) equipped with a meter capable of reading from 0 to 1,000 μseconds/cm on a linear scale.

4.1.5 Pump, capable of delivering a constant flow of approximately 2 to 5 mL/min throughout the test and tolerating a pressure of 200 to 700 psi (1.3 to 4.8 MPa).

4.2 Recorder, compatible with the detector output with a full-scale response time in 2 seconds or less.

4.3 Syringe, minimum capacity of 2 mL and equipped with a male pressure fitting.

4.4 Eluent and regenerant reservoirs, suitable containers for storing eluents and regenerant. For example, 4 L collapsible bags can be used.

4.5 Integrator, to integrate the area under the chromatogram. Different integrators can perform this task when compatible with the electronics of the detector meter or recorder. If an integrator is used, the maximum area measurement must be within the linear range of the integrator.

4.6 Analytical balance, capable of weighing to the nearest 0.0001 g.

4.7 Pipets, Class A volumetric flasks, beakers: assorted sizes.

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 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One. Column life may be extended by passing reagent water through a 0.22-μm filter prior to use.

5.3 Eluent, 0.003M $NaHCO_3$/0.0024M Na_2CO_3. Dissolve 1.0080 g of sodium bicarbonate (0.003M $NaHCO_3$) and 1.0176 g of sodium carbonate (0.0024M Na_2CO_3) in reagent water and dilute to 4 L with reagent water.

5.4 Suppressor regenerant solution. Add 100 mL of 1N H_2SO_4 to 3 L of reagent water in a collapsible bag and dilute to 4 L with reagent water.

5.5 Stock solutions (1,000 mg/L).

5.5.1 Bromide stock solution (1.00 mL = 1.00 mg Br^-). Dry approximately 2 g of sodium bromide (NaBr) for 6 hours at 150°C, and cool in a desiccator. Dissolve 1.2877 g of the dried salt in reagent water, and dilute to 1 L with reagent water.

5.5.2 Chloride stock solution (1.00 mL = 1.00 mg Cl^-). Dry sodium chloride (NaCl) for 1 hour at 600°C, and cool in a desiccator. Dissolve 1.6484 g of the dry salt in reagent water, and dilute to 1 L with reagent water.

5.5.3 Fluoride stock solution (1.00 mL = 1.00 mg F^-). Dissolve 2.2100 g of sodium fluoride (NaF) in reagent water, and dilute to 1 L with reagent water. Store in chemical-resistant glass or polyethylene.

5.5.4 Nitrate stock solution (1.00 mL = 1.00 mg NO_3^-). Dry approximately 2 g of sodium nitrate ($NaNO_3$) at 105°C for 24 hours. Dissolve exactly 1.3707 g of the dried salt in reagent water, and dilute to 1 L with reagent water.

5.5.5 Nitrite stock solution (1.00 mL = 1.00 mg NO_2^-). Place approximately 2 g of sodium nitrate ($NaNO_2$) in a 125 mL beaker and dry to constant weight (about 24 hours) in a desiccator containing concentrated H_2SO_4. Dissolve 1.4998 g of the dried salt in reagent water, and dilute to 1 L with reagent water. Store in a sterilized glass bottle. Refrigerate and prepare monthly.

NOTE: Nitrite is easily oxidized, especially in the presence of moisture, and only fresh reagents are to be used.

NOTE: Prepare sterile bottles for storing nitrite solutions by heating for 1 hour at 170°C in an air oven.

5.5.6 Phosphate stock solution (1.00 mL = 1.00 mg PO_4^{3-}). Dissolve 1.4330 g of potassium dihydrogen phosphate (KH_2PO_4) in reagent water, and dilute to 1 L with reagent water. Dry sodium sulfate (Na_2SO_4) for 1 hour at 105°C and cool in a desiccator.

5.5.7 Sulfate stock solution (1.00 mL = 1.00 mg SO_4^{2-}). Dissolve 1.4790 g of the dried salt in reagent water, and dilute to 1 L with reagent water.

5.6 Anion working solutions. Prepare a blank and at least three different working solutions containing the following combinations of anions. The combination anion solutions must be prepared in Class A volumetric flasks. See Table 2.

5.6.1 Prepare a high-range standard solution by diluting the volumes of each anion specified in Table 2 together to 1 L with reagent water.

5.6.2 Prepare the intermediate-range standard solution by diluting 10.0 mL of the high-range standard solution (see Table 2) to 100 mL with reagent water.

5.6.3 Prepare the low-range standard solution by diluting 20.0 mL of the intermediate-range standard solution (see Table 2) to 100 mL with reagent water.

5.7 Stability of standards. Stock standards are stable for at least 1 month when stored at 4°C. Dilute working standards should be prepared weekly, except those that contain nitrite and phosphate, which should be prepared fresh daily.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Analyze the samples as soon as possible after collection. Preserve by refrigeration at 4°C.

7.0 PROCEDURE

7.1 Calibration

7.1.1 Establish ion chromatographic operating parameters equivalent to those indicated in Table 1.

7.1.2 For each analyte of interest, prepare calibration standards at a minimum of three concentration levels and a blank by adding accurately measured volumes of one or more stock standards to a Class A volumetric flask and diluting to volume with reagent water. If the working range exceeds the linear range of the system, a sufficient number of standards must be analyzed to allow an accurate calibration curve to be established. One of the standards should be representative of a concentration near, but above, the method detection limit if the system is operated on an applicable attenuator range. The other standards should correspond to the range of concentrations expected in the sample or should define the working range of the detector. Unless the attenuator range settings are proven to be linear, each setting must be calibrated individually.

7.1.3 Using injections of 0.1 to 1.0 mL (determined by injection loop volume) of each calibration standard, tabulate peak height or area responses against the concentration. The results are used to prepare a calibration curve for each analyte. During this procedure, retention times must be recorded. The retention time is inversely proportional to the concentration.

7.1.4 The working calibration curve must be verified on each working day, or whenever the anion eluent is changed, and for every batch of samples. If the response or retention time for any analyte varies from the expected values by more than $\pm$ 10%, the test must be repeated, using fresh calibration standards. If the results are still more than $\pm$ 10%, an entirely new calibration curve must be prepared for that analyte.

7.1.5 Nonlinear response can result when the separator column capacity is exceeded (overloading). Maximum column loading (all anions) should not exceed about 400 ppm.

7.2 Analyses

7.2.1 Sample preparation. When aqueous samples are injected, the water passes rapidly through the columns, and a negative "water dip" is observed that may interfere with the early-eluting fluoride and/or chloride ions. The water dip should not be observed in the combustate

samples; the collecting solution is a concentrated eluent solution that will "match" the eluent strength when diluted to 100-mL with reagent water according to the bomb combustion procedure. Any dilutions required in analyzing other water samples should be made with the eluent solution. The water dip, if present, may be removed by adding concentrated eluent to all samples and standards. When a manual system is used, it is necessary to micropipet concentrated buffer into each sample. The recommended procedures follow:

(1) Prepare a 100-mL stock of eluent 100 times normal concentration by dissolving 2.5202 g $NaHCO_3$ and 2.5438 g Na_2CO_3 in 100-mL reagent water. Protect the volumetric flask from air.

(2) Pipet 5 mL of each sample into a clean polystyrene micro-beaker. Micropipet 50 μL of the concentrated buffer into the beaker and stir well.

Dilute the samples with eluent, if necessary, to concentrations within the linear range of the calibration.

7.2.2 Sample analysis.

7.2.2.1 Start the flow of regenerant through the supressor column.

7.2.2.2 Set up the recorder range for maximum sensitivity and any additional ranges needed.

7.2.2.3 Begin to pump the eluent through the columns. After a stable baseline is obtained, inject a midrange standard. If the peak height deviates by more than 10% from that of the previous run, prepare fresh standards.

7.2.2.4 Begin to inject standards starting with the highest concentration standard and decreasing in concentration. The first sample should be a quality control reference sample to check the calibration.

7.2.2.5 Using the procedures described in Step 7.2.1, calculate the regression parameters for the initial standard curve. Compare these values with those obtained in the past. If they exceed the control limits, stop the analysis and look for the problem.

7.2.2.6 Inject a quality control reference sample. A spiked sample or a sample of known content must be analyzed with each batch of samples. Calculate the concentration from the calibration curve and compare the known value. If the control limits are exceeded, stop the analysis until the problem is found. Recalibration is necessary.

7.2.2.7 When an acceptable value has been obtained for the quality control sample, begin to inject the samples.

7.2.2.8 Load and inject a fixed amount of well-mixed sample. Flush injection loop thoroughly, using each new sample. Use the same size loop for standards and samples. Record the resulting peak size in area or peak height units. An automated constant volume injection system may also be used.

7.2.2.9 The width of the retention time window used to make identifications should be based on measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

7.2.2.10 If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.

7.2.2.11 If the resulting chromatogram fails to produce adequate resolution, or if identification of specific anions is questionable, spike the sample with an appropriate amount of standard and reanalyze.

NOTE: Retention time is inversely proportional to concentration. Nitrate and sulfate exhibit the greatest amount of change, although all anions are affected to some degree. In some cases, this peak migration can produce poor resolution or misidentification.

7.3 Calculation

7.3.1 Prepare separate calibration curves for each anion of interest by plotting peak size in area, or peak height units of standards against concentration values. Compute sample concentration by comparing sample peak response with the standard curve.

7.3.2 Enter the calibration standard concentrations and peak heights from the integrator or recorder into a calculator with linear least squares capabilities.

7.3.3 Calculate the following parameters: slope (s), intercept (I), and correlation coefficient (r). The slope and intercept define a relationship between the concentration and instrument response of the form:

$$y_i = s_i\, x_i + I \quad (1)$$

where:
y_i = predicted instrument response
s_i = response slope
x_i = concentration of standard i
I = intercept

Rearrangement of the above equation yields the concentration corresponding to an instrumental measurement:

$$x_j = (y_j - I)/s_j \quad (2)$$

where:

x_j = calculated concentration for a sample
y_j = actual instrument response for a sample
s_j and I are calculated slope and intercept from calibration above.

7.3.4 Enter the sample peak height into the calculator, and calculate the sample concentration in milligrams per liter.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference and inspection. Refer to Chapter One for additional quality control guidelines.

8.2 After every 10 injections, analyze a midrange calibration standard. If the instrument response has changed by more than 5%, recalibrate.

8.3 Analyze all samples in duplicate. Take the duplicate sample through the entire sample preparation and analytical process.

8.4 A matrix spiked sample should be run for each analytical batch or twenty samples, whatever is more frequent, to determine matrix effects.

9.0 METHOD PERFORMANCE

9.1 Single-operator accuracy and precision for reagent, drinking and surface water, and mixed domestic and industrial wastewater are listed in Table 3.

9.2 Combustate samples. These data are based on 41 data points obtained by six laboratories who each analyzed four used crankcase oils and three fuel oil blends with crankcase in duplicate. The oil samples were combusted using Method 5050. A data point represents one duplicate analysis of a sample. One data point was judged to be an outlier and was not included in the results.

9.2.1 Precision. The precision of the method as determined by the statistical examination of interlaboratory test results is as follows:

Repeatability - The difference between successive results obtained by the sample operator with the same apparatus under constant operating conditions on identical test material would exceed, in the long run, in the normal and correct operation of the test method, the following values only in 1 case in 20 (see Table 4):

$$Repeatability = 20.9\sqrt{x}*$$

*where x is the average of two results in µg/g.

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would exceed, in the long run, the following values only in 1 case in 20:

$$Reproducibility = 42.1\sqrt{x}*$$

*where x is the average value of two results in µg/g.

9.2.2 Bias. The bias of this method varies with concentration, as shown in Table 5:

Bias = Amount found - Amount expected

10.0 REFERENCES

1. Environmental Protection Agency. Test Method for the Determination of Inorganic Anions in Water by Ion Chromatography. EPA Method 300.0. EPA-600/4-84-017. 1984.

2. Annual Book of ASTM Standards, Volume 11.01 Water D4327, Standard Test Method for Anions in Water by Ion Chromatography, pp. 696-703. 1988.

3. Standard Methods for the Examination of Water and Wastewater, Method 429, "Determination of Anions by Ion Chromatography with Conductivity Measurement," 16th Edition of Standard Methods.

4. Dionex, IC 16 Operation and Maintenance Manual, PN 30579, Dionex Corp., Sunnyvale, CA 94086.

5. Method detection limit (MDL) as described in "Trace Analyses for Wastewater," J. Glaser, D. Foerst, G. McKee, S. Quave, W. Budde, Environmental Science and Technology, Vol. 15, Number 12, p. 1426, December 1981.

6. Gaskill, A.; Estes, E. D.; Hardison, D. L.; and Myers, L. E. Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels. Prepared for U.S. Environmental Protection Agency Office of Solid Waste. EPA Contract No. 68-01-7075, WA 80. July 1988.

TABLE 1.
CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS IN REAGENT WATER

Analyte	Retention[a] time min	Relative retention time	Method[b] detection limit, mg/L
Fluoride	1.2	1.0	0.005
Chlorine	3.4	2.8	0.015
Nitrite-N	4.5	3.8	0.004
O-Phosphate-P	9.0	7.5	0.061
Nitrate-N	11.3	9.4	0.013
Sulfate	21.4	17.8	0.206

Standard conditions:

Columns - As specified in 4.1.4
Detector - As specified in 4.1.4
Eluent - As specified in 5.3

Sample loop - 100 μL
Pump volume - 2.30 mL/min

[a]Concentrations of mixed standard (mg/L):

Fluoride 3.0
Chloride 4.0
Nitrite-N 10.0
O-Phosphate-P 9.0
Nitrate-N 30.0
Sulfate 50.0

[b]MDL calculated from data obtained using an attentuator setting of 1 umho full scale. Other settings would produce an MDL proportional to their value.

TABLE 2.
PREPARATION OF STANDARD SOLUTIONS FOR INSTRUMENT CALIBRATION

	High-range standard (see 5.6.1) Milliliters of each stock solution (1.00 mL = 1.00 mg) diluted to 1,000 mL	Anion concentration mg/L	Intermediate-range standard, mg/L (see 5.6.2)	Low-range standard, mg/L (see 5.6.3)
Fluoride (F^-)	10	10	1.0	0.2
Chloride (Cl^-)	10	10	1.0	0.2
Nitrite (NO_2^-)	20	20	2.0	0.4
Phosphate (PO_4^{3-})	50	50	5.0	1.0
Bromide (Br^-)	10	10	1.0	0.2
Nitrate (NO_3^-)	30	30	3.0	0.6
Sulfate (SO_4^{2-})	100	100	10.0	2.0

TABLE 3.
SINGLE-OPERATOR ACCURACY AND PRECISION

Analyte	Sample type	Spike mg/L	Number of replicates	Mean recovery, %	Standard deviation, mg/L
Chloride	RW	0.050	7	97.7	0.0047
	DW	10.0	7	98.2	0.289
	SW	1.0	7	105.0	0.139
	WW	7.5	7	82.7	0.445
Fluoride	RW	0.24	7	103.1	0.0009
	DW	9.3	7	87.7	0.075
	SW	0.50	7	74.0	0.0038
	WW	1.0	7	92.0	0.011
Nitrate-N	RW	0.10	7	100.9	0.0041
	DW	31.0	7	100.7	0.356
	SW	0.50	7	100.0	0.0058
	WW	4.0	7	94.3	0.058
Nitrite-N	RW	0.10	7	97.7	0.0014
	DW	19.6	7	103.3	0.150
	SW	0.51	7	88.2	0.0053
	WW	0.52	7	100.0	0.018
O-Phosphate-P	RW	0.50	7	100.4	0.019
	DE	45.7	7	102.5	0.386
	SW	0.51	7	94.1	0.020
	WW	4.0	7	97.3	0.04
Sulfate	RW	1.02	7	102.1	0.066
	DW	98.5	7	104.3	1.475
	SW	10.0	7	111.6	0.709
	WW	12.5	7	134.9	0.466

RW = Reagent water.
DW = Drinking water.
SW = Surface water.
WW = Wastewater.

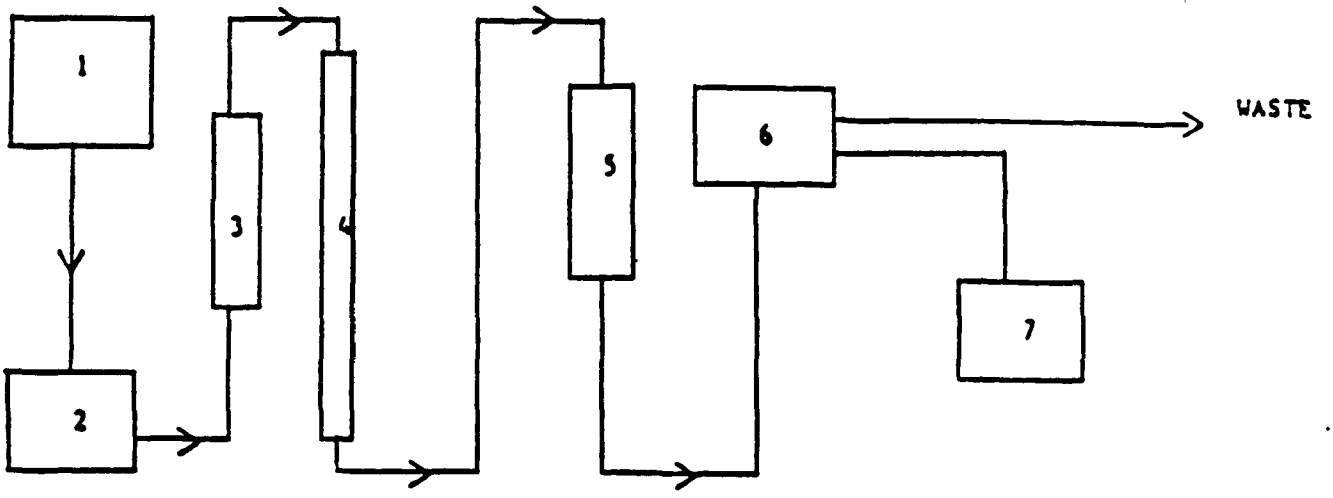
TABLE 4.
REPEATABILITY AND REPRODUCIBILITY FOR CHLORINE IN USED OILS BY BOMB OXIDATION AND ION CHROMATOGRAPHY

Average value, µg/g	Repeatability, µg/g	Reproducibility, µg/g
500	467	941
1,000	661	1,331
1,500	809	1,631
2,000	935	1,883
2,500	1,045	2,105
3,000	1,145	2,306

TABLE 5.
RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS BY BOMB OXIDATION AND ION CHROMATOGRAPHY

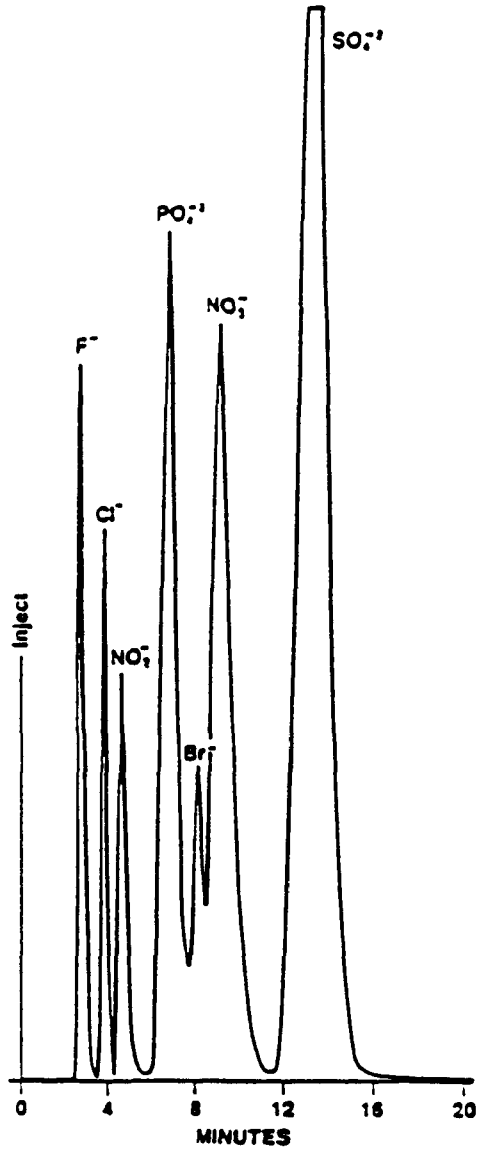
Amount Expected µg/g	Amount found µg/g	Bias, µg/g	Percent, bias
320	567	247	+77
480	773	293	+61
920	1,050	130	+14
1,498	1,694	196	+13
1,527	1,772	245	+16
3,029	3,026	-3	0
3,045	2,745	-300	-10

FIGURE 1
SCHEMATIC OF ION CHROMATOGRAPH

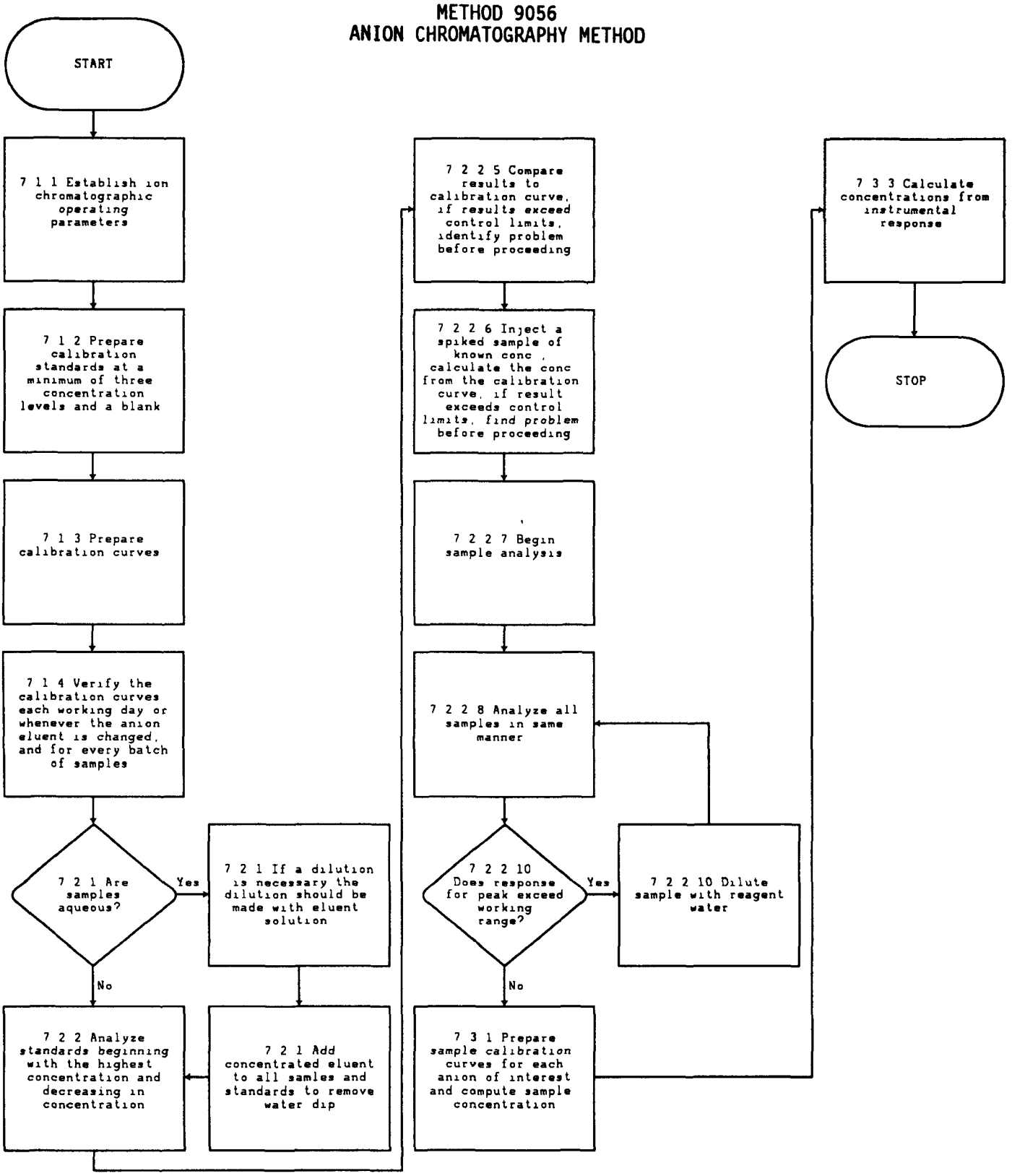


(1) Eluent reservoir
(2) Pump
(3) Precolumn
(4) Separator column
(5) Suppressor column
(6) Detector
(7) Recorder or integrator, or both

FIGURE 2
TYPICAL ANION PROFILE



METHOD 9056
ANION CHROMATOGRAPHY METHOD



METHOD 9071A

OIL AND GREASE EXTRACTION METHOD FOR SLUDGE AND SEDIMENT SAMPLES

1.0 SCOPE AND APPLICATION

1.1 Method 9071 is used to recover low levels of oil and grease (10 mg/L) by chemically drying a wet sludge sample and then extracting via the Soxhlet apparatus.

1.2 Method 9071 is used when relatively polar, heavy petroleum fractions are present, or when the levels of nonvolatile greases challenge the solubility limit of the solvent.

1.3 Specifically, Method 9071 is suitable for biological lipids, mineral hydrocarbons, and some industrial wastewaters.

1.4 Method 9071 is not recommended for measurement of low-boiling fractions that volatilize at temperatures below 70°C.

2.0 SUMMARY OF METHOD

2.1 A 20-g sample of wet sludge with a known dry-solids content is acidified to pH 2.0 with 0.3 mL concentrated HCl.

2.2 Magnesium sulfate monohydrate will combine with 75% of its own weight in water in forming $MgSO_4 \cdot 7H_2O$ and is used to dry the acidified sludge sample.

2.3 Anhydrous sodium sulfate is used to dry samples of soil and sediment.

2.4 After drying, the oil and grease are extracted with trichlorotrifluoroethane (Fluorocarbon-113)[1] using the Soxhlet apparatus.

3.0 INTERFERENCES

3.1 The method is entirely empirical, and duplicate results can be obtained only by strict adherence to all details of the processes.

3.2 The rate and time of extraction in the Soxhlet apparatus must be exactly as directed because of varying solubilities of the different greases.

3.3 The length of time required for drying and cooling extracted material must be constant.

3.4 A gradual increase in weight may result due to the absorption of oxygen; a gradual loss of weight may result due to volatilization.

---

[1]Replacement solvent will be specified in a forthcoming regulation.

4.0 APPARATUS AND MATERIALS

4.1 Extraction apparatus: Soxhlet.

4.2 Analytical balance.

4.3 Vacuum pump or some other vacuum source.

4.4 Extraction thimble: Filter paper.

4.5 Glass wool or small glass beads to fill thimble.

4.6 Grease-free cotton: Extract nonabsorbent cotton with solvent.

4.7 Beaker: 150-mL.

4.8 pH Indicator to determine acidity.

4.9 Porcelain mortar.

4.10 Extraction flask: 150-mL.

4.11 Distilling apparatus: Waterbath at 70°C.

4.12 Desiccator.

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 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Concentrated hydrochloric acid (HCl).

5.4 Magnesium sulfate monohydrate: Prepare $MgSO_4 \cdot H_2O$ by spreading a thin layer in a dish and drying in an oven at 150°C overnight.

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 Trichlorotrifluoroethane (1,1,2-trichloro-1,2,2-trifluoroethane): Boiling point, 47°C. The solvent should leave no measurable residue on evaporation; distill if necessary.[2]

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Transfers of the solvent trichlorotrifluoroethane should not involve any plastic tubing in the assembly.

6.2 Sample transfer implements: Implements are required to transfer portions of solid, semisolid, and liquid wastes from sample containers to laboratory glassware. Liquids may be transferred using a glass hypodermic syringe. Solids may be transferred using a spatula, spoon, or coring device.

6.3 Any turbidity or suspended solids in the extraction flask should be removed by filtering through grease-free cotton or glass wool.

7.0 PROCEDURE

7.1 Determination of Sample Dry Weight Fraction

7.1.1 Weigh 5-10 g of the sample into a tared crucible. Determine the dry weight fraction of the sample by drying overnight at 105°C.

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

Allow to cool in a desiccator before weighing:

$$\text{dry weight fraction} = \frac{\text{g of dry sample}}{\text{g of sample}}$$

7.2 Sample Handling

7.2.1 Sludge Samples

7.2.1.1 Weigh out 20 $\pm$ 0.5 g of wet sludge with a known dry-weight fraction (Section 7.1). Place in a 150-mL beaker.

7.2.1.2 Acidify to a pH of 2 with approximately 0.3 mL concentrated HCl.

7.2.1.3 Add 25 g prepared $Mg_2SO4 \cdot H_2O$ and stir to a smooth paste.

7.2.1.4 Spread paste on sides of beaker to facilitate evaporation. Let stand about 15-30 min or until substance is solidified.

---

[2]Replacement solvent will be specified in a forthcoming regulation.

7.2.1.5 Remove solids and grind to fine powder in a mortar.

7.2.1.6 Add the powder to the paper extraction thimble.

7.2.1.7 Wipe beaker and mortar with pieces of filter paper moistened with solvent and add to thimble.

7.2.1.8 Fill thimble with glass wool (or glass beads).

7.2.2 Sediment/Soil Samples

7.2.2.1 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.

7.2.2.2 Blend 10 g of the solid sample of known dry weight fraction 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.

7.3 Extraction

7.3.1 Extract in Soxhlet apparatus using trichlorotrifluorocarbon at a rate of 20 cycles/hr for 4 hr.

7.3.2 Using grease-free cotton, filter the extract into a pre-weighed 250-mL boiling flask. Use gloves to avoid adding fingerprints to the flask.

7.3.3 Rinse flask and cotton with solvent.

7.3.4 Connect the boiling flask to the distilling head and evaporate the solvent by immersing the lower half of the flask in water at 70°C. Collect the solvent for reuse. A solvent blank should accompany each analytical batch of samples.

7.3.5 When the temperature in the distilling head reaches 50°C or the flask appears dry, remove the distilling head. To remove solvent vapor, sweep out the flask for 15 sec with air by inserting a glass tube that is connected to a vacuum source. Immediately remove the flask from the heat source and wipe the outside to remove excess moisture and fingerprints.

7.3.6 Cool the boiling flask in a desiccator for 30 min and weigh.

7.3.7 Calculate oil and grease as a percentage of the total dry solids. Generally:

$$\% \text{ of oil and grease} = \frac{\text{gain in weight of flask (g)} \times 100}{\text{wt. of wet solids (g)} \times \text{dry weight fraction}}$$

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference and inspection. Refer to Chapter One for additional quality control guidelines.

8.2 Employ a minimum of one blank per analytical batch or twenty samples, whichever is more frequent, to determine if contamination has occurred.

8.3 Run one matrix duplicate and matrix spike sample every twenty samples or analytical batch, whichever is more frequent. Matrix duplicates and spikes are brought through the whole sample preparation and analytical process.

8.3 The use of corn oil is recommended as a reference sample solution.

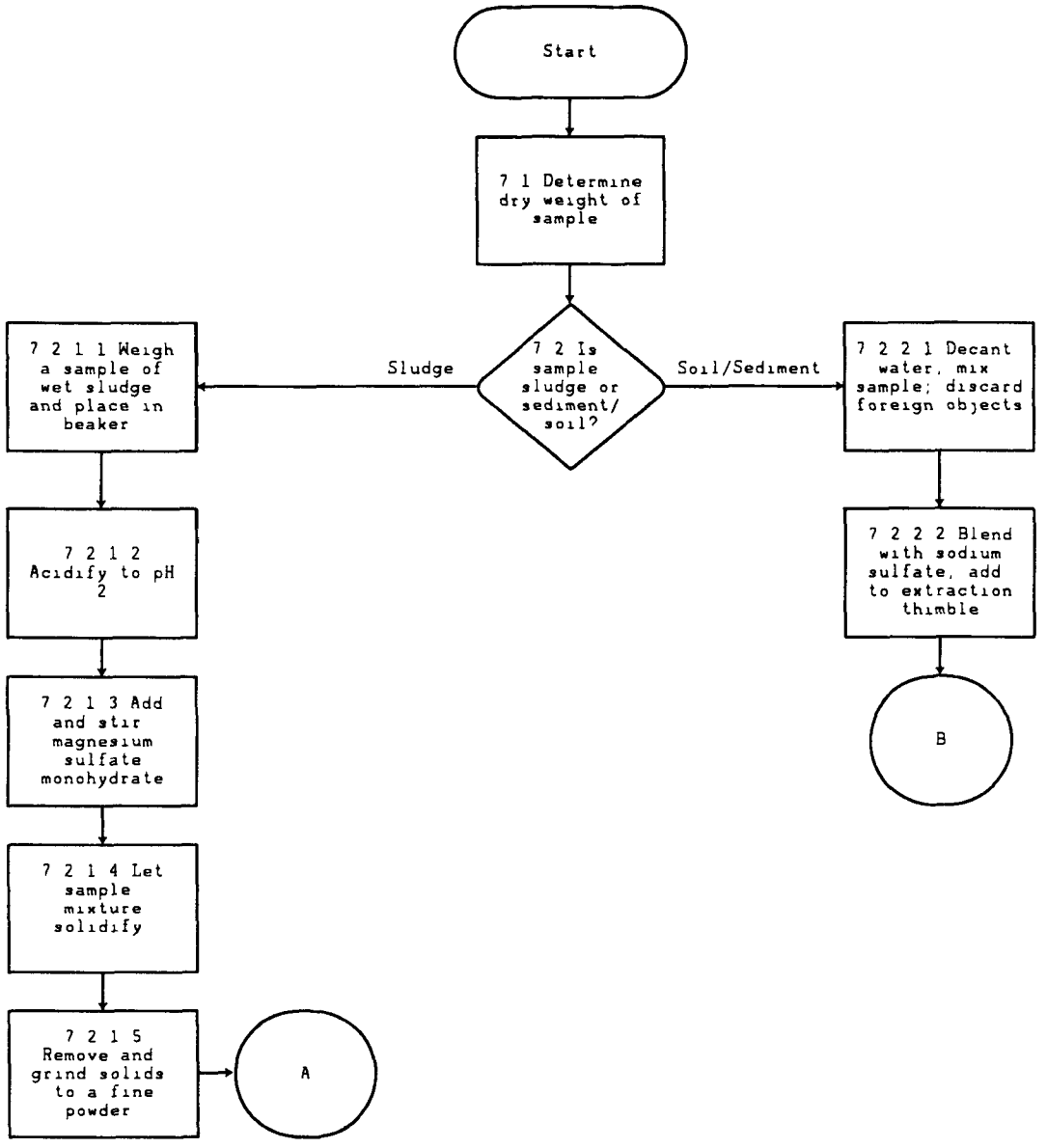
9.0 METHOD PERFORMANCE

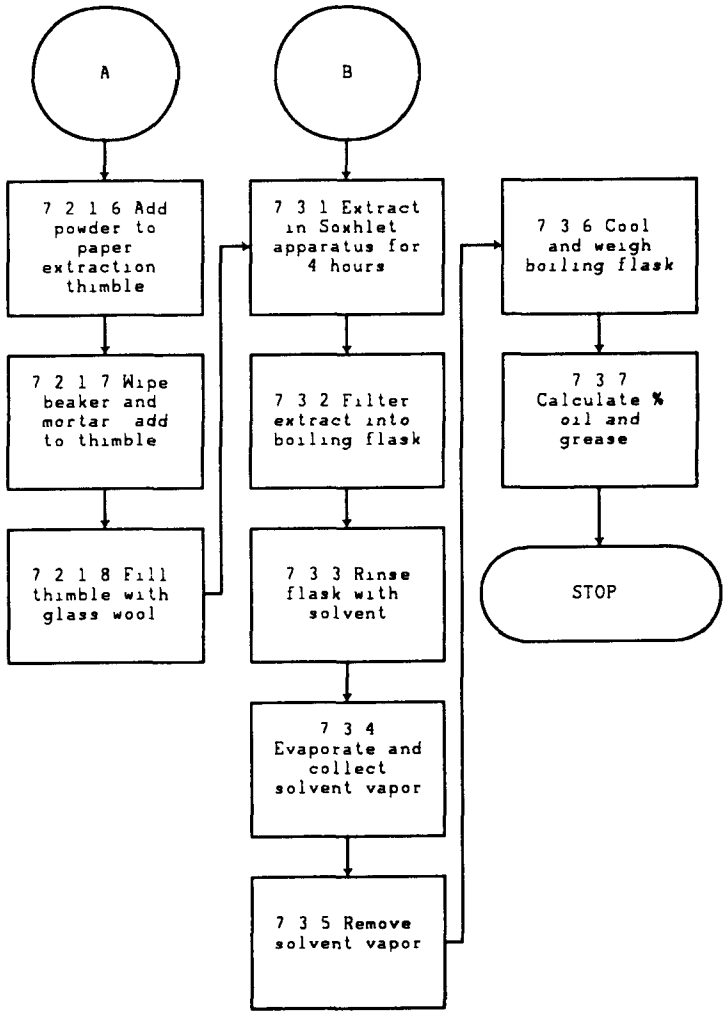
9.1 The two oil and grease methods (Methods 9070 and 9071) in this manual were tested on sewage by a single laboratory. When 1-liter portions of the sewage were dosed with 14.0 mg of a mixture of No. 2 fuel oil and Wesson oil, the recovery was 93%, with a standard deviation of $\pm$ 0.9 mg/L.

10.0 REFERENCES

1. Blum, K.A. and M.J. Taras, "Determination of Emulsifying Oil in Industrial Wastewater," JWPCF Research Suppl., 40, R404 (1968).

2. Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 515, Method 502A (1975).


Start
7 1 Determine dry weight of sample
7 2 Is sample sludge or sediment/ soil?
Sludge
Soil/Sediment
7 2 1 1 Weigh a sample of wet sludge and place in beaker
7 2 1 2 Acidify to pH 2
7 2 1 3 Add and stir magnesium sulfate monohydrate
7 2 1 4 Let sample mixture solidify
7 2 1 5 Remove and grind solids to a fine powder
A
7 2 2 1 Decant water, mix sample; discard foreign objects
7 2 2 2 Blend with sodium sulfate, add to extraction thimble
B


A
B
7 2 1 6 Add powder to paper extraction thimble
7 2 1 7 Wipe beaker and mortar add to thimble
7 2 1 8 Fill thimble with glass wool
7 3 1 Extract in Soxhlet apparatus for 4 hours
7 3 2 Filter extract into boiling flask
7 3 3 Rinse flask with solvent
7 3 4 Evaporate and collect solvent vapor
7 3 5 Remove solvent vapor
7 3 6 Cool and weigh boiling flask
7 3 7 Calculate % oil and grease
STOP

METHOD 9075

TEST METHOD FOR TOTAL CHLORINE IN NEW AND USED PETROLEUM PRODUCTS BY X-RAY FLUORESCENCE SPECTROMETRY (XRF)

1.0 SCOPE AND APPLICATION

1.1 This test method covers the determination of total chlorine in new and used oils, fuels, and related materials, including crankcase, hydraulic, diesel, lubricating and fuel oils, and kerosene. The chlorine content of petroleum products is often required prior to their use as a fuel.

1.2 The applicable range of this method is from 200 μg/g to percent levels.

2.0 SUMMARY OF METHOD

2.1 A well-mixed sample, contained in a disposable plastic sample cup, is loaded into an X-ray fluorescence (XRF) spectrometer. The intensities of the chlorine K alpha and sulfur K alpha lines are measured, as are the intensities of appropriate background lines. After background correction, the net intensities are used with a calibration equation to determine the chlorine content. The sulfur intensity is used to correct for absorption by sulfur.

3.0 INTERFERENCES

3.1 Possible interferents include metals, water, and sediment in the oil. Results of spike recovery measurements and measurements on diluted samples can be used to check for interferences.

Each sample, or one sample from a group of closely related samples, should be spiked to confirm that matrix effects are not significant. Dilution of samples that may contain water or sediment can product incorrect results, so dilution should be undertaken with caution and checked by spiking. Sulfur interferes with the chlorine determination, but a correction is made.

Spike recovery measurements of used crankcase oil showed that diluting samples five to one allowed accurate measurements on approximately 80% of the samples. The other 20% of the samples were not accurately analyzed by XRF.

3.2 Water in samples absorbs X-rays due to chlorine. For this interference, using as short an X-ray counting time as possible is beneficial. This appears to be related to stratification of samples into aqueous and nonaqueous layers while in the analyzer.

Although a correction for water may be possible, none is currently available. In general, the presence of any free water as a separate phase or a water content greater than 25% will reduce the chlorine signal by 50 to 90%.

4.0 APPARATUS AND MATERIALS

4.1 XRF spectrometer, either energy dispersive or wavelength dispersive. The instrument must be able to accurately resolve and measure the intensity of the chlorine and sulfur lines with acceptable precision.

4.2 Disposable sample cups with suitable plastic film such as Mylar®.

5.0 REAGENTS

5.1 Purity of reagents. 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 Mineral oil, mineral spirits or paraffin oil, sulfur and chlorine free, for preparing standards and dilutions.

5.3 1-Chlorodecane (Aldrich Chemical Co.), 20.1% chlorine, or similar chlorine compound.

5.4 Di-n-butyl sulfide (Aldrich Chemical Co.), 21.9% sulfur by weight.

5.5 Quality control standards such as the standard reference materials NBS 1620, 1621, 1622, 1623, and 1624, sulfur in oil standards, and NBS 1818, chlorine in oil standards.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine.

6.2 The collected sample should be kept headspace free prior to preparation and analysis to minimize volatilization losses of organic halogens. Because waste oils may contain toxic and/or carcinogenic substances, appropriate field and laboratory safety procedures should be followed.

6.3 Laboratory sampling of the sample should be performed on a well-mixed sample of oil. The mixing should be kept to a minimum and carried out as nearly headspace free as possible to minimize volatilization losses of organic halogens.

6.4 Free water, as a separate phase, should be removed and cannot be analyzed by this method.

7.0 PROCEDURE

7.1 Calibration and standardization.

7.1.1 Prepare primary calibration standards by diluting the chlorodecane and n-butyl sulfide with mineral spirits or similar material.

7.1.2 Prepare working calibration standards that contain sulfur, chlorine, or both according to the following table:

Cl: 500, 1,000, 2,000, 4,000, and 6,000 μg/g
S: 0.5, 1.0, and 1.5% sulfur

1.	0.5% S, 1,000 μg/g Cl	5.	1.0% S, 6,000 μg/g Cl
2.	0.5% S, 4,000 μg/g Cl	6.	1.5% S, 1,000 μg/g Cl
3.	1.0% S, 500 μg/g Cl	7.	1.5% S, 4,000 μg/g Cl
4.	1.0% S, 2,000 μg/g Cl	8.	1.5% S, 6,000 μg/g Cl

Once the correction factor for sulfur interference with chlorine is determined, fewer standards may be required.

7.1.3 Measure the intensity of the chlorine K alpha line and the sulfur K alpha line as well as the intensity of a suitably chosen background. Based on counting statistics, the relative standard deviation of each peak measurement should be 1% or less.

7.1.4 Determine the net chlorine and sulfur intensities by correcting each peak for background. Do this for all of the calibration standards as well as for a paraffin blank.

7.1.5 Obtain a linear calibration curve for sulfur by performing a least squares fit of the net sulfur intensity to the standard concentrations, including the blank. The chlorine content of a standard should have little effect on the net sulfur intensity.

7.1.6 The calibration equation for chlorine must include a correction term for the sulfur concentration. A suitable equation follows:

$$Cl = (mI + b)\ (1 + k^*S) \qquad (1)$$

where:

I = net chlorine intensity
m, b, k* = adjustable parameters.

Using a least squares procedure, the above equation or a suitable substitute should be fitted to the data. Many XRF instruments are equipped with suitable computer programs to perform this fit. In any case, the resulting equation should be shown to be accurate by analysis of suitable standard materials.

7.2 Analysis.

7.2.1 Prepare a calibration curve as described in Step 7.1. By periodically measuring a very stable sample containing both sulfur and chlorine, it may be possible to use the calibration equations for more than 1 day. During each day, the suitability of the calibration curve should be checked by analyzing standards.

7.2.2 Determine the net chlorine and sulfur intensities for a sample in the same manner as was done for the standards.

7.2.3 Determine the chlorine and sulfur concentrations of the samples from the calibration equations. If the sample concentration for either element is beyond the range of the standards, the sample should be diluted with mineral oil and reanalyzed.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 One sample in ten should be analyzed in triplicate and the relative standard deviation reported. For each triplicate, a separate preparation should be made, starting from the original sample.

8.3 Each sample, or one sample in ten from a group of similar samples, should be spiked with the elements of interest by adding a known amount of chlorine or sulfur to the sample. The spiked amount should be between 50% and 200% of the sample concentration, but the minimum addition should be at least five times the limit of detection. The percent recovery should be reported and should be between 80% and 120%. Any sample suspected of containing >25% water should also be spiked with organic chlorine.

8.4 Quality control standard check samples should be analyzed every day and should agree within 10% of the expected value of the standard.

9.0 METHOD PERFORMANCE

9.1 These data are based on 47 data points obtained by seven laboratories who each analyzed four used crankcase oils and three fuel oil blends with crankcase in duplicate. A data point represents one duplicate analysis of a sample. Two data points were determined to be outliers and are not included in these results.

9.2 Precision. The precision of the method as determined by the statistical examination of interlaboratory test results is as follows:

Repeatability - The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would exceed, in the long run, in the normal and correct operation of the test method, the following values only in 1 case in 20 (see Table 1):

$$Repeatability = 5.72\sqrt{x}*$$

*where x is the average of two results in μg/g.

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories

on identical test material would exceed, in the long run, the following values only in 1 case in 20:

$$Reproducibility = 9.83\sqrt{x}*$$

*where x is the average value of two results in μg/g.

9.3 Bias. The bias of this test method varies with concentration, as shown in Table 2:

Bias = Amount found - Amount expected.

10.0 REFERENCE

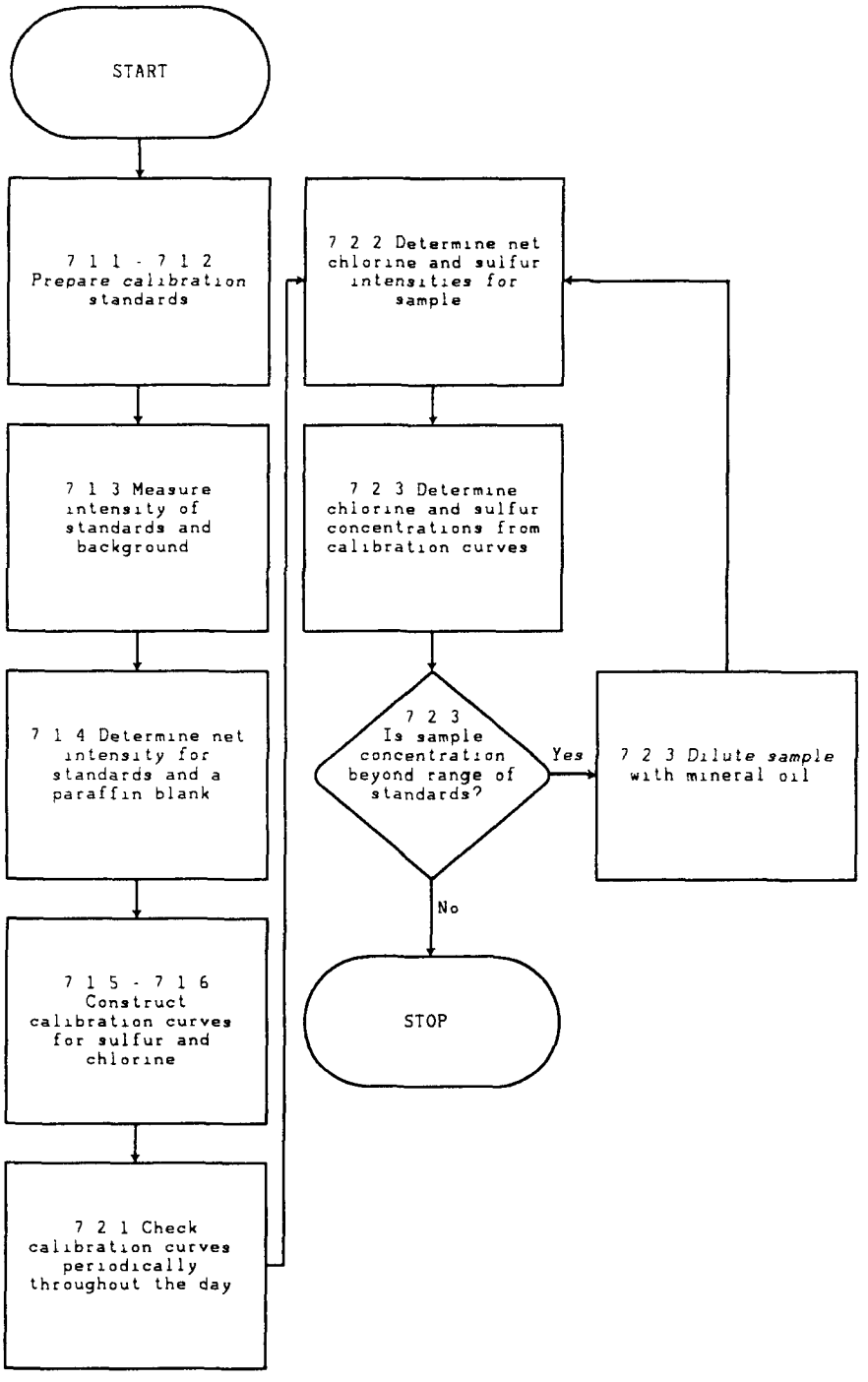
1. Gaskill, A.; Estes, E.D.; Hardison, D.L.; and Myers, L.E. Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels. Prepared for U.S. Environmental Protection Agency, Office of Solid Waste. EPA Contract No. 68-01-7075, WA 80. July 1988.

TABLE 1. REPEATABILITY AND REPRODUCIBILITY FOR CHLORINE IN USED OILS BY X-RAY FLUORESCENCE SPECTROMETRY

Average value, µg/g	Repeatability, µg/g	Reproducibility, µg/g
500	128	220
1,000	181	311
1,500	222	381
2,000	256	440
2,500	286	492
3,000	313	538

TABLE 2. RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS BY X-RAY FLUORESCENCE SPECTROMETRY

Amount expected, µg/g	Amount found, µg/g	Bias, µg/g	Percent bias
320	278	-42	-13
480	461	-19	-4
920	879	-41	-4
1,498	1,414	-84	-6
1,527	1,299	-228	-15
3,029	2,806	-223	-7
3,045	2,811	-234	-8


START
7 1 1 - 7 1 2 Prepare calibration standards
7 1 3 Measure intensity of standards and background
7 1 4 Determine net intensity for standards and a paraffin blank
7 1 5 - 7 1 6 Construct calibration curves for sulfur and chlorine
7 2 1 Check calibration curves periodically throughout the day
7 2 2 Determine net chlorine and sulfur intensities for sample
7 2 3 Determine chlorine and sulfur concentrations from calibration curves
7 2 3 Is sample concentration beyond range of standards?
Yes
7 2 3 Dilute sample with mineral oil
No
STOP

TEST METHOD FOR TOTAL CHLORINE IN NEW AND USED PETROLEUM PRODUCTS BY OXIDATIVE COMBUSTION AND MICROCOULOMETRY

1.0 SCOPE AND APPLICATION

1.1 This test method covers the determination of total chlorine in new and used oils, fuels and related materials, including crankcase, hydraulic, diesel, lubricating and fuel oils, and kerosene by oxidative combustion and microcoulometry. The chlorine content of petroleum products is often required prior to their use as a fuel.

1.2 The applicable range of this method is from 10 to 10,000 μg/g chlorine.

2.0 SUMMARY OF METHOD

2.1 The sample is placed in a quartz boat at the inlet of a high-temperature quartz combustion tube. An inert carrier gas such as argon, carbon dioxide, or nitrogen sweeps across the inlet while oxygen flows into the center of the combustion tube. The boat and sample are advanced into a vaporization zone of approximately 300°C to volatilize the light ends. Then the boat is advanced to the center of the combustion tube, which is at 1,000°C. The oxygen is diverted to pass directly over the sample to oxidize any remaining refractory material. All during this complete combustion cycle, the chlorine is converted to chloride and oxychlorides, which then flow into an attached titration cell where they quantitatively react with silver ions. The silver ions thus consumed are coulometrically replaced. The total current required to replace the silver ions is a measure of the chlorine present in the injected samples.

2.2 The reaction occurring in the titration cell as chloride enters is:

$$Cl^- + Ag^+ \text{-------} > AgCl \qquad (1)$$

The silver ion consumed in the above reaction is generated coulometrically thus:

$$Ag^\circ \text{-------} > Ag^+ + e^- \qquad (2)$$

2.3 These microequivalents of silver are equal to the number of microequivalents of titratable sample ion entering the titration cell.

3.0 INTERFERENCES

3.1 Other titratable halides will also give a positive response. These titratable halides include HBr and HI (HOBr + HOI do not precipitate silver). Because these oxyhalides do not react in the titration cell, approximately 50% microequivalent response is detected from bromine and iodine.

3.2 Fluorine as fluoride does not precipitate silver, so it is not an interferant nor is it detected.

3.3 This test method is applicable in the presence of total sulfur concentrations of up to 10,000 times the chlorine level.

4.0 APPARATUS AND MATERIALS[1]

4.1 Combustion furnace. The sample should be oxidized in an electric furnace capable of maintaining a temperature of 1,000°C to oxidize the organic matrix.

4.2 Combustion tube, fabricated from quartz and constructed so that a sample, which is vaporized completely in the inlet section, is swept into the oxidation zone by an inert gas where it mixes with oxygen and is burned. The inlet end of the tube connects to a boat insertion device where the sample can be placed on a quartz boat by syringe, micropipet, or by being weighed externally. Two gas ports are provided, one for an inert gas to flow across the boat and one for oxygen to enter the combustion tube.

4.3 Microcoulometer, Stroehlein Coulomat 702 CL or equivalent, having variable gain and bias control, and capable of measuring the potential of the sensing-reference electrode pair, and comparing this potential with a bias potential, and applying the amplified difference to the working-auxiliary electrode pair so as to generate a titrant. The microcoulometer output signal shall be proportional to the generating current. The microcoulometer may have a digital meter and circuitry to convert this output signal directly to nanograms or micrograms of chlorine or micrograms per gram chlorine.

4.4 Titration cell. Two different configurations have been applied to coulometrically titrate chlorine for this method.

4.4.1 Type I uses a sensor-reference pair of electrodes to detect changes in silver ion concentration and a generator anode-cathode pair of electrodes to maintain constant silver ion concentration and an inlet for a gaseous sample from the pyrolysis tube. The sensor, reference, and anode electrodes are silver electrodes. The cathode electrode is a platinum wire. The reference electrode resides in a saturated silver acetate half-cell. The electrolyte contains 70% acetic acid in water.

4.4.2 Type II uses a sensor-reference pair of electrodes to detect changes in silver ion concentration and a generator anode-cathode pair of electrodes to maintain constant silver ion concentration, an inlet for a gaseous sample that passes through a 95% sulfuric acid dehydrating tube from the pyrolysis tube, and a sealed two-piece titration cell with an exhaust tube to vent fumes to an external exhaust. All electrodes can be removed and replaced independently without reconstructing the cell assembly. The anode electrode is constructed of silver. The cathode electrode is constructed of platinum. The anode is separated from the cathode by a 10% KNO_3 agar bridge, and continuity is maintained through an aqueous 10% KNO_3 salt bridge. The sensor electrode is constructed of

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[1]Three commercial analyzers fulfill the requirements for apparatus Steps 4.1 through 4.4 and have been found satisfactory for this method. They are the two Dohrmann Models DX-20B and MCTS-20 and Mitsubishi Model TSX-10 available from Cosa Instrument.

silver. The reference electrode is a silver/silver chloride ground glass sleeve, double-junction electrode with aqueous 1M KNO_3 in the outer chamber and aqueous 1M KCl in the inner chamber.

4.5 Sampling syringe, a microliter syringe of 10 μL capacity capable of accurately delivering 2 to 5 μL of a viscous sample into the sample boat.

4.6 Micropipet, a positive displacement micropipet capable of accurately delivering 2 to 5 μL of a viscous sample into the sample boat.

4.7 Analytical balance. When used to weigh a sample of 2 to 5 mg onto the boat, the balance shall be accurate to $\pm$ 0.01 mg. When used to determine the density of the sample, typically 8 g per 10 mL, the balance shall be accurate to $\pm$ 0.1 g.

4.8 Class A volumetric flasks: 100 mL.

5.0 REAGENTS

5.1 Purity of Reagents. 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 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Acetic acid, CH_3CO_2H. Glacial.

5.4 Isooctane, $(CH_3)_2CHCH_2C(CH_3)_3$ (2,2,4-Trimethylpentane).

5.5 Chlorobenzene, C_6H_5Cl.

5.6 Chlorine, standard stock solution - 10,000 ng Cl/μL, weigh accurately 3.174 g of chlorobenzene into 100-mL Class A volumetric flask. Dilute to the mark with isooctane.

5.7 Chlorine, standard solution. 1,000 ng Cl/μL, pipet 10.0 mL of chlorine stock solution (Step 5.6) into a 100-mL volumetric flask and dilute to volume with isooctane.

5.8 Argon, helium, nitrogen, or carbon dioxide, high-purity grade (HP) used as the carrier gas. High-purity grade gas has a minimum purity of 99.995%.

5.9 Oxygen, high-purity grade (HP), used as the reactant gas.

5.10 Gas regulators. Two-stage regulator must be used on the reactant and carrier gas.

5.11 Cell Type 1.

5.11.1 Cell electrolyte solution. 70% acetic acid: combine 300 mL reagent water with 700 mL acetic acid (Step 5.3) and mix well.

5.11.2 Silver acetate, CH_3CO_2Ag. Powder purified for saturated reference electrode.

5.12 Cell Type 2.

5.12.1 Sodium acetate, CH_3CO_2Na.

5.12.2 Potassium nitrate, KNO_3.

5.12.3 Potassium chloride, KCl.

5.12.4 Sulfuric acid (concentrated), H_2SO_4.

5.12.5 Agar, (jelly strength 450 to 600 g/cm^2).

5.12.6 Cell electrolyte solution - 85% acetic acid: combine 150 mL reagent water with 1.35 g sodium acetate (Step 5.12.1) and mix well; add 850 mL acetic acid (Step 5.3) and mix well.

5.12.7 Dehydrating solution - Combine 95 mL sulfuric acid (Step 5.12.4) with 5 mL reagent water and mix well.

CAUTION: This is an exothermic reaction and may proceed with bumping unless controlled by the addition of sulfuric acid. Slowly add sulfuric acid to reagent water. Do not add water to sulfuric acid.

5.12.8 Potassium nitrate (10%), KNO_3. Add 10 g potassium nitrate (Step 5.12.2) to 100 mL reagent water and mix well.

5.12.9 Potassium nitrate (1M), KNO_3. Add 10.11 g potassium nitrate (Step 5.12.2) to 100 mL reagent water and mix well.

5.12.10 Potassium chloride (1M), KCl. Add 7.46 g potassium chloride (Step 5.12.3) to 100 mL reagent water and mix well.

5.12.11 Agar bridge solution - Mix 0.7 g agar (Step 5.12.5), 2.5g potassium nitrate (Step 5.12.2), and 25 mL reagent water and heat to boiling.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine.

6.2 Because the collected sample will be analyzed for total halogens, it should be kept headspace free and refrigerated prior to preparation and analysis to minimize volatilization losses of organic halogens. Because waste oils may contain toxic and/or carcinogenic substances, appropriate field and laboratory safety procedures should be followed.

6.3 Laboratory subsampling of the sample should be performed on a well-mixed sample of oil.

7.0 PROCEDURES

7.1 Preparation of apparatus.

7.1.1 Set up the analyzer as per the equipment manufacturer's instructions.

7.1.2 Typical operating conditions: Type 1.

Furnace temperature	1,000°C
Carrier gas flow	43 cm^3/min
Oxygen gas flow	160 cm^3/min
Coulometer	
Bias	250 mV
Gain	25%

7.1.3 Typical operating conditions: Type 2.

Furnace temperature	H-1 850°C
	H-2 1,000°C
Carrier gas flow	250 cm^3/min
Oxygen gas flow	250 cm^3/min
Coulometer	
End point potential (bias)	300 mV
Gain G-1	1.5 coulombs/Δ mV
G-2	3.0 coulombs/Δ mV
G-3	3.0 coulombs/Δ mV
ES-1 (range 1)	25 mV
ES-2 (range 2)	30 mV

NOTE: Other conditions may be appropriate. Refer to the instrumentation manual.

7.2 Sample introduction.

7.2.1 Carefully fill a 10-μL syringe with 2 to 5 μL of sample depending on the expected concentration of total chlorine. Inject the sample through the septum onto the cool boat, being certain to touch the boat with the needle tip to displace the last droplet.

7.2.2 For viscous samples that cannot be drawn into the syringe barrel, a positive displacement micropipet may be used. Here, the 2-5 μL of sample is placed on the boat from the micropipet through the opened hatch port. The same technique as with the syringe is used to displace the last droplet into the boat. A tuft of quartz wool in the boat can aid in completely transferring the sample from the micropipet into the boat.

NOTE: Dilution of samples to reduce viscosity is not recommended due to uncertainty about the solubility of the sample and its chlorinated constituents. If a positive displacement micropipet is not available, dilution may be attempted to enable injection of viscous samples.

7.2.3 Alternatively, the sample boat may be removed from the instrument and tared on an analytical balance. A sample of 2-5 mg is accurately weighed directly into the boat and the boat and sample returned to the inlet of the instrument.

$$2\text{-}5\ \mu L = 2\text{-}5\ mg$$

NOTE: Sample dilution may be required to ensure that the titration system is not overloaded with chlorine. This will be somewhat system dependent and should be determined before analysis is attempted. For example, the MCTS-20 can titrate up to 10,000 ng chlorine in a single injection or weighed sample, while the DX-20B has an upper limit of 50,000 ng chlorine. For 2 to 5 μL sample sizes, these correspond to nominal concentrations in the sample of 800 to 2,000 μg/g and 4,000 to 10,000 μg/g, respectively. If the system is overloaded, especially with inorganic chloride, residual chloride may persist in the system and affect results of subsequent samples. In general, the analyst should ensure that the baseline returns to normal before running the next sample. To speed baseline recovery, the electrolyte can be drained from the cell and replaced with fresh electrolyte.

NOTE: To determine total chlorine, do not extract the sample either with reagent water or with an organic solvent such as toluene or isooctane. This may lower the inorganic chlorine content as well as result in losses of volatile solvents.

7.2.4 Follow the manufacturer's recommended procedure for moving the sample and boat into the combustion tube.

7.3 Calibration and standardization.

7.3.1 System recovery - The fraction of chlorine in a standard that is titrated should be verified every 4 hours by analyzing the standard solution (Step 5.7). System recovery is typically 85% or better. The pyrolysis tube should be replaced whenever system recovery drops below 75%.

NOTE: The 1,000 μg/g system recovery sample is suitable for all systems except the MCTS-20 for which a 100 μg/g sample should be used.

7.3.2 Repeat the measurement of this standard at least three times.

7.3.3 System blank - The blank should be checked daily with isooctane. It is typically less than 1 μg/g chlorine. The system blank should be subtracted from both samples and standards.

7.4 Calculations.

7.4.1 For systems that read directly in mass units of chloride, the following equations apply:

$$\text{Chlorine, } \mu g/g \text{ (wt/wt)} = \frac{\text{Display}_S}{(V_S)\ (D_S)\ (RF)} - B \qquad (3)$$

or

$$\text{Chlorine, } \mu g/g \text{ (wt/wt)} = \frac{\text{Display}_S}{(M)\ (RF)} - B \qquad (4)$$

where:

Display = Integrated value in nanograms (when the integrated values are displayed in micrograms, they must be multiplied by 10^3)
Display_B = blank measurement Display_S = sample measurement

V = Volume of sample injected in microliters
V_B = blank volume V_S = sample volume

D = Density of sample, grams per cubic centimeters
D_B = blank density D_S = sample density

RF = Recovery factor = ratio of chlorine determined in standard minus the system blank, divided by known standard content = $\frac{\text{Found - Blank}}{\text{Known}}$

B = System blank, $\mu g/g$ chlorine = $\frac{\text{Display}_B}{(V_B)\ (D_B)}$

M = Mass of sample, mg

7.4.2 Other systems internally compensate for recovery factor, volume, density, or mass and blank, and thus read out directly in parts per million chlorine units. Refer to instrumentation manual.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 Each sample should be analyzed twice. If the results do not agree to within 10%, expressed as the relative percent difference of the results, repeat the analysis.

8.3 Analyze matrix spike and matrix spike duplicates - spike samples with a chlorinated organic at a level of total chlorine commensurate with the levels being determined. The spike recovery should be reported and should be between 80 and 120% of the expected value. Any sample suspected of containing >25% water should also be spiked with organic chlorine.

9.0 METHOD PERFORMANCE

9.1 These data are based on 66 data points obtained by 10 laboratories who each analyzed four used crankcase oils and three fuel oil blends with crankcase in duplicate. A data point represents one duplicate analysis of a sample. One laboratory and four additional data points were determined to be outliers and are not included in these results.

9.2 Precision. The precision of the method as determined by the statistical examination of interlaboratory test results is as follows:

Repeatability - The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would exceed, in the long run, in the normal and correct operation of the test method the following values only in 1 case in 20 (see Table 1):

$$Repeatability = 0.137\ x*$$

*where x is the average of two results in µg/g.

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would exceed, in the long run, the following values only in 1 case in 20:

$$Reproducibility = 0.455\ x*$$

*where x is the average value of two results in µg/g.

9.3 Bias. The bias of this test method varies with concentration, as shown in Table 2:

Bias = Amount found - Amount expected

10.0 REFERENCE

1. Gaskill, A.; Estes, E.D.; Hardison, D.L.; and Myers, L.E. "Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels." Prepared for U.S. Environmental Protection Agency, Office of Solid Waste. EPA Contract No. 68-01-7075, WA80. July 1988.

2. Rohrobough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

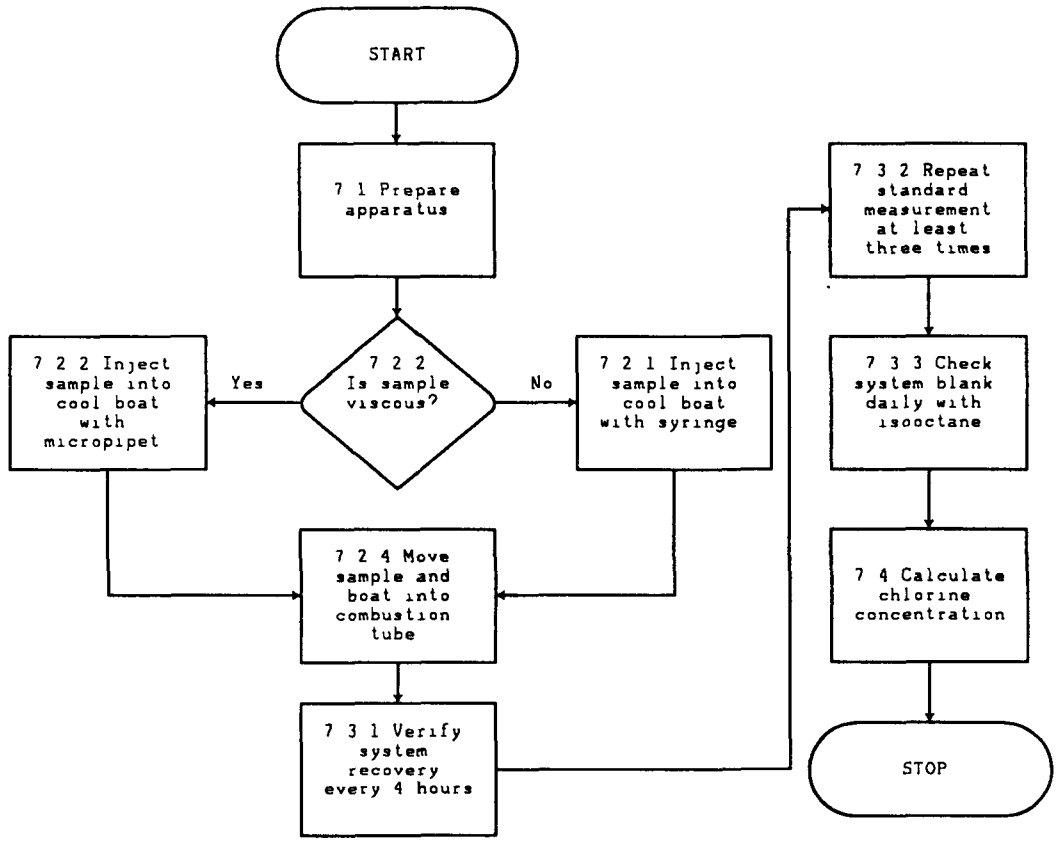
3. Standard Instrumentation, 3322 Pennsylvania Avenue, Charleston, WV 25302.

TABLE 1.
REPEATABILITY AND REPRODUCIBILITY FOR CHLORINE IN USED OILS BY MICROCOULOMETRIC TITRATION

Average value µg/g	Repeatability, µg/g	Reproducibility, µg/g
500	69	228
1,000	137	455
1,500	206	683
2,000	274	910
2,500	343	1,138
3,000	411	1,365

TABLE 2.
RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS BY MICROCOULOMETRIC TITRATION

Amount expected, µg/g	Amount found µg/g	Bias, µg/g	Percent bias
320	312	-8	-3
480	443	-37	-8
920	841	-79	-9
1,498	1,483	-15	-1
1,527	1,446	-81	-5
3,029	3,016	-13	0
3,045	2,916	-129	-4


START
7 1 Prepare apparatus
7 2 2 Is sample viscous?
Yes
No
7 2 2 Inject sample into cool boat with micropipet
7 2 1 Inject sample into cool boat with syringe
7 2 4 Move sample and boat into combustion tube
7 3 1 Verify system recovery every 4 hours
7 3 2 Repeat standard measurement at least three times
7 3 3 Check system blank daily with isooctane
7 4 Calculate chlorine concentration
STOP

METHOD 9077

TEST METHODS FOR TOTAL CHLORINE IN NEW AND USED PETROLEUM PRODUCTS (FIELD TEST KIT METHODS)

1.0 SCOPE AND APPLICATION

1.1 The method may be used to determine if a new or used petroleum product meets or exceeds requirements for total halogen measured as chloride. An analysis of the chlorine content of petroleum products is often required prior to their use as a fuel. The method is specifically designed for used oils permitting onsite testing at remote locations by nontechnical personnel to avoid the delays for laboratory testing.

1.2 In these field test methods, the entire analytical sequence, including sampling, sample pretreatment, chemical reactions, extraction, and quantification, are combined in a single kit using predispensed and encapsulated reagents. The overall objective is to provide a simple, easy to use procedure, permitting nontechnical personnel to perform a test with analytical accuracy outside of a laboratory environment in under 10 minutes. One of the kits is preset at 1,000 μg/g total chlorine to meet regulatory requirements for used oils. The other kits provide quantitative results over a range of 750 to 7,000 μg/g and 300 to 4,000 μg/g.

2.0 SUMMARY OF METHOD

2.1 The oil sample (around 0.4 g by volume) is dispersed in a solvent and reacted with a mixture of metallic sodium catalyzed with naphthalene and diglyme at ambient temperature. This process converts all organic halogens to their respective sodium halides. All halides in the treated mixture, including those present prior to the reaction, are then extracted into an aqueous buffer, which is then titrated with mercuric nitrate using diphenyl carbazone as the indicator. The end point of the titration is the formation of the blue-violet mercury diphenylcarbazone complex. Bromide and iodide are titrated and reported as chloride.

2.2 Reagent quantities are preset in the fixed end point kit (Method A) so that the color of the solution at the end of the titration indicates whether the sample is above 1,000 μg/g chlorine (yellow) or below 1,000 μg/g chlorine (blue).

2.3 The first quantitative kit (Method B) involves a reverse titration of a fixed volume of mercuric nitrate with the extracted sample such that the end point is denoted by a change from blue to yellow in the titration vessel over the range of the kit (750 to 7,000 μg/g). The final calculation is based on the assumption that the oil has a specific gravity of 0.9.

2.4 The second quantitative kit (Method C) involves a titration of the extracted sample with mercuric nitrate by means of a 1-mL microburette such that the end point is denoted by a change from pale yellow to red-violet over the range of the kit (300 to 4,000 μg/g). The concentration of chlorine in the original oil is then read from a scale on the microburette.

NOTE: Warning--All reagents are encapsulated or contained within ampoules. Strict adherence to the operational procedures included with the kits as well as accepted safety procedures (safety glasses and gloves) should be observed.

NOTE: Warning--When crushing the glass ampoules, press firmly in the center of the ampoule once. Never attempt to recrush broken glass because the glass may come through the plastic and cut fingers.

NOTE: Warning--In case of accidental breakage onto skin or clothing, wash with large amounts of water. All the ampoules are poisonous and should not be taken internally.

NOTE: Warning--The gray ampoules contain metallic sodium. Metallic sodium is a flammable water-reactive solid.

NOTE: Warning--Do not ship kits on passenger aircraft. Dispose of used kits properly.

NOTE: Caution--When the sodium ampoule in either kit is crushed, oils that contain more than 25% water will cause the sample to turn clear to light gray. Under these circumstances, the results may be biased excessively low and should be disregarded.

3.0 INTERFERENCES

3.1 Free water, as a second phase, should be removed. However, this second phase can be analyzed separately for chloride content if desired.

METHOD A

FIXED END POINT TEST KIT METHOD

4.0A APPARATUS AND MATERIALS

4.1A The CLOR-D-TECT 1000[1] is a complete self-contained kit. It includes: a sampling tube to withdraw a fixed sample volume for analysis; a polyethylene test tube #1 into which the sample is introduced for dilution and reaction with metallic sodium; and a polyethylene tube #2 containing a buffered aqueous extractant, the mercuric nitrate titrant, and diphenyl carbazone indicator. Included are instructions to conduct the test and a color chart to aid in determining the end point.

5.0A REAGENTS

5.1A Purity of reagents. 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.

5.2A All necessary reagents are contained within the kit.

5.3A The kit should be examined upon opening to see that all of the components are present and that all the ampoules (4) are in place and not leaking. The liquid in Tube #2 (yellow cap) should be approximately 1/2 in. above the 5-mL line and the tube should not be leaking. The ampoules are not supposed to be completely full.

6.0A SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1A All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine.

6.2A Because the collected sample will be analyzed for total halogens, it should be kept headspace free and refrigerated prior to preparation and analysis to minimize volatilization losses of organic halogens. Because waste oils may contain toxic and/or carcinogenic substances, appropriate field and laboratory safety procedures should be followed.

7.0A PROCEDURE

7.1A Preparation. Open analysis carton, remove contents, mount plastic test tubes in the provided holder. Remove syringe and glass sampling capillary from foil pouch.

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[1]Available from Dexsil Corporation, One Hamden Park Drive, Hamden, CT 06517.

NOTE: Perform the test in a warm, dry area with adequate light. In cold weather, a truck cab is sufficient. If a warm area is not available, Step 7.3A should be performed while warming Tube #1 in palm of hand.

7.2A Sample introduction. Remove white cap from Tube #1. Using the plastic syringe, slowly draw the oil up the capillary tube until it reaches the flexible adapter tube. Wipe excess oil from the tube with the provided tissue, keeping capillary vertical. Position capillary tube into Tube #1, and detach adapter tubing, allowing capillary to drop to the bottom of the tube. Replace white cap on tube. Crush the capillary by squeezing the test tube several times, being careful not to break the glass reagent ampoules.

7.3A Reaction. Break the lower (colorless) capsule containing the clear diluent solvent by squeezing the sides of the test tube. Mix thoroughly by shaking the tube vigorously for 30 seconds. Crush the upper grey ampoule containing metallic sodium, again by squeezing the sides of the test tube. Shake vigorously for 20 seconds. Allow reaction to proceed for 60 seconds, shaking intermittently several times while timing with a watch.

NOTE: Caution--Always crush the clear ampoule in each tube first. Otherwise, stop the test and start over using another complete kit. False (low) results may occur and allow a contaminated sample to pass without detection if clear ampoule is not crushed first.

7.4A Extraction. Remove caps from both tubes. Pour the clear buffered extraction solution from Tube #2 into Tube #1. Replace the white cap on Tube #1, and shake vigorously for 10 seconds. Vent tube by partially unscrewing the dispenser cap. Close cap securely, and shake for an additional 10 seconds. Vent again, tighten cap, and stand tube upside down on white cap. Allow phases to separate for 2 minutes.

7.5A Analysis. Put filtration funnel into Tube #2. Position Tube #1 over funnel and open nozzle on dispenser cap. Squeeze the sides of Tube #1 to dispense the clear aqueous lower phase through the filter into Tube #2 to the 5-mL line on Tube #2. Remove the filter funnel. Replace the yellow cap on Tube #2 and close the nozzle on the dispenser cap. Break the colorless lower capsule containing mercuric nitrate solution by squeezing the sides of the tube, and shake for 10 seconds. Then break the upper colored ampoule containing the diphenylcarbazone indicator, and shake for 10 seconds. Observe color immediately.

7.6A Interpretation of results

7.6.1A Because all reagent levels are preset, calculations are not required. A blue solution in Tube #2 indicates a chlorine content in the original oil of less than 1,000 μg/g, and a yellow color indicates that the chlorine concentration is greater than 1,000 μg/g. Refer to the color chart enclosed with the kit in interpreting the titration end point.

7.6.2A Report the results as < or > 1,000 μg/g chlorine in the oil sample.

8.0A QUALITY CONTROL

8.1A Refer to Chapter One for specific quality control procedures.

8.2A Each sample should be tested two times. If the results do not agree, then a third test must be performed. Report the results of the two that agree.

9.0A METHOD PERFORMANCE

9.1A No formal statement is made about either the precision or bias of the overall test kit method for determining chlorine in used oil because the result merely states whether there is conformance to the criteria for success specified in the procedure, (i.e., a blue or yellow color in the final solution). In a collaborative study, eight laboratories analyzed four used crankcase oils and three fuel oil blends with crankcase in duplicate using the test kit. Of the resulting 56 data points, 3 resulted in incorrect classification of the oil's chlorine content (Table 1). A data point represents one duplicate analysis of a sample. There were no disagreements within a laboratory on any duplicate determinations.

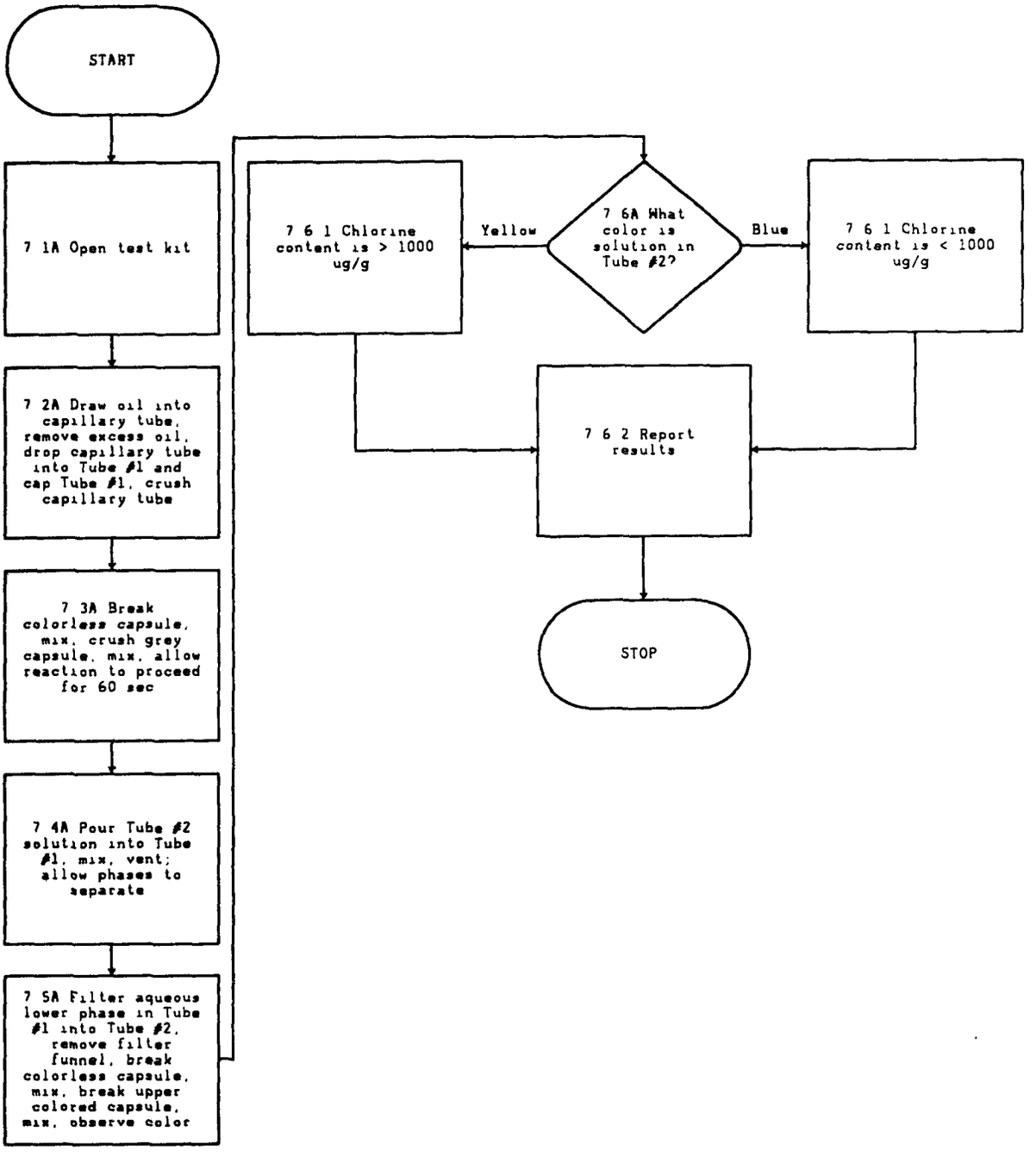
TABLE 1.
PRECISION AND BIAS INFORMATION FOR METHOD A-
FIXED END POINT TEST KIT METHOD

Expected concentration, µg/g	Expected results, µg/g	Percent correct[a]	Percent agreement[b]	
			Within	Between
320	< 1,000	100	100	100
480	< 1,000	100	100	100
920	< 1,000	100	100	100
1,498	> 1,000	87	100	87
1,527	> 1,000	75	100	75
3,029	> 1,000	100	100	100
3,045	> 1,000	100	100	100

[a]Percent correct--percent correctly identified as above or below 1,000 µg/g.

[b]Percent agreement--percent agreement within or between laboratories.

METHOD 9077 A
FIXED END POINT TEST KIT METHOD



METHOD B

REVERSE TITRATION QUANTITATIVE END POINT TEST KIT METHOD

4.0B APPARATUS AND MATERIALS

4.1B QuantiClor[2] kit components (see Figure 1).

4.1.1B Plastic reaction bottle: 1 oz, with flip-top dropper cap and a crushable glass ampoule containing sodium.

4.1.2B Plastic buffer bottle: contains 9.5 mL of aqueous buffer solution.

4.1.3B Titration vial: contains buffer bottle and indicator-impregnated paper.

4.1.4B Glass vial: contains 2.0 mL of solvents.

4.1.5B Micropipet and plunger, 0.25 mL.

4.1.6B Activated carbon filtering column.

4.1.7B Titret and valve assembly.

4.2B The reagents needed for the test are packaged in disposable containers.

4.3B The procedure utilizes a Titret. Titrets® are hand-held, disposable cells for titrimetric analysis. A Titret is an evacuated glass ampoule (13 mm diameter) that contains an exact amount of a standardized liquid titrant. A flexible valve assembly is attached to the tip of the ampoule. Titrets® employ the principle of reverse titration; that is, small doses of sample are added to the titrant to the appearance of the end point color. The color change indicates that the equivalency point has been reached. The flow of the sample into the Titret may be controlled by using an accessory called a Titrettor™.

5.0B REAGENTS

5.1B The crushable glass ampoule, which is inside the reaction bottle, contains 85 mg of metallic sodium in a light oil dispersion.

5.2B The buffer bottle contains 0.44 g of $NaH_2PO_4 \cdot 2H_2O$ and 0.32 mL of HNO_3 in distilled water.

5.3B The glass vial contains 770 mg Stoddard Solvent (CAS No. 8052-41-3), 260 mg toluene, 260 mg butyl ether, 260 mg diglyme, 130 mg naphthalene, and 70 mg demulsifier.

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[2]Quanti-Chlor Kit, Titrets®, and Titrettor™ are manufactured by Chemetrics, Inc., Calverton, VA 22016. U.S. Patent No. 4,332,769.

5.4B The Titret contains 1.12 mg mercuric nitrate in distilled water.

5.5B The indicator-impregnated paper contains approximately 0.3 mg of diphenylcarbazone and 0.2 mg of brilliant yellow.

6.0B SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See Section 6.0A of Method A.

7.0B PROCEDURE

7.1B Shake the glass vial and pour its contents into the reaction bottle.

7.2B Fill the micropipet with a well-shaken oil sample by pulling the plunger until its top edge is even with the top edge of the micropipet. Wipe off the excess oil and transfer the sample into the reaction bottle (see Figure 2.1).

7.3B Gently squeeze most of the air out of the reaction bottle (see Figure 2.2). Cap the bottle securely, and shake vigorously for 30 seconds.

7.4B Crush the sodium ampoule by pressing against the outside wall of the reaction bottle (see Figure 2.3).

CAUTION: Samples containing a high percentage of water will generate heat and gas, causing the reaction bottle walls to expand. To release the gas, briefly loosen the cap.

7.5B Shake the reaction bottle vigorously for 30 seconds.

7.6B Wait 1 minute. Shake the reaction bottle occasionally during this time.

7.7B Remove the buffer bottle from the titration vial, and slowly pour its contents into the reaction bottle (see Figure 2.4).

7.8B Cap the reaction bottle and shake gently for a few seconds. As soon as the foam subsides, release the gas by loosening the cap. Tighten the cap, and shake vigorously for 30 seconds. As before, release any gas that has formed, then turn the reaction bottle upside down (see Figure 2.5).

7.9B Wait 1 minute.

7.10B While holding the filtering column in a vertical position, remove the plug. Gently tap the column to settle the carbon particles.

7.11B Keeping the reaction bottle upside down, insert the flip top into the end of the filtering column and position the column over the titration vial (see Figure 2.6). Slowly squeeze the lower aqueous layer out of the reaction bottle and into the filtering column. Keep squeezing until the first drop of oil is squeezed out.

NOTE: Caution--The aqueous layer should flow through the filtering column into the titration vial in about 1 minute. In rare cases, it may be necessary to gently tap the column to begin the flow. The indicator paper should remain in the titration vial.

7.12B Cap the titration vial and shake it vigorously for 10 seconds.

7.13B Slide the flexible end of the valve assembly over the tapered tip of the Titret so that it fits snugly (see Figure 3.1).

7.14B Lift (see Figure 3.2) the control bar and insert the assembled Titret into the Titrettor™.

7.15B Hold the Titrettor™ with the sample pipe in the sample, and press the control bar to snap the pre-scored tip of the Titret (see Figure 3.3).

NOTE: Caution--Because the Titret is sealed under vacuum, the fluid inside may be agitated when the tip snaps.

7.16B With the tip of the sample pipe in the sample, briefly press the control bar to pull in a SMALL amount of sample (see Figure 3.3). The contents of the Titret will turn purple.

CAUTION: During the titration, there will be some undissolved powder inside the Titret. <u>This does not interfere with the accuracy of the test.</u>

7.17B Wait 30 seconds.

7.18B Gently press the control bar again to allow another SMALL amount of the sample to be drawn into the Titret.

CAUTION: Do not press the control bar unless the sample pipe is immersed in the sample. This prevents air from being drawn into the Titret.

7.19B After each addition, rock the entire assembly to mix the contents of the Titret. Watch for a color change from purple to very pale yellow.

7.20B Repeat Steps 7.18B and 7.19B until the color change occurs.

CAUTION: The end point color change (from purple to pale yellow) actually goes through an intermediate gray color. During this intermediate stage, extra caution should be taken to bring in SMALL amounts of sample and to mix the Titret contents well.

7.21B When the color of the liquid in the Titret changes to PALE YELLOW, remove the Titret from the Titrettor™. Hold the Titret in a vertical position and carefully read the test result on the scale opposite the liquid level.

7.22B Calculation

7.22.1B To obtain results in micrograms per gram total chlorine, multiply scale units on the Titret by 1.3 and then subtract 200.

8.0B QUALITY CONTROL

8.1B Refer to Chapter One for specific quality control procedures.

8.2B Each sample should be tested two times. If the results do not agree to within 10%, expressed as the relative percent difference of the results, a third test must be performed. Report the results of the two that agree.

9.0B METHOD PERFORMANCE

9.1B These data are based on 49 data points obtained by seven laboratories who each analyzed four used crankcase oils and three fuel oil blends with crankcase in duplicate. A data point represents one duplicate analysis of a sample. There were no outlier data points or laboratories.

9.2B Precision. The precision of the method as determined by the statistical examination of interlaboratory test results is as follows:

Repeatability - The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would exceed, in the long run, in the normal and correct operation of the test method, the following values only in 1 case in 20 (see Table 2):

$$Repeatability = 0.31\ x*$$

*where x is the average of two results in μg/g.

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would exceed, in the long run, the following values only in 1 case in 20:

$$Reproducibility = 0.60\ x*$$

*where x is the average value of two results in μg/g.

9.3B Bias. The bias of this test method varies with concentration, as shown in Table 3:

Bias = Amount found - Amount expected

TABLE 2.
REPEATABILITY AND REPRODUCIBILITY FOR CHLORINE IN USED OILS BY THE QUANTITATIVE END POINT TEST KIT METHOD

Average value, μg/g	Repeatability, μg/g	Reproducibility, μg/g
1,000	310	600
1,500	465	900
2,000	620	1,200
2,500	775	1,500
3,000	930	1,800

TABLE 3.
RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS BY THE QUANTITATIVE END POINT TEST KIT METHOD

Amount expected, μg/g	Amount found, μg/g	Bias, μg/g	Percent bias
320 (< 750)[a]	776	+16	+3
480 (< 750)[a]	782	+32	+4
920	1,020	+100	+11
1,498	1,129	-369	-25
1,527	1,434	-93	-6
3,029	1,853	-1,176	-39
3,045	2,380	-665	-22

[a] The lower limit of the kit is 750 μg/g.

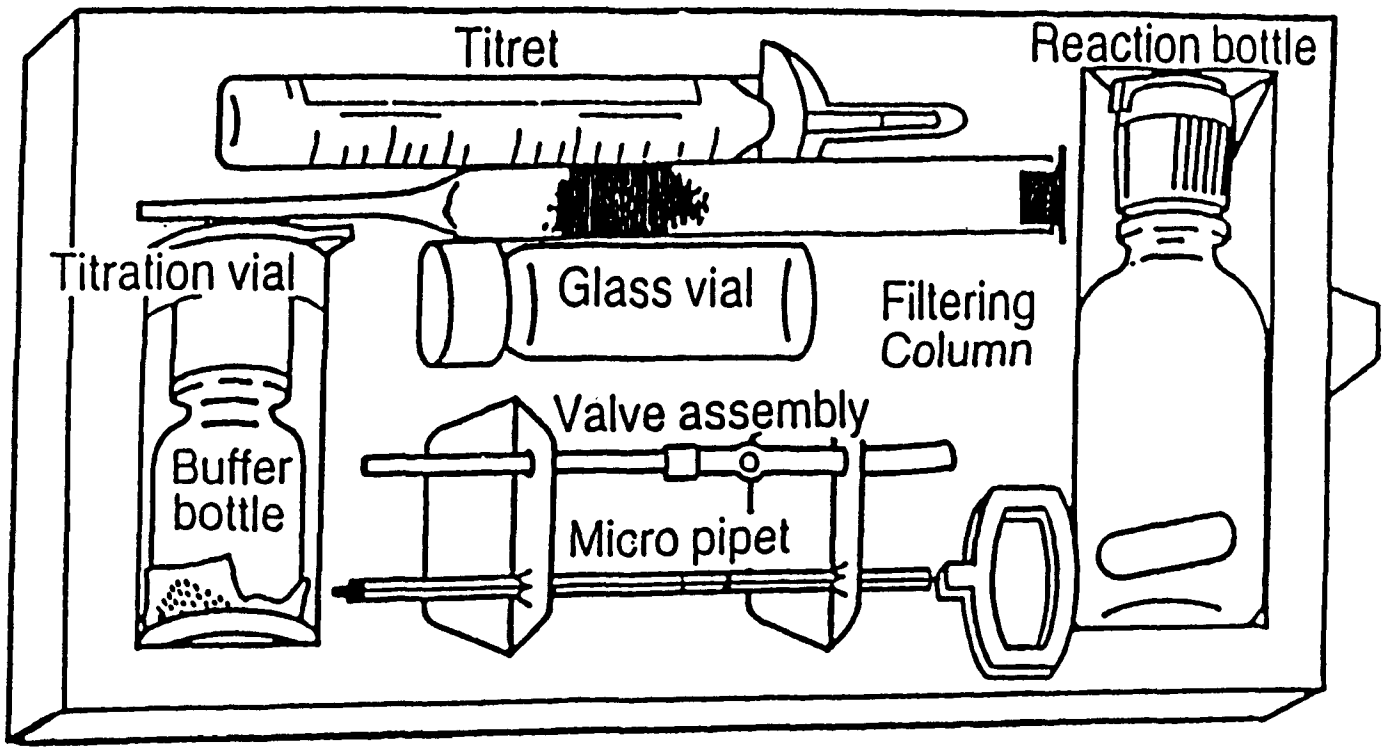


Figure 1. Components of CHEMetrics Total Chlorine in Waste Oil Test Kit (Cat. No. K2610).

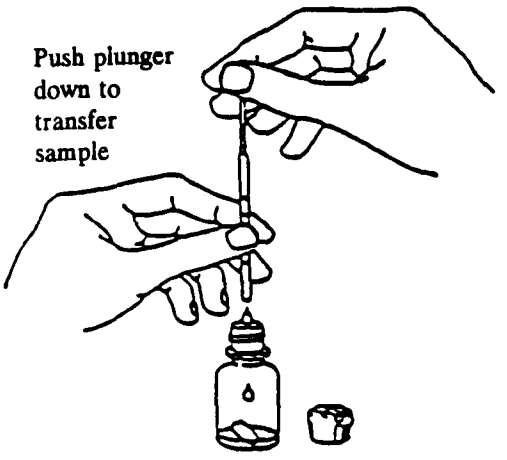


Figure 2.1

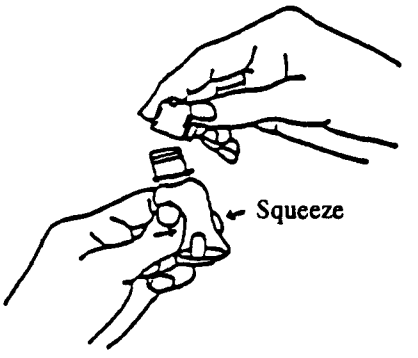


Figure 2.2

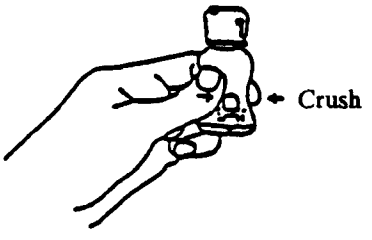


Figure 2.3

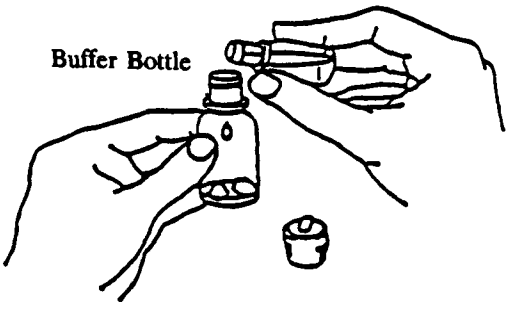


Figure 2.4

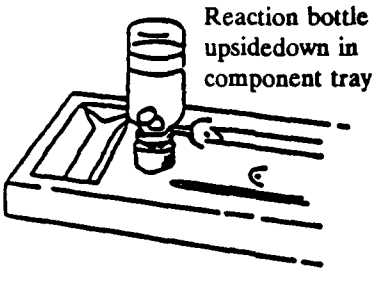


Figure 2.5

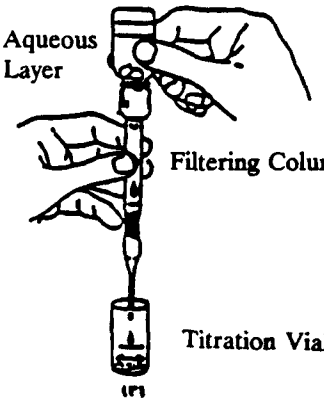


Figure 2.6

Figure 2. Reaction-Extraction Procedure.

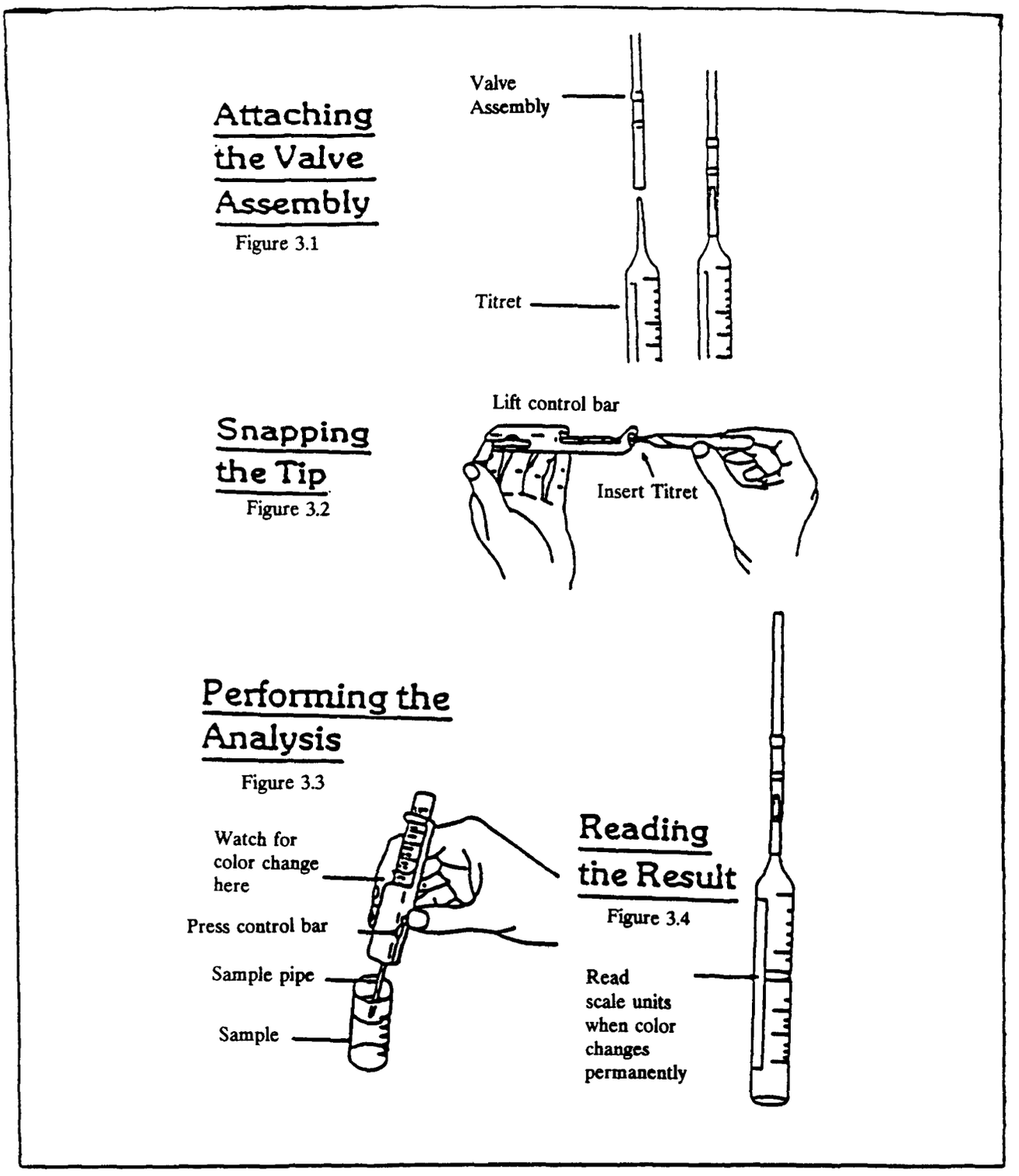
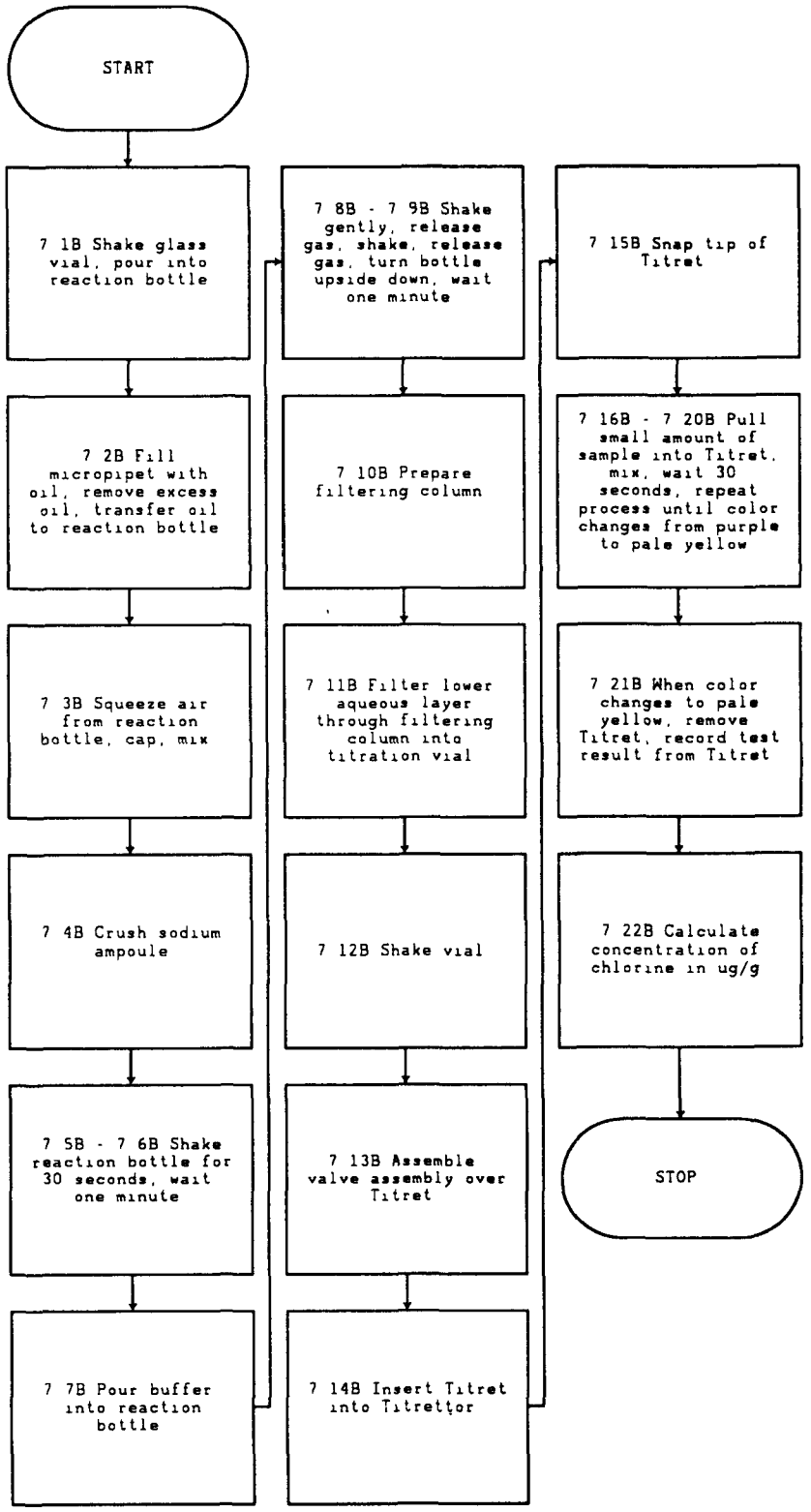


Figure 3. Titration Procedure

METHOD 9077 B
REVERSE TITRATION QUANTITATIVE END POINT TEST KIT METHOD



METHOD C

DIRECT TITRATION QUANTITAVE END POINT TEST KIT METHOD

4.0C APPARATUS AND MATERIALS

4.1C The CHLOR-D-TECT Q4000[3] is a complete self-contained kit. It includes: a sampling syringe to withdraw a fixed sample volume for analysis; a polyethylene test tube #1 into which the sample is introduced for dilution and reaction with metallic sodium; a polyethylene tube #2 containing a buffered aqueous extractant and the diphenylcarbazone indicator; a microburette containing the mercuric nitrate titrant; and a plastic filtration funnel. Also included are instructions to conduct the test.

5.0C REAGENTS

5.1C All necessary reagents are contained within the kit. The diluent solvent containing the catalyst, the metallic sodium, and the diphenylcarbazone are separately glass-encapsulated in the precise quantity required for analysis. A predispensed volume of buffer is contained in the second polyethylene tube. Mercuric nitrate titrant is also supplied in a sealed titration burette.

5.2C The kit should be examined upon opening to see that all of the components are present and that all ampoules (3) are in place and not leaking. The liquid in Tube #2 (clear cap) should be approximately 1/2 in. above the 5-mL line and the tube should not be leaking. The ampoules are not supposed to be completely full.

6.0C SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1C See Section 6.0A of Method A.

7.0C PROCEDURE

7.1C Preparation. Open analysis carton, remove contents, mount plastic test tubes in the provided holder.

NOTE: Perform the test in a warm, dry area with adequate light. In cold weather, a truck cab is sufficient. If a warm area is not available, Step 7.3C should be performed while warming Tube #1 in palm of hand.

7.2C Sample introduction. Unscrew the white dispenser cap from Tube #1. Slide the plunger in the empty syringe a few times to make certain that it slides easily. Place the top of the syringe in the oil sample to be tested, and pull back on the plunger until it reaches the stop and cannot be pulled further. Remove the syringe from the sample container, and wipe any excess oil from the outside of the syringe with the enclosed tissue. Place the tip of the syringe in Tube #1, and dispense the oil sample by depressing the plunger. Replace the white cap on the tube.

---

[3]Available from Dexsil Corporation, One Hamden Park Drive, Hamden, CT 06517.

7.3C Reaction. Break the lower (colorless) capsule containing the clear diluent solvent by squeezing the sides of the test tube. Mix thoroughly by shaking the tube vigorously for 30 seconds. Crush the upper grey ampoule containing metallic sodium, again by squeezing the sides of the test tube. Shake vigorously for 20 seconds. Allow reaction to proceed for 60 seconds, shaking intermittently several times while timing with a watch.

CAUTION: Always crush the clear ampoule in each tube first. Otherwise, stop the test and start over using another complete kit. False (low) results may occur and allow a contaminated sample to pass without detection if clear ampoule is not crushed first.

7.4C Extraction. Remove caps from both tubes. Pour the clear buffered extraction solution from Tube #2 into Tube #1. Replace the white cap on Tube #1, and shake vigorously for 10 seconds. Vent tube by partially unscrewing the dispenser cap. Close cap securely, and shake for an additional 10 seconds. Vent again, tighten cap, and stand tube upside down on white cap. Allow phases to separate for 2 minutes.

NOTE: Tip Tube #2 to an angle of only about 45°. This will prevent the holder from sliding out.

7.5C Analysis. Put filtration funnel into Tube #2. Position Tube #1 over funnel and open nozzle on dispenser cap. Squeeze the sides of Tube #1 to dispense the clear aqueous lower phase through the filter into Tube #2 to the 5-mL line on Tube #2. Remove the filter funnel, and close the nozzle on the dispenser cap. Place the plunger rod in the titration burette and press until it clicks into place. Break off (do not pull off) the tip on the titration burette. Insert the burette into Tube #2, and tighten the cap. Break the colored ampoule, and shake gently for 10 seconds. Dispense titrant dropwise by pushing down on burette rod in small increments. Shake the tube gently to mix titrant with solution in Tube #2 after each increment. Continue adding titrant until solution turns from yellow to red-violet. An intermediate pink color may develop in the solution, but should be disregarded. Continue titrating until a true red-violet color is realized. The chlorine concentration of the original oil sample is read directly off the titrating burette at the tip of the black plunger. Record this result immediatley as the red-violet color will fade with time.

8.0C QUALITY CONTROL

8.1C Refer to Chapter One for specific quality control procedures.

8.2C Each sample should be tested two times. If the results do not agree to within 10%, expressed as the relative percent difference of the results, a third test must be performed. Report the results of the two that agree.

9.0C METHOD PERFORMANCE

9.1C These data are based on 96 data points obtained by 12 laboratories who each analyzed six used crankcase oils and two fuel oil blends with crankcase in duplicate. A data point represents one duplicate analysis of a sample.

9.2C Precision. The precision of the method as determined by the statistical examination of interlaboratory test results is as follows:

Repeatability - The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would exceed, in the long run, in the normal and correct operation of the test method, the following values only in 1 case in 20 (see Table 4):

$$Repeatability = 0.175\ x*$$

*where x is the average of two results in μg/g.

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would exceed, in the long run, the following values only in 1 case in 20:

$$Reproducibility = 0.331\ x*$$

*where x is the average value of two results in μg/g.

9.3C Bias. The bias of this test method varies with concentration, as shown in Table 5:

Bias = Amount found - Amount expected

10.0 REFERENCE

1. Gaskill, A.; Estes, E.D.; Hardison, D.L.; and Myers, L.E. Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels. Prepared for U.S. Environmental Protection Agency, Office of Solid Waste. EPA Contract No. 68-01-7075, wA 80. July 1988.

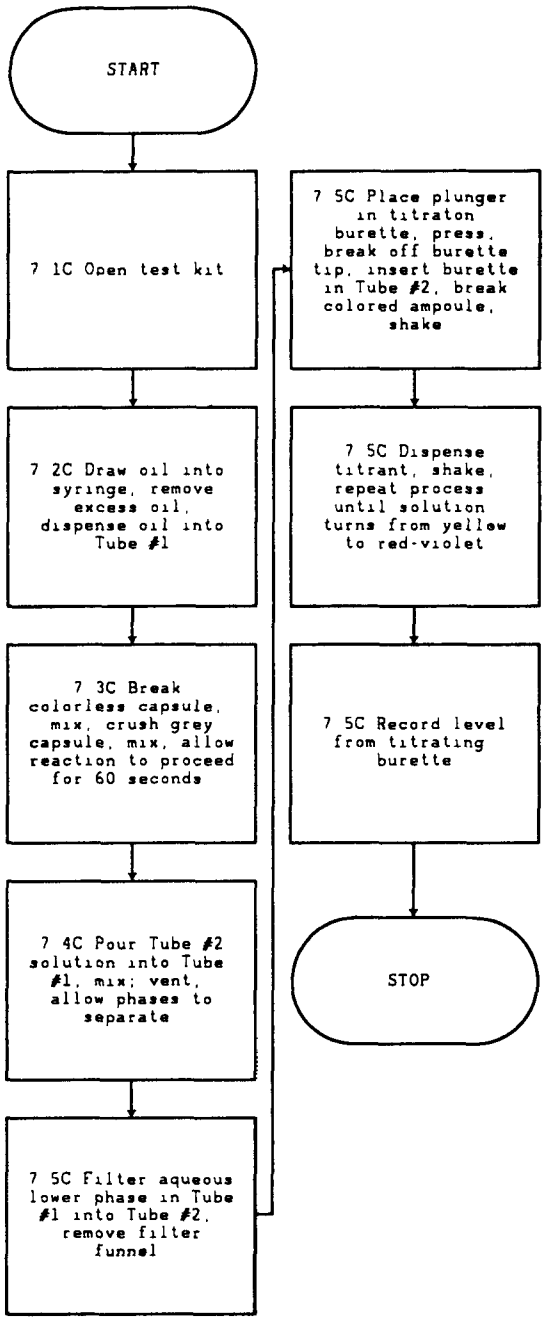
TABLE 4.
REPEATABILITY AND REPRODUCIBILITY FOR CHLORINE IN USED OILS BY THE QUANTITATIVE END POINT TEST KIT METHOD

Average value, µg/g	Repeatability, µg/g	Reproducibility, µg/g
500	88	166
1,000	175	331
1,500	263	497
2,000	350	662
2,500	438	828
3,000	525	993
4,000	700	1,324

TABLE 5.
RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS BY THE QUANTITATIVE END POINT TEST KIT METHOD

Amount expected, µg/g	Amount found, µg/g	Bias, µg/g	Percent bias
664	695	31	+5
964	906	-58	-6
1,230	1,116	-114	-9
1,445	1,255	-190	-13
2,014	1,618	-396	-20
2,913	2,119	-794	-27
3,812	2,776	-1,036	-27
4,190	3,211	-979	-23

METHOD 9077 C
DIRECT TITRATION QUANTITAVE END POINT TEST KIT METHOD



METHOD 9090

COMPATIBILITY TEST FOR WASTES AND MEMBRANE LINERS

1.0 SCOPE AND APPLICATION

1.1 Method 9090 is intended for use in determining the effects of chemicals in a surface impoundment, waste pile, or landfill on the physical properties of flexible membrane liner (FML) materials intended to contain them. Data from these tests will assist in deciding whether a given liner material is acceptable for the intended application.

2.0 SUMMARY OF METHOD

2.1 In order to estimate waste/liner compatibility, the liner material is immersed in the chemical environment for minimum periods of 120 days at room temperature (23 ± 2°C) and at 50 ± 2°C. In cases where the FML will be used in a chemical environment at elevated temperatures, the immersion testing shall be run at the elevated temperatures if they are expected to be higher than 50°C. Whenever possible, the use of longer exposure times is recommended. Comparison of measurements of the membrane's physical properties, taken periodically before and after contact with the waste fluid, is used to estimate the compatibility of the liner with the waste over time.

3.0 INTERFERENCES (Not Applicable)

4.0 APPARATUS AND MATERIALS

NOTE: In general, the following definitions will be used in this method:

1. Sample -- a representative piece of the liner material proposed for use that is of sufficient size to allow for the removal of all necessary specimens.
2. Specimen -- a piece of material, cut from a sample, appropriately shaped and prepared so that it is ready to use for a test.

4.1 Exposure tank - Of a size sufficient to contain the samples, with provisions for supporting the samples so that they do not touch the bottom or sides of the tank or each other, and for stirring the liquid in the tank. The tank should be compatible with the waste fluid and impermeable to any of the constituents they are intended to contain. The tank shall be equipped with a means for maintaining the solution at room temperature (23 ± 2°C) and 50 ± 2°C and for preventing evaporation of the solution (e.g., use a cover equipped with a reflux condenser, or seal the tank with a Teflon gasket and use an airtight cover). Both sides of the liner material shall be exposed to the chemical environment. The pressure inside the tank must be the same as that outside the tank. If the liner has a side that (1) is not exposed to the waste in actual use and (2) is not designed to withstand exposure to the chemical environment, then such a liner may be treated with only the barrier surface exposed.

4.2 Stress-strain machine suitable for measuring elongation, tensile strength, tear resistance, puncture resistance, modulus of elasticity, and ply adhesion.

4.3 Jig for testing puncture resistance for use with FTMS 101C, Method 2065.

4.4 Liner sample labels and holders made of materials known to be resistant to the specific wastes.

4.5 Oven at 105 $\pm$ 2°C.

4.6 Dial micrometer.

4.7 Analytical balance.

4.8 Apparatus for determining extractable content of liner materials.

NOTE: A minimum quantity of representative waste fluid necessary to conduct this test has not been specified in this method because the amount will vary depending upon the waste compostion and the type of liner material. For example, certain organic waste constituents, if present in the representative waste fluid, can be absorbed by the liner material, thereby changing the concentration of the chemicals in the waste. This change in waste composition may require the waste fluid to be replaced at least monthly in order to maintain representative conditions in the waste fluid. The amount of waste fluid necessary to maintain representative waste conditions will depend on factors such as the volume of constituents absorbed by the specific liner material and the concentration of the chemical constituents in the waste.

5.0 REAGENTS (Not Applicable)

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 For information on what constitutes a representative sample of the waste fluid, refer to the following guidance document:

Permit Applicants' Guidance Manual for Hazardous Waste Land Treatment, Storage, and Disposal Facilities; Final Draft; Chap. 5, pp. 15-17; Chap. 6, pp. 18-21; and Chap. 8, pp. 13-16, May 1984.

7.0 PROCEDURE

7.1 Obtain a representative sample of the waste fluid. If a waste sample is received in more than one container, blend thoroughly. Note any signs of stratification. If stratification exists, liner samples must be placed in each of the phases. In cases where the waste fluid is expected to stratify and the phases cannot be separated, the number of immersed samples per exposure period can be increased (e.g. if the waste fluid has two phases, then 2 samples per exposure period are needed) so that test samples exposed at each level of the waste can be tested. If the waste to be contained in the

land disposal unit is in solid form, generate a synthetic leachate (see Step 7.9.1).

7.2 Perform the following tests on unexposed samples of the polymeric membrane liner material at 23 ± 2°C (see Steps 7.9.2 and 7.9.3 below for additional tests suggested for specific circumstances). Tests for tear resistance and tensile properties are to be performed according to the protocols referenced in Table 1. See Figure 1 for cutting patterns for nonreinforced liners, Figure 2 for cutting patterns for reinforced liners, and Figure 3 for cutting patterns for semicrystalline liners. (Table 2, at the end of this method, gives characteristics of various polymeric liner materials.)

1. Tear resistance, machine and transverse directions, three specimens each direction for nonreinforced liner materials only. See Table 1 for appropriate test method, the recommended test speed, and the values to be reported.

2. Puncture resistance, two specimens, FTMS 101C, Method 2065. See Figure 1, 2, or 3, as applicable, for sample cutting patterns.

3. Tensile properties, machine and transverse directions, three tensile specimens in each direction. See Table 1 for appropriate test method, the recommended test speed, and the values to be reported. See Figure 4 for tensile dumbbell cutting pattern dimensions for nonreinforced liner samples.

4. Hardness, three specimens, Duro A (Duro D if Duro A reading is greater than 80), ASTM D2240. The hardness specimen thickness for Duro A is 1/4 in., and for Duro D it is 1/8 in. The specimen dimensions are 1 in. by 1 in.

5. Elongation at break. This test is to be performed only on membrane materials that do not have a fabric or other nonelastomeric support as part of the liner.

6. Modulus of elasticity, machine and transverse directions, two specimens each direction for semicrystalline liner materials only, ASTM D882 modified Method A (see Table 1).

7. Volatiles content, SW 870, Appendix III-D.

8. Extractables content, SW 870, Appendix III-E.

9. Specific gravity, three specimens, ASTM D792 Method A.

10. Ply adhesion, machine and transverse directions, two specimens each direction for fabric reinforced liner materials only, ASTM D413 Machine Method, Type A -- 180 degree peel.

11. Hydrostatic resistance test, ASTM D751 Method A, Procedure 1.

7.3 For each test condition, cut five pieces of the lining material of a size to fit the sample holder, or at least 8 in. by 10 in. The fifth sample is an extra sample. Inspect all samples for flaws and discard unsatisfactory ones. Liner materials with fabric reinforcement require close inspection to ensure that threads of the samples are evenly spaced and straight at 90°. Samples containing a fiber scrim support may be flood-coated along the exposed edges with a solution recommended by the liner manufacturer, or another procedure should be used to prevent the scrim from being directly exposed. The flood-coating solution will typically contain 5-15% solids dissolved in a solvent. The solids content can be the liner formula or the base polymer.

Measure the following:

1. Gauge thickness, in. -- average of the four corners.

2. Mass, lb. -- to one-hundredth of a lb.

3. Length, in. -- average of the lengths of the two sides plus the length measured through the liner center.

4. Width, in. -- average of the widths of the two ends plus the width measured through the liner center.

NOTE: Do not cut these liner samples into the test specimen shapes shown in Figure 1, 2, or 3 at this time. Test specimens will be cut as specified in Step 7.7, after exposure to the waste fluid.

7.4 Label the liner samples (e.g. notch or use metal staples to identify the sample) and hang in the waste fluid by a wire hanger or a weight. Different liner materials should be immersed in separate tanks to avoid exchange of plasticizers and soluble constituents when plasticized membranes are being tested. Expose the liner samples to the stirred waste fluid held at room temperature and at 50 $\pm$ 2°C.

7.5 At the end of 30, 60, 90, and 120 days of exposure, remove one liner sample from each test condition to determine the membrane's physical properties (see Steps 7.6 and 7.7). Allow the liner sample to cool in the waste fluid until the waste fluid has a stable room temperature. Wipe off as much waste as possible and rinse briefly with water. Place wet sample in a labeled polyethylene bag or aluminum foil to prevent the sample from drying out. The liner sample should be tested as soon as possible after removal from the waste fluid at room temperature, but in no case later than 24 hours after removal.

7.6 To test the immersed sample, wipe off any remaining waste and rinse with deionized water. Blot sample dry and measure the following as in Step 7.3:

1. Gauge thickness, in.

2. Mass, lb.

3. Length, in.

4. Width, in.

7.7 Perform the following tests on the exposed samples (see Steps 7.9.2 and 7.9.3 below for additional tests suggested for specific circumstances). Tests for tear resistance and tensile properties are to be performed according to the protocols referenced in Table 1. Die-cut test specimens following suggested cutting patterns. See Figure 1 for cutting patterns for nonreinforced liners, Figure 2 for cutting patterns for reinforced liners, and Figure 3 for semicrystalline liners.

1. Tear resistance, machine and transverse directions, three specimens each direction for materials without fabric reinforcement. See Table 1 for appropriate test method, the recommended test specimen and speed of test, and the values to be reported.

2. Puncture resistance, two specimens, FTMS 101C, Method 2065. See Figure 1, 2, or 3, as applicable, for sample cutting patterns.

3. Tensile properties, machine and transverse directions, three specimens each direction. See Table 1 for appropriate test method, the recommended test specimen and speed of test, and the values to be reported. See Figure 4 for tensile dumbbell cutting pattern dimensions for nonreinforced liner samples.

4. Hardness, three specimens, Duro A (Duro D if Duro A reading is greater than 80), ASTM 2240. The hardness specimen thickness for Duro A is 1/4 in., and for Duro D is 1/8 in. The specimen dimensions are 1 in. by 1 in.

5. Elongation at break. This test is to be performed only on membrane materials that do not have a fabric or other nonelastomeric support as part of the liner.

6. Modulus of elasticity, machine and transverse directions, two specimens each direction for semicrystalline liner materials only, ASTM D882 modified Method A (see Table 1).

7. Volatiles content, SW 870, Appendix III-D.

8. Extractables content, SW 870, Appendix III-E.

9. Ply adhesion, machine and transverse directions, two specimens each direction for fabric reinforced liner materials only, ASTM D413 Machine Method, Type A -- 180 degree peel.

10. Hydrostatic resistance test, ASTM D751 Method A, Procedure 1.

7.8 Results and reporting

7.8.1 Plot the curve for each property over the time period 0 to 120 days and display the spread in data points.

7.8.2 Report all raw, tabulated, and plotted data. Recommended methods for collecting and presenting information are described in the documents listed under Step 6.1 and in related agency guidance manuals.

7.8.3 Summarize the raw test results as follows:

1. Percent change in thickness.

2. Percent change in mass.

3. Percent change in area (provide length and width dimensions).

4. Percent retention of physical properties.

5. Change, in points, of hardness reading.

6. The modulus of elasticity calculated in pounds-force per square inch.

7. Percent volatiles of unexposed and exposed liner material.

8. Percent extractables of unexposed and exposed liner material.

9. The adhesion value, determined in accordance with ASTM D413, Step 12.2.

10. The pressure and time elapsed at the first appearance of water through the flexible membrane liner for the hydrostatic resistance test.

7.9 The following additional procedures are suggested in specific situations:

7.9.1 For the generation of a synthetic leachate, the Agency suggests the use of the Toxicity Characteristic Leaching Procedure (TCLP) that was proposed in the Federal Register on June 13, 1986, Vol. 51, No. 114, p. 21685.

7.9.2 For semicrystalline membrane liners, the Agency suggests the determination of the potential for environmental stress cracking. The test that can be used to make this determination is either ASTM D1693 or the National Bureau of Standards Constant Tensile Load. The evaluation of the results should be provided by an expert in this field.

7.9.3 For field seams, the Agency suggests the determination of seam strength in shear and peel modes. To determine seam strength in peel mode, the test ASTM D413 can be used. To determine seam strength in shear mode for nonreinforced FMLs, the test ASTM D3083 can be used, and for reinforced FMLs, the test ASTM D751, Grab Method, can be used at a

speed of 12 in. per minute. The evaluation of the results should be provided by an expert in this field.

8.0 QUALITY CONTROL

8.1 Determine the mechanical properties of identical nonimmersed and immersed liner samples in accordance with the standard methods for the specific physical property test. Conduct mechanical property tests on nonimmersed and immersed liner samples prepared from the same sample or lot of material in the same manner and run under identical conditions. Test liner samples immediately after they are removed from the room temperature test solution.

9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. None required.

Table 1. Physical testing of exposed membranes in liner-waste liquid compatibility test

Type of compound and construction	Crosslinked or vulcanized	Thermoplastic	Semicrystalline	Fabric-reinforced[a]
Tensile properties method	ASTM D412	ASTM D638	ASTM D638	ASTM D751, Method B
Type of specimen	Dumbbell[b]	Dumbbell[b]	Dumbbell[b]	1-in. wide strip and 2-in. jaw separation
Number of specimens	3 in each direction	3 in each direction	3 in each direction	3 in each direction
Speed of test	20 ipm	20 ipm	2 ipm	12 ipm
Values to be reported	Tensile strength, psi Elongation at break, % Tensile set after break, % Stress at 100 and 200% elongation, psi	Tensile strength, psi Elongation at break, % Tensile set after break, % Stress at 100 and 200% elongation, psi	Tensile strength at yield, psi Elongation at yield, % Tensile set at break, psi Elongation at break, psi Tensile set after break, % Stress at 100 and 200% elongation, psi	Tensile at fabric break, ppi Elongation at fabric break, % Tensile at ultimate break, ppi Elongation at ultimate break, ppi Tensile set after break, % Stress at 100 and 200% elongation, psi
Modulus of elasticity method	c	c	ASTM D882, Method A	c
Type of specimen	—	—	Strip: 0.5 in. wide and 6. in long at a 2 in. jaw separation	—
Number of specimens	—	—	2 in each direction	—
Speed of test	—	—	0.2 ipm	—
Values reported	—	—	Greatest slope of initial stress - strain curve, psi	—
Tear resistance method	ASTM D624	ASTM 1004	ASTM D1004	d
Type of specimen	Die C	e	e	—
Number of specimens	3 in each direction	3 in each direction	2 in each direction	—
Speed of test	20 ipm	20 ipm	2 ipm	—
Values reported	Stress, ppi	Stress, ppi	Maximum stress, ppi	—
Puncture resistance method	FTMS 101C, Method 2065	FTMS 101C, Method 2065	FTMS 101C, Method 2065	FTMS 101C, Method 2065
Type of specimen	2 in. square	2 in. square	2 in. square	2 in. square
Number of specimens	2	2	2	2
Speed of test	20 ipm	20 ipm	20 ipm	20 ipm
Values reported	Gage, mil Stress, lb[b] Elongation, in.	Gage, mil Stress, lb[b] Elongation, in.	Gage, mil Stress, lb[b] Elongation, in.	Gage, mil Stress, lb[b] Elongation, in.

[a]Can be thermoplastic, crosslinked, or vulcanized membrane.
[b]See Figure 4.
[c]Not performed on this material.
[d]No tear resistance test is recommended for fabric-reinforced sheetings in the immersion study.
[e]Same as ASTM D624, Die C.

TABLE 2.
POLYMERS USED IN FLEXIBLE MEMBRANE LINERS

Thermoplastic Materials (TP)

CPE (Chlorinated polyethylene)[a]

A family of polymers produced by a chemical reaction of chlorine on polyethylene. The resulting thermoplastic elastomers contain 25 to 45% chlorine by weight and 0 to 25% crystallinity.

CSPE (Chlorosulfonated polyethylene)[a]

A family of polymers that are produced by the reaction of polyethylene with chlorine and sulfur dioxide, usually containing 25 to 43% chlorine and 1.0 to 1.4% sulfur. Chlorosulfonated polyethylene is also known as hypalon.

EIA (Ethylene interpolymer alloy)[a]

A blend of EVA and polyvinyl chloride resulting in a thermoplastic elastomer.

PVC (Polyvinyl chloride)[a]

A synthetic thermoplastic polymer made by polymerizing vinyl chloride monomer or vinyl chloride/vinyl acetate monomers. Normally rigid and containing 50% of plasticizers.

PVC-CPE (Polyvinyl chloride - chlorinated polyethylene alloy)[a]

A blend of polyvinyl chloride and chlorinated polyethylene.

TN-PVC (Thermoplastic nitrile-polyvinyl choloride)[a]

An alloy of thermoplastic unvulcanized nitrile rubber and polyvinyl chloride.

Vulcanized Materials (XL)

Butyl rubber[a]

A synthetic rubber based on isobutylene and a small amount of isoprene to provide sites for vulcanization.

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[a]Also supplied reinforced with fabric.

TABLE 2. (Continued)

EPDM (Ethylene propylene diene monomer)[a,b]

A synthetic elastomer based on ethylene, propylene, and a small amount of nonconjugated diene to provide sites for vulcanization.

CM (Cross-linked chlorinated polyethylene)

No definition available by EPA.

CO, ECO (Epichlorohydrin polymers)[a]

Synthetic rubber, including two epichlorohydrin-based elastomers that are saturated, high-molecular-weight aliphatic polyethers with chloromethyl side chains. The two types include homopolymer (CO) and a copolymer of epichlorohydrin and ethylene oxide (ECO).

CR (Polychloroprene)[a]

Generic name for a synthetic rubber based primarily on chlorobutadiene. Polychloroprene is also known as neoprene.

Semicrystalline Materials (CX)

HDPE - (High-density polyethylene)

A polymer prepared by the low-pressure polymerization of ethylene as the principal monomer.

HDPE - A (High-density polyethylene/rubber alloy)

A blend of high-density polyethylene and rubber.

LLDPE (Liner low-density polyethylene)

A low-density polyethylene produced by the copolymerization of ethylene with various alpha olefins in the presence of suitable catalysts.

PEL (Polyester elastomer)

A segmented thermoplastic copolyester elastomer containing recurring long-chain ester units derived from dicarboxylic acids and long-chain glycols and short-chain ester units derived from dicarboxylic acids and low-molecular-weight diols.

---

[a]Also supplied reinforced with fabric.
[b]Also supplied as a thermoplastic.

TABLE 2. (Continued)

PE-EP-A (Polyethylene ethylene/propylene alloy)

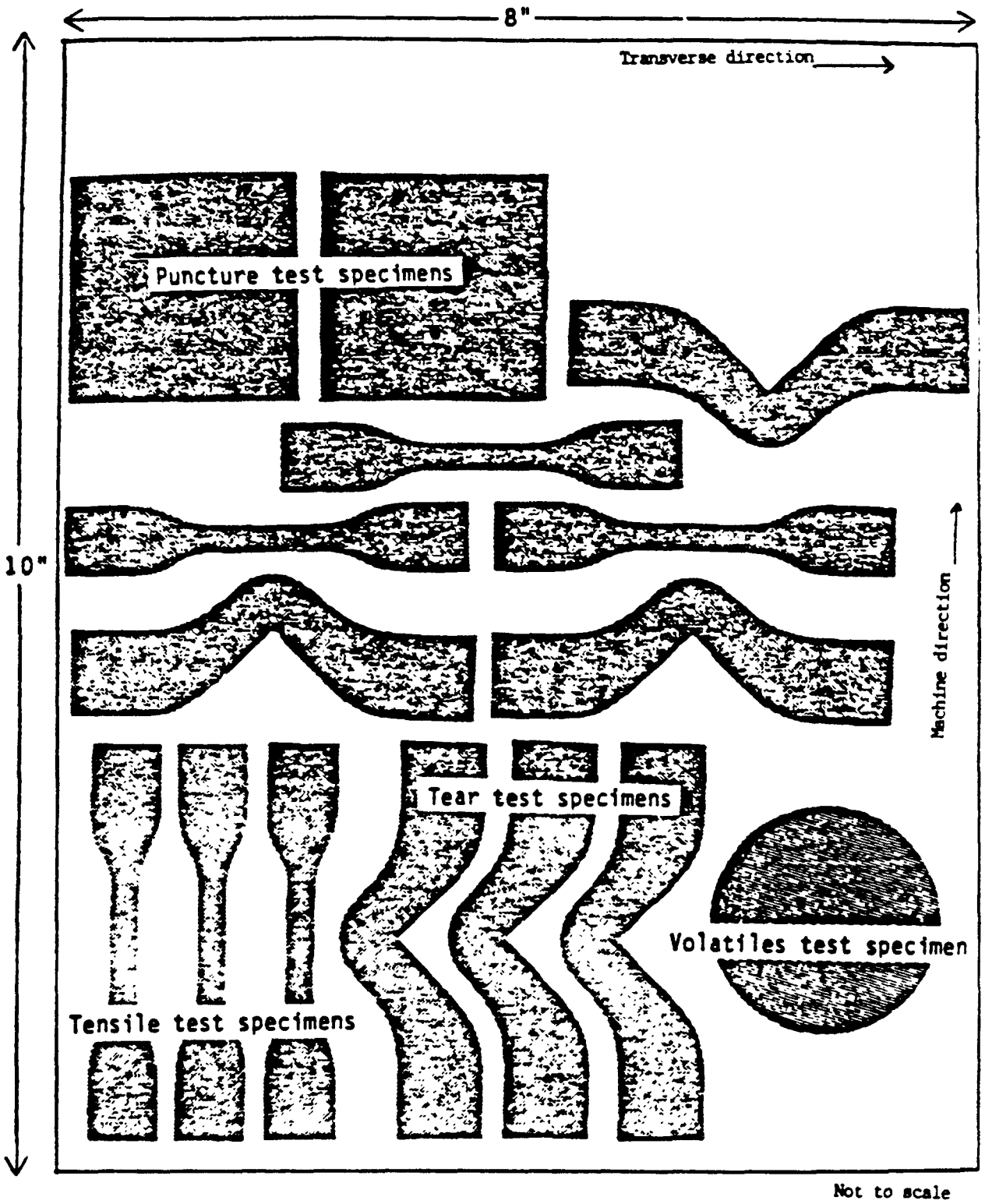
A blend of polyethylene and ethylene and propylene polymer resulting in a thermoplastic elastomer.

T-EPDM (Thermoplastic EPDM)

An ethylene-propylene diene monomer blend resulting in a thermoplastic elastomer.

Figure 1 .

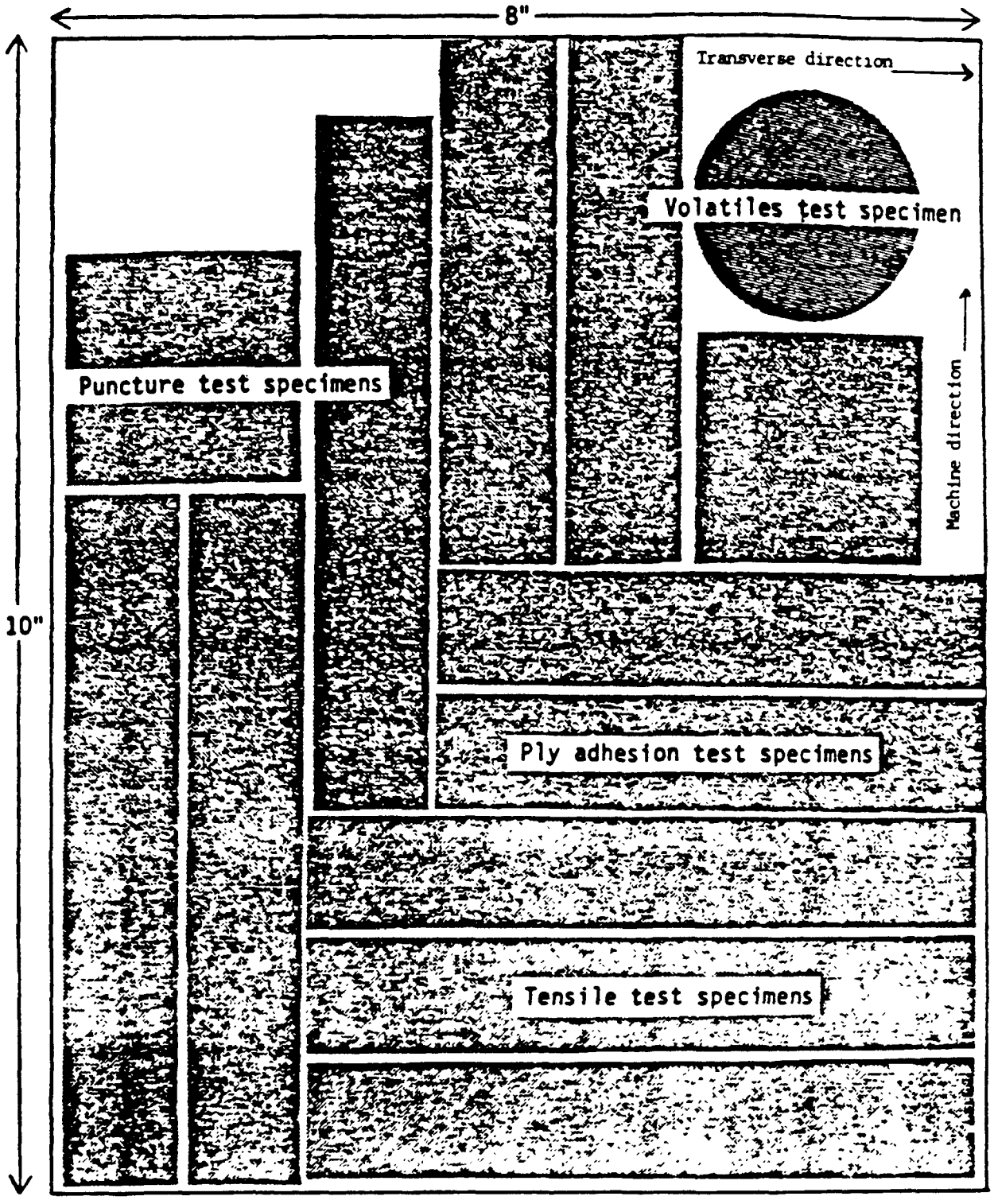
Suggested pattern for cutting test specimens from nonreinforced crosslinked or thermoplastic immersed liner samples.



Not to scale

Figure 2 .

Suggested pattern for cutting test specimens from fabric reinforced immersed liner samples. Note: To avoid edge effects, cut specimens 1/8 - 1/4 inch in from edge of immersed sample.



Not to scale

Figure 3 .

Suggested pattern for cutting test specimens from semicrystalline immersed liner samples. Note: To avoid edge effects, cut specimens 1/8 - 1/4 inch in from edge of immersed sample.

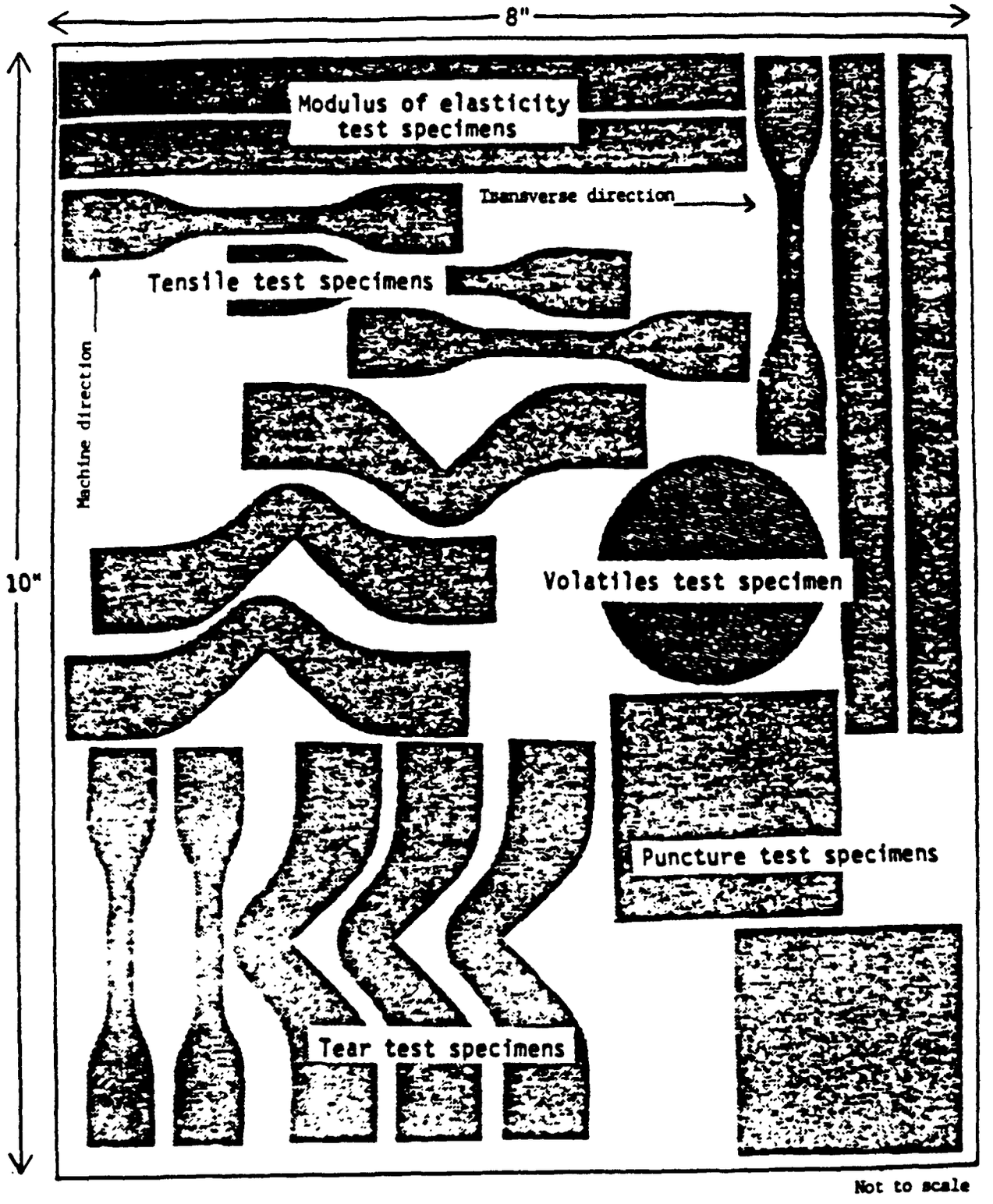
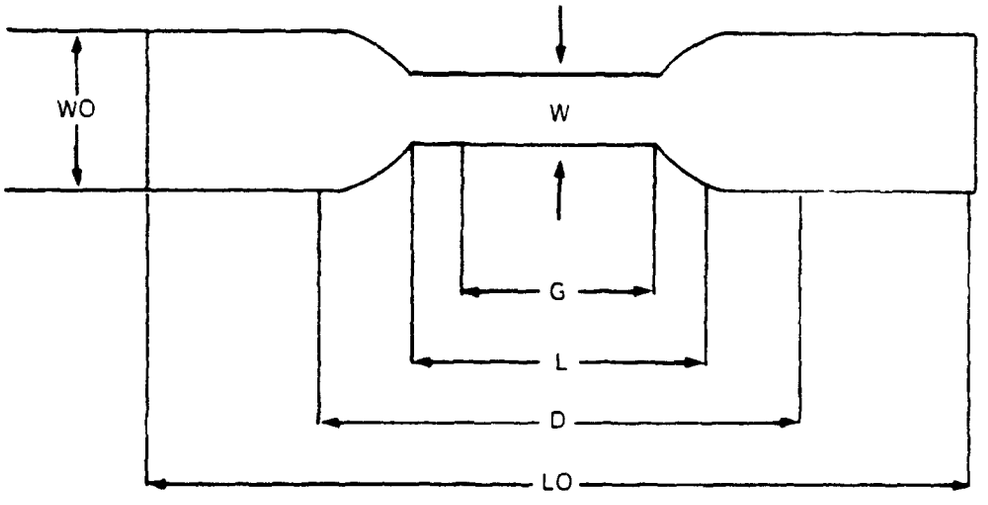


Figure 4.

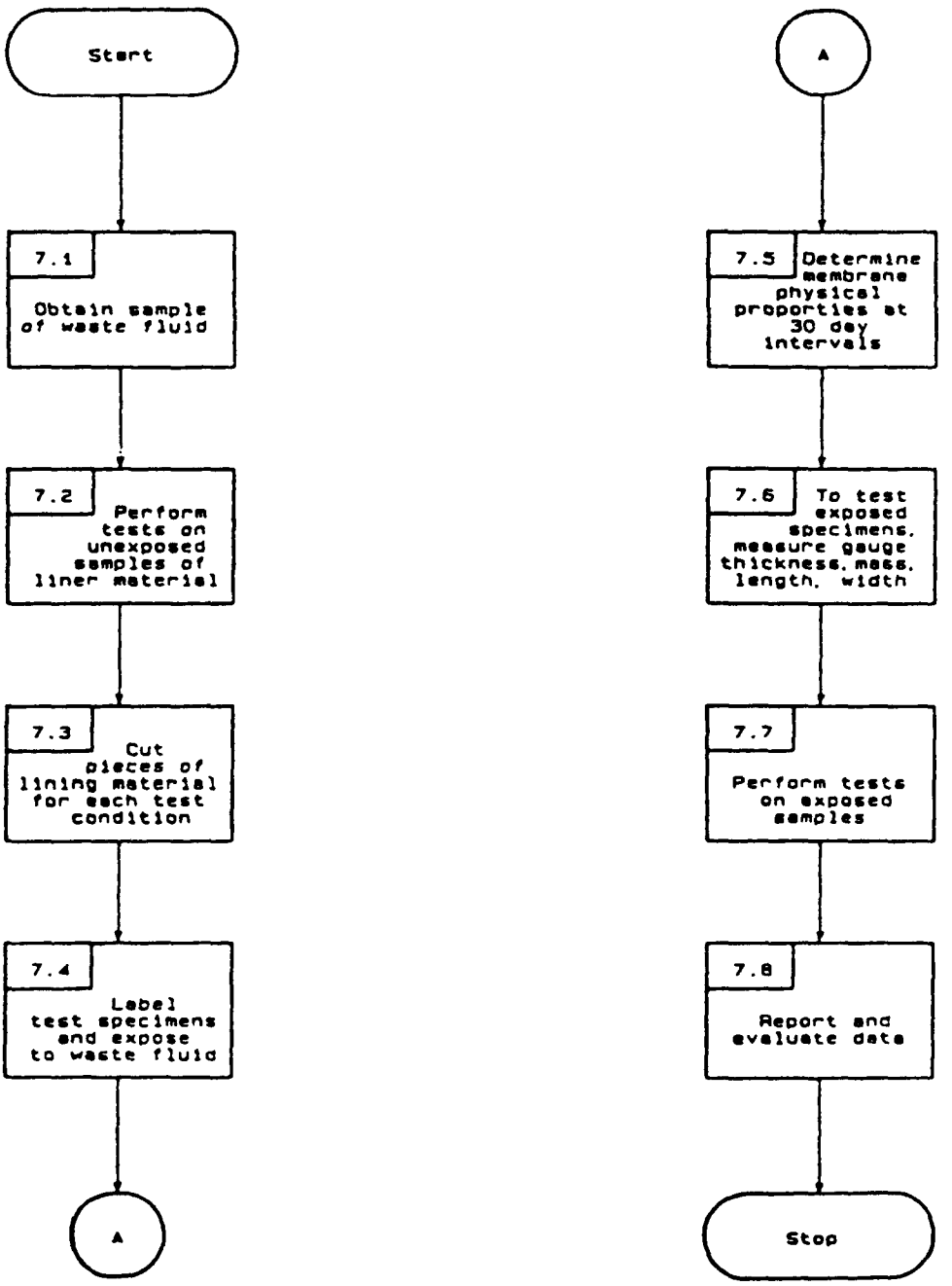
Die for tensile dumbbell (nonreinforced liners) having the following dimensions



W	-	Width of narrow section	0.25 inches
L	-	Length of narrow section	1.25 inches
WO	-	Width overall	0.625 inches
LO	-	Length overall	3.50 inches
G	-	Gage length	1.00 inches
D		Distance between grips	2.00 inches

METHOD 9090

COMPATIBILITY TEST FOR WASTES AND MEMBRANE LINERS



METHOD 9200A

NITRATE

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the analysis of groundwater, drinking, surface, and saline waters, and domestic and industrial wastes. Modifications can be made to remove or correct for turbidity, color, salinity, or dissolved organic compounds in the sample.

1.2 The applicable range of concentration is 0.1 to 2 mg NO_3-N per liter of sample.

2.0 SUMMARY OF METHOD

2.1 This method is based upon the reaction of the nitrate ion with brucine sulfate in a 13 N H_2SO_4 solution at a temperature of 100°C. The color of the resulting complex is measured at 410 nm. Temperature control of the color reaction is extremely critical.

3.0 INTERFERENCES

3.1 Dissolved organic matter will cause an off color in 13 N H_2SO_4 and must be compensated for by additions of all reagents except the brucine-sulfanilic acid reagent. This also applies to natural color, not due to dissolved organics, that is present.

3.2 If the sample is colored or if the conditions of the test cause extraneous coloration, this interference should be corrected by running a concurrent sample under the same conditions but in the absence of the brucine-sulfanilic acid reagent.

3.3 Strong oxidizing or reducing agents cause interference. The presence of oxidizing agents may be determined by a residual chlorine test; reducing agents may be detected with potassium permanganate.

3.3.1 Oxidizing agents' interference is eliminated by the addition of sodium arsenite.

3.3.2 Reducing agents may be oxidized by addition of H_2O_2.

3.4 Ferrous and ferric ion and quadrivalent manganese give slight positive interferences, but in concentrations less than 1 mg/L these are negligible.

3.5 Uneven heating of the samples and standards during the reaction time will result in erratic values. The necessity for absolute control of temperature during the critical color development period cannot be too strongly emphasized.

4.0 APPARATUS AND MATERIALS

4.1 Spectrophotometer or filter photometer suitable for measuring absorbance at 410 nm.

4.2 Sufficient number of 40- to 50-mL glass sample tubes for reagent blanks, standards, and samples.

4.3 Neoprene-coated wire racks to hold sample tubes.

4.4 Water bath suitable for use at 100°C. This bath should contain a stirring mechanism so that all tubes are at the same temperature and should be of sufficient capacity to accept the required number of tubes without a significant drop in temperature when the tubes are immersed.

4.5 Water bath suitable for use at 10-15°C.

4.6 Analytical balance: capable of weighing to 0.0001 g.

4.7 Class A volumetric flasks: 1 L.

4.8 pH Indicator paper.

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 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Sodium chloride solution (30%): Dissolve 300 g NaCl in reagent water and dilute to 1 liter with reagent water.

5.4 Sulfuric acid solution: Carefully add 500 mL concentrated H_2SO_4 to 125 mL reagent water. Cool and keep tightly stoppered to prevent absorption of atmospheric moisture.

5.5 Brucine-sulfanilic acid reagent: Dissolve 1 g brucine sulfate -- $(C_{23}H_{26}N_2O_4)_2 \cdot H_2SO_4 \cdot 7H_2O$ -- and 0.1 g sulfanilic acid ($NH_2C_6H_4SO_3H \cdot H_2O$) in 70 mL hot reagent water. Add 3 mL concentrated HCl, cool, mix, and dilute to 100 mL with reagent water. Store in a dark bottle at 5°C. This solution is stable for several months; the pink color that develops slowly does not affect its usefulness. Mark bottle with warning, **"CAUTION: Brucine Sulfate is toxic; do not ingest."**

5.6 Potassium nitrate stock solution (1.0 mL = 0.1 mg NO_3-N): Dissolve 0.7218 g anhydrous potassium nitrate (KNO_3) in reagent water and dilute to 1

liter in a Class A volumetric flask. Preserve with 2 mL chloroform per liter. This solution is stable for at least 6 months.

5.7 Potassium nitrate standard solution (1.0 mL = 0.001 mg NO_3-N): Dilute 10.0 mL of the stock solution (Step 5.6) to 1 liter in a Class A volumetric flask. This standard solution should be prepared fresh weekly.

5.8 Acetic acid (1+3): Dilute 1 volume glacial acetic acid (CH_3COOH) with 3 volumes of reagent water.

5.9 Sodium hydroxide (1 N): Dissolve 40 g of NaOH in reagent water. Cool and dilute to 1 liter with reagent water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Analysis should be performed within 48 hours. If analysis can be done within 24 hours, the sample should be preserved by refrigeration at 4°C. When samples must be stored for more than 24 hours, they should be preserved with sulfuric acid (2 mL/L concentrated H_2SO_4) and refrigerated.

7.0 PROCEDURE

7.1 Adjust the pH of the samples to approximately 7 with acetic acid (Step 5.8) or sodium hydroxide (Step 5.9). If necessary, filter to remove turbidity. Sulfuric acid can be used in place of acetic acid, if preferred.

7.2 Set up the required number of sample tubes in the rack to handle the reagent blank, standards, and samples. Space tubes evenly throughout the rack to allow for even flow of bath water between the tubes. This should assist in achieving uniform heating of all tubes.

7.3 If it is necessary to correct for color or dissolved organic matter which will cause color on heating, run a set of duplicate samples with all of the reagents, except the brucine-sulfanilic acid.

7.4 Pipet 10.0 mL of standards and samples or an aliquot of the samples diluted to 10.0 mL into the sample tubes.

7.5 If the samples are saline, add 2 mL of the 30% sodium chloride solution (Step 5.3) to the reagent blank, standards, and samples. For freshwater samples, sodium chloride solution may be omitted. Mix contents of tubes by swirling; place rack in cold-water bath (0-10°C).

7.6 Pipet 10.0 mL of sulfuric acid solution (Step 5.4) into each tube and mix by swirling. Allow tubes to come to thermal equilibrium in the cold bath. Be sure that temperatures have equilibrated in all tubes before continuing.

7.6.1 Add 0.5 mL brucine-sulfanilic acid reagent (Step 5.5) to each tube (except the interference control tubes) and carefully mix by swirling; place the rack of tubes in the 100°C water bath for exactly 25 minutes.

CAUTION: Immersion of the tube rack into the bath should not decrease the temperature of the bath by more than 1-2°C. In order to keep this temperature decrease to an absolute minimum, flow of bath water between the tubes should not be restricted by crowding too many tubes into the rack. If color development in the standards reveals discrepancies in the procedure, the operator should repeat the procedure after reviewing the temperature control steps.

7.7 Remove rack of tubes from the hot-water bath, immerse in the cold-water bath, and allow to reach thermal equilibrium (20-25°C).

7.8 Read absorbance against the reagent blank at 410 nm using a 1-cm or longer cell.

7.9 Calculation:

7.9.1 Obtain a standard curve by plotting the absorbance of standards run by the above procedure against mg/L NO_3-N. (The color reaction does not always follow Beer's law.)

7.9.2 Subtract the absorbance of the sample without the brucine-sulfanilic reagent from the absorbance of the sample containing brucine-sulfanilic acid and determine mg/L NO_3-N. Multiply by an appropriate dilution factor if less than 10 mL of sample is taken.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Linear calibration curves must be composed of a minimum of a blank and five standards. A set of standards must be included with each batch of samples.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 After calibrating, verify calibration with an independently prepared check standard.

8.5 Run one matrix spike and matrix spike duplicate sample for every 10 samples. Matrix spikes and matrix spike duplicates are brought through the whole sample preparation and analytical process.

9.0 METHOD PERFORMANCE

9.1 Twenty-seven analysts in fifteen laboratories analyzed natural-water samples containing exact increments of inorganic nitrate, with the following results:

Increment as Nitrogen, Nitrate (mg/L N)	Precision as Standard Deviation (mg/L N)	Accuracy as Bias (%)	Accuracy as Bias (mg/L N)
0.16	0.092	-6.79	-0.01
0.19	0.083	+8.30	+0.02
1.08	0.245	+4.12	+0.04
1.24	0.214	+2.82	+0.04

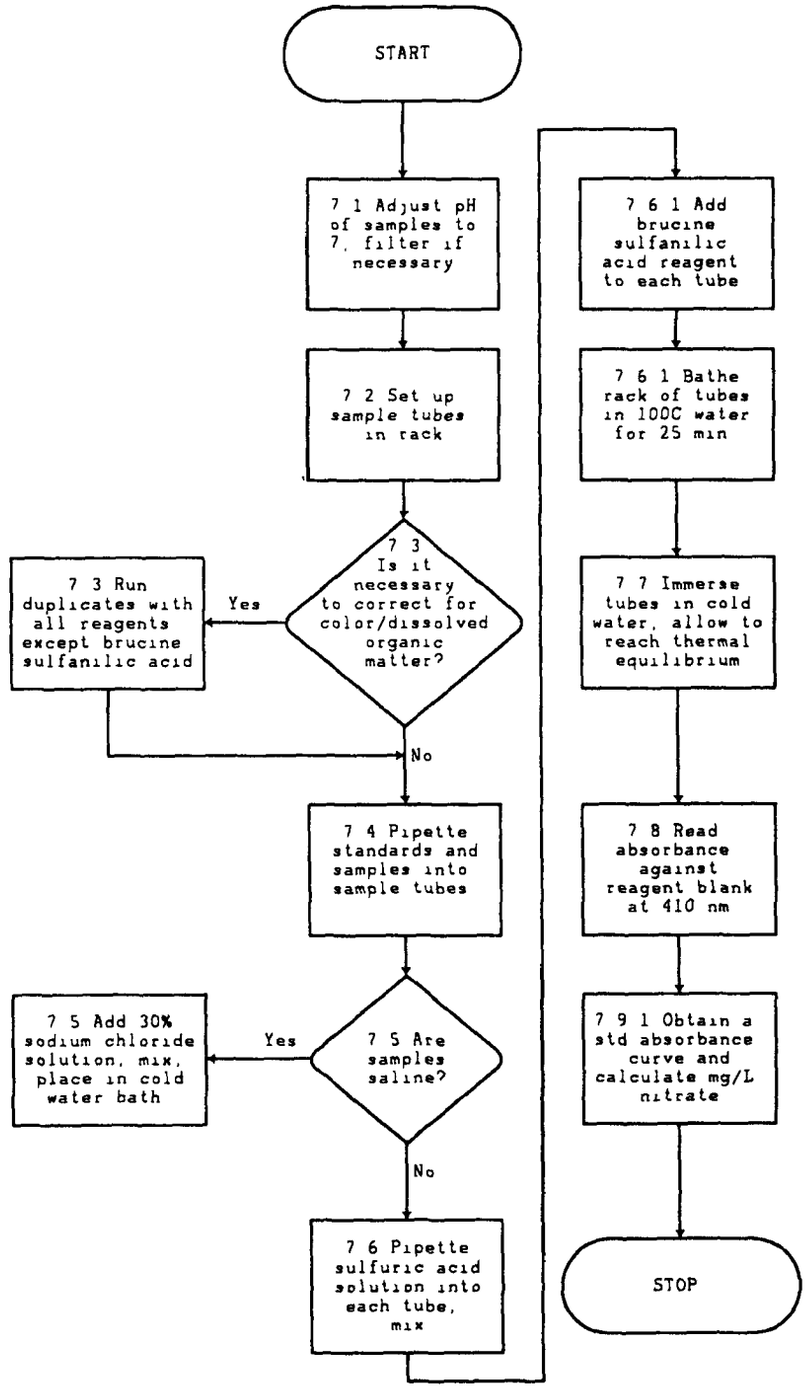
10.0 REFERENCES

1. Annual Book of ASTM Standards, Part 31, "Water," Standard D992-71, p. 363 (1976).

2. Jenkins, D. and L. Medsken, "A Brucine Method for the Determination of Nitrate in Ocean, Estuarine, and Fresh Water," Anal.Chem., 36, p. 610 (1964).

3. Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 427, Method 419D (1975).

NITRATE


START
7 1 Adjust pH of samples to 7, filter if necessary
7 2 Set up sample tubes in rack
7 3 Is it necessary to correct for color/dissolved organic matter?
Yes
7 3 Run duplicates with all reagents except brucine sulfanilic acid
No
7 4 Pipette standards and samples into sample tubes
7 5 Are samples saline?
Yes
7 5 Add 30% sodium chloride solution, mix, place in cold water bath
No
7 6 Pipette sulfuric acid solution into each tube, mix
7 6 1 Add brucine sulfanilic acid reagent to each tube
7 6 1 Bathe rack of tubes in 100C water for 25 min
7 7 Immerse tubes in cold water, allow to reach thermal equilibrium
7 8 Read absorbance against reagent blank at 410 nm
7 9 1 Obtain a std absorbance curve and calculate mg/L nitrate
STOP

METHOD 9252A

CHLORIDE (TITRIMETRIC, MERCURIC NITRATE)

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to ground water, drinking, surface, and saline waters, and domestic and industrial wastes.

1.2 The method is suitable for all concentration ranges of chloride content; however, in order to avoid large titration volume, a sample aliquot containing not more than 10 to 20 mg Cl^- per 50 mL is used.

1.3 Automated titration may be used.

2.0 SUMMARY OF METHOD

2.1 An acidified sample is titrated with mercuric nitrate in the presence of mixed diphenylcarbazone-bromophenol blue indicator. The end point of the titration is the formation of the blue-violet mercury diphenylcarbazone complex.

3.0 INTERFERENCES

3.1 Anions and cations at concentrations normally found in surface waters do not interfere. However, at the higher concentration often found in certain wastes, problems may occur.

3.2 Sulfite interference can be eliminated by oxidizing the 50 mL of sample solution with 0.5-1 mL of H_2O_2.

4.0 APPARATUS AND MATERIALS

4.1 Standard laboratory titrimetric equipment, including 1 mL or 5 mL microburet with 0.01 mL gradations.

4.2 Class A volumetric flasks: 1 L and 100 mL.

4.3 pH Indicator paper.

4.4 Analytical balance: capable of weighing to 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 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Standard sodium chloride solution, 0.025 N: Dissolve 1.4613 g ± 0.0002 g of sodium chloride (dried at 600°C for 1 hr) in chloride-free water in a 1 liter Class A volumetric flask and dilute to the mark with reagent water.

5.4 Nitric acid (HNO_3) solution: Add 3.0 mL concentrated nitric acid to 997 mL of reagent water ("3 + 997" solution).

5.5 Sodium hydroxide (NaOH) solution (10 g/L): Dissolve approximately 10 g of NaOH in reagent water and dilute to 1 L with reagent water.

5.6 Hydrogen peroxide (H_2O_2): 30%.

5.7 Hydroquinone solution (10 g/L): Dissolve 1 g of purified hydroquinone in reagent water in a 100 mL Class A volumetric flask and dilute to the mark.

5.8 Mercuric nitrate titrant (0.141 N): Dissolve 24.2 g $Hg(NO_3)_2 \cdot H_2O$ in 900 mL of reagent water acidified with 5.0 mL concentrated HNO_3 in a 1 liter volumetric flask and dilute to the mark with reagent water. Filter, if necessary. Standardize against standard sodium chloride solution (Step 5.3) using the procedures outlined in Section 7.0. Adjust to exactly 0.141 N and check. Store in a dark bottle. A 1.00 mL aliquot is equivalent to 5.00 mg of chloride.

5.9 Mercuric nitrate titrant (0.025 N): Dissolve 4.2830 g $Hg(NO_3)_2 \cdot H_2O$ in 50 mL of reagent water acidified with 0.05 mL of concentrated HNO_3 (sp. gr. 1.42) in a 1 liter volumetric flask and dilute to the mark with reagent water. Filter, if necessary. Standardize against standard sodium chloride solution (Step 5.3) using the procedures outlined in Section 7.0. Adjust to exactly 0.025 N and check. Store in a dark bottle.

5.10 Mercuric nitrate titrant (0.0141 N): Dissolve 2.4200 g $Hg(NO_3)_2 \cdot H_2O$ in 25 mL of reagent water acidified with 0.25 mL of concentrated HNO_3 (sp. gr. 1.42) in a 1 liter Class A volumetric flask and dilute to the mark with reagent water. Filter, if necessary. Standardize against standard sodium chloride solution (Step 5.3) using the procedures outlined in Section 7.0. Adjust to exactly 0.0141 N and check. Store in a dark bottle. A 1 mL aliquot is equivalent to 500 μg of chloride.

5.11 Mixed indicator reagent: Dissolve 0.5 g crystalline diphenylcarbazone and 0.05 g bromophenol blue powder in 75 mL 95% ethanol in a 100 mL Class A volumetric flask and dilute to the mark with 95% ethanol. Store in brown bottle and discard after 6 mo.

5.12 Alphazurine indicator solution: Dissolve 0.005 g of alphazurine blue-green dye in 95% ethanol or isopropanol in 100 mL Class A volumetric flask and dilute to the mark with 95% ethanol or isopropanol.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 There are no special requirements for preservation.

7.0 PROCEDURE

7.1 Place 50 mL of sample in a vessel for titration. If the concentration is greater than 20 mg/L chloride, use 0.141 N mercuric nitrate titrant (Step 5.8) in Step 7.6, or dilute sample with reagent water. If the concentration is less than 2.5 mg/L of chloride, use 0.0141 N mercuric nitrate titrant (Step 5.10) in Step 7.6. Using a 1 mL or 5 mL microburet, determine an indicator blank on 50 mL chloride-free water using Step 7.6. If the concentration is less than 0.1 mg/L of chloride, concentrate an appropriate volume to 50 mL.

7.2 Add 5 to 10 drops of mixed indicator reagent (Step 5.11); shake or swirl solution.

7.3 If a blue-violet or red color appears, add HNO_3 solution (Step 5.4) dropwise until the color changes to yellow. Proceed to Step 7.5.

7.4 If a yellow or orange color forms immediately on addition of the mixed indicator, add NaOH solution (Step 5.5) dropwise until the color changes to blue-violet; then add HNO_3 solution (Step 5.4) dropwise until the color changes to yellow.

7.5 Add 1 mL excess HNO_3 solution (Step 5.4).

7.6 Titrate with 0.025 N mercuric nitrate titrant (Step 5.9) until a blue-violet color persists throughout the solution. If volume of titrant exceeds 10 mL or is less than 1 mL, use the 0.141 N or 0.0141 N mercuric nitrate solutions, respectively. If necessary, take a small sample aliquot. Alphazurine indicator solution (Step 5.12) may be added with the indicator to sharpen the end point. This will change color shades. Practice runs should be made.

Note: The use of indicator modifications and the presence of heavy metal ions can change solution colors without affecting the accuracy of the determination. For example, solutions containing alphazurine may be bright blue when neutral, grayish purple when basic, blue-green when acidic, and blue-violet at the chloride end point. Solutions containing about 100 mg/L nickel ion and normal mixed indicator are purple when neutral, green when acidic, and gray at the chloride end point. When applying this method to samples that contain colored ions or that require modified indicator, it is recommended that the operator become familiar with the specific color changes involved by experimenting with solutions prepared as standards for comparison of color effects.

7.6.1 If chromate is present at <100 mg/L and iron is not present, add 5-10 drops of alphazurine indicator solution (Step 5.12) and acidify to a pH of 3 (indicating paper). End point will then be an olive-purple color.

7.6.2 If chromate is present at >100 mg/L and iron is not present, add 2 mL of fresh hydroquinone solution (Step 5.7).

7.6.3 If ferric ion is present use a volume containing no more than 2.5 mg of ferric ion or ferric ion plus chromate ion. Add 2 mL fresh hydroquinone solution (Step 5.7).

7.6.4 If sulfite ion is present, add 0.5 mL of H_2O_2 solution (Step 5.6) to a 50 mL sample and mix for 1 min.

7.7 Calculation:

$$\text{mg chloride/liter} = \frac{(A - B)N \times 35{,}450}{\text{mL of sample}}$$

where:

A = mL titrant for sample;

B = mL titrant for blank; and

N = normality of mercuric nitrate titrant.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection. Refer to Chapter One for specific quality control guidelines.

8.2 Analyze a standard reference material to ensure that correct procedures are being followed and that all standard reagents have been prepared properly.

8.3 Employ a minimum of one blank per analytical batch or twenty samples, whichever is more frequent, to determine if contamination has occurred.

8.4 Run one matrix spike and matrix duplicate every analytical batch or twenty samples, whichever is more frequent. Matrix spikes and duplicates are brought through the whole sample preparation and analytical process.

9.0 METHOD PERFORMANCE

9.1 Water samples--A total of 42 analysts in 18 laboratories analyzed synthetic water samples containing exact increments of chloride, with the results shown in Table 1.

In a single laboratory, using surface water samples at an average concentration of 34 mg Cl^-/L, the standard deviation was $\pm$1.0.

A synthetic unknown sample containing 241 mg/L chloride, 108 mg/L Ca, 82 mg/L Mg, 3.1 mg/L K, 19.9 mg/L Na, 1.1 mg/L nitrate N, 0.25 mg/L nitrate N, 259 mg/L sulfate and 42.5 mg/L total alkalinity (contributed by $NaHCO_3$) in reagent water was analyzed in 10 laboratories by the mercurimetric method, with a relative standard deviation of 3.3% and a relative error of 2.9%.

9.2 Oil combustates--These data are based on 34 data points obtained by five laboratories who each analyzed four used crankcase oils and three fuel oil blends with crankcase oil in duplicate. The samples were combusted using Method 5050. A data point represents one duplicate analysis of a sample. One data point was judged to be an outlier and was not included in these results.

9.2.1 Precision and bias.

9.2.1.1 Precision. The precision of the method as determined by the statistical examination of interlaboratory test results is as follows:

Repeatability - The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would exceed, in the long run, in the normal and correct operation of the test method, the following values only in 1 case in 20 (see Table 2):

$$Repeatability = 7.61\sqrt{x}*$$

*where x is the average of two results in μg/g.

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would exceed, in the long run, the following values only in 1 case in 20:

$$Reproducibility = 20.02\sqrt{x}*$$

*where x is the average value of two results in μg/g.

9.2.1.2 Bias. The bias of this method varies with concentration, as shown in Table 3:

Bias = Amount found - Amount expected

10.0 REFERENCES

1. Annual Book of ASTM Standards, Part 31, "Water," Standard D512-67, Method A, p. 270 (1976).

2. Standard Methods for the Examination of Water and Wastewater, 15th ed., (1980).

3. U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020 (1983), Method 325.3.

TABLE 1. ANALYSES OF SYNTHETIC WATER SAMPLES FOR CHLORIDE BY MERCURIC NITRATE METHOD

Increment as Chloride (mg/L)	Precision as Standard Deviation (mg/L)	Accuracy as Bias (%)	Accuracy as Bias (mg/L)
17	1.54	+2.16	+0.4
18	1.32	+3.50	+0.6
91	2.92	+0.11	+0.1
97	3.16	-0.51	-0.5
382	11.70	-0.61	-2.3
398	11.80	-1.19	-4.7

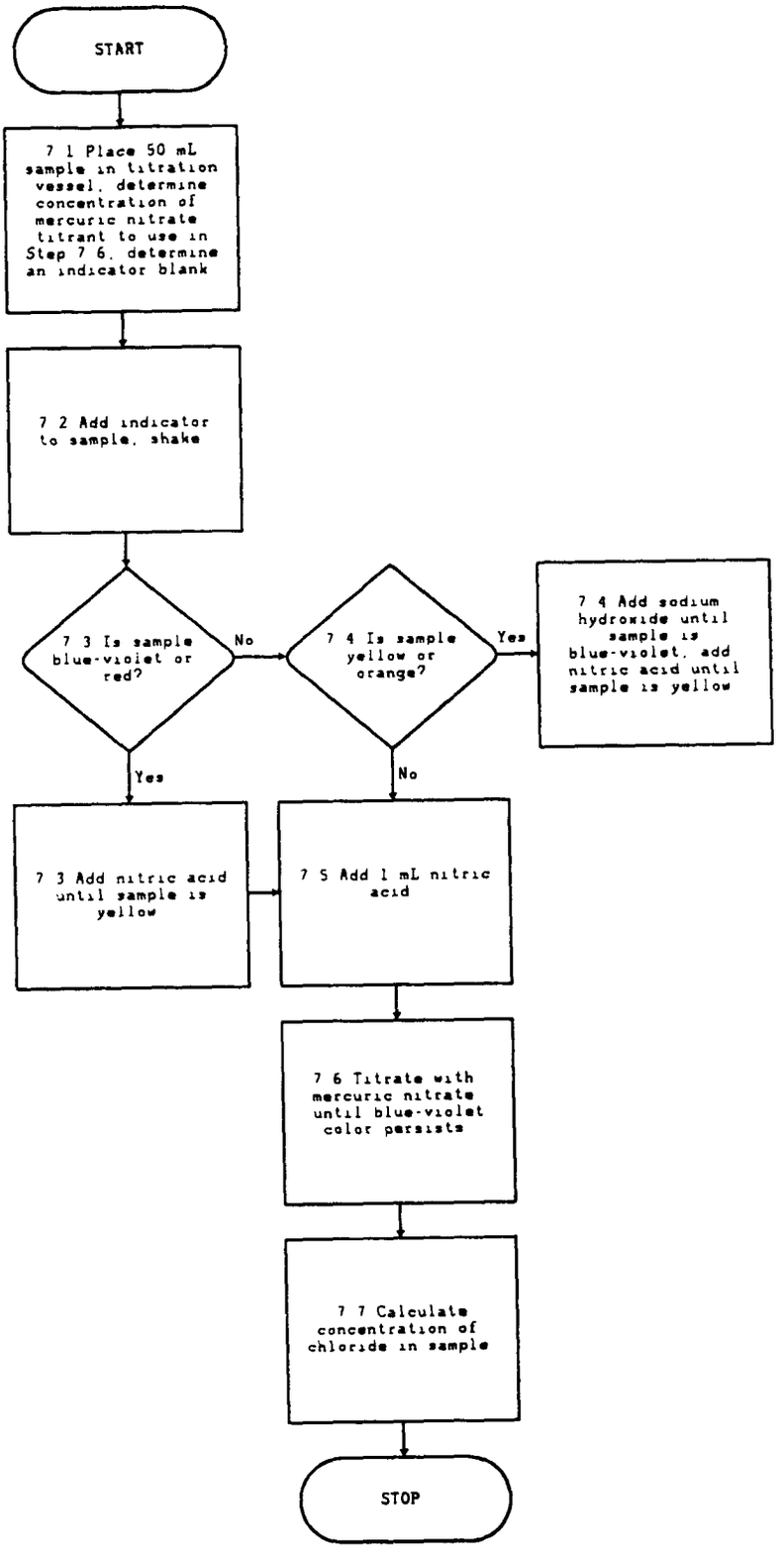
TABLE 2. REPEATABILITY AND REPRODUCIBILITY FOR CHLORINE IN USED OILS BY BOMB OXIDATION AND MERCURIC NITRATE TITRATION

Average value, µg/g	Repeatability, µg/g	Reproducibility, µg/g
500	170	448
1,000	241	633
1,500	295	775
2,000	340	895
2,500	381	1,001
3,000	417	1,097

TABLE 3. RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS BY BOMB OXIDATION AND MERCURIC NITRATE TITRATION

Amount expected, µg/g	Amount found, µg/g	Bias, µg/g	Percent bias
320	460	140	+44
480	578	98	+20
920	968	48	+ 5
1,498	1,664	166	+11
1,527	1,515	- 12	- 1
3,029	2,809	-220	- 7
3,045	2,710	-325	-11

METHOD 9252
CHLORIDE (TITRIMETRIC, MERCURIC NITRATE)



Revision 1
November 1992

METHOD 9253

CHLORIDE (TITRIMETRIC, SILVER NITRATE)

1.0 SCOPE AND APPLICATION

1.1 This method is intended primarily for oxygen bomb combustates or other waters where the chloride content is 5 mg/L or more and where interferences such as color or high concentrations of heavy metal ions render Method 9252 impracticable.

2.0 SUMMARY OF METHOD

2.1 Water adjusted to pH 8.3 is titrated with silver nitrate solution in the presence of potassium chromate indicator. The end point is indicated by persistence of the orange-silver chromate color.

3.0 INTERFERENCES

3.1 Bromide, iodide, and sulfide are titrated along with the chloride. Orthophosphate and polyphosphate interfere if present in concentrations greater than 250 and 25 mg/L, respectively. Sulfite and objectionable color or turbidity must be eliminated. Compounds that precipitate at pH 8.3 (certain hydroxides) may cause error by occlusion.

3.2 Residual sodium carbonate from the bomb combustion may react with silver nitrate to produce the precipitate, silver carbonate. This competitive reaction may interfere with the visual detection of the end point. To remove carbonate from the test solution, add small quantities of sulfuric acid followed by agitation.

4.0 APPARATUS AND MATERIALS

4.1 Standard laboratory titrimetric equipment, including 1 mL or 5 mL microburet with 0.01 mL gradations, and 25 mL buret.

4.2 Analytical balance: capable of weighing to 0.0001 g.

4.3 Class A volumetric flask: 1 L.

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 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Hydrogen peroxide (30%), H_2O_2.

5.4 Phenolphthalein indicator solution (10 g/L).

5.5 Potassium chromate indicator solution. Dissolve 50 g of potassium chromate (K_2CrO_4) in 100 mL of reagent water and add silver nitrate ($AgNO_3$) until a slightly red precipitate is produced. Allow the solution to stand, protected from light, for at least 24 hours after the addition of $AgNO_3$. Then filter the solution to remove the precipitate and dilute to 1 L with reagent water.

5.6 Silver nitrate solution, standard (0.025N). Crush approximately 5 g of silver nitrate ($AgNO_3$) crystals and dry to constant weight at 40°C. Dissolve 4.2473 $\pm$ 0.0002 g of the crushed, dried crystals in reagent water and dilute to 1 L with reagent water. Standardize against the standard NaCl solution, using the procedure given in Section 7.0.

5.7 Sodium chloride solution, standard (0.025N). Dissolve 1.4613 g $\pm$ 0.0002 g of sodium chloride (dried at 600°C for 1 hr) in chloride-free water in a 1 liter Class A volumetric flask and dilute to the mark with reagent water.

5.8 Sodium hydroxide solution (0.25N). Dissolve approximately 10 g of NaOH in reagent water and dilute to 1 L with reagent water.

5.9 Sulfuric acid (1:19), H_2SO_4. Carefully add 1 volume of concentrated sulfuric acid to 19 volumes of reagent water, while mixing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 There are no special requirements for preservation.

7.0 PROCEDURE

7.1 Pour 50 mL or less of the sample, containing between 0.25 mg and 20 mg of chloride ion, into a white porcelain container. Dilute to approximately 50 mL with reagent water, if necessary. Adjust the pH to the phenolphthalein end point (pH 8.3) using H_2SO_4 (Step 5.9) or NaOH solution (Step 5.8).

7.2 Add approximately 1.0 mL of K_2CrO_4 indicator solution and mix. Add standard $AgNO_3$ solution dropwise from a 25 mL buret until the orange color persists throughout the sample when illuminated with a yellow light or viewed with yellow goggles.

7.3 Repeat the procedure described in Steps 7.1 and 7.2 using exactly one-half as much original sample, diluted to 50 mL with halide-free water.

7.4 If sulfite ion is present, add 0.5 mL of H_2O_2 to the samples described in Steps 7.2 and 7.3 and mix for 1 minute. Adjust the pH, then proceed as described in Steps 7.2 and 7.3.

7.5 Calculation

7.5.1 Calculate the chloride ion concentration in the original sample, in milligrams per liter, as follows:

$$\text{Chloride (mg/L)} = [(V_1 - V_2) \times N \times 71{,}000] / S$$

where:

V_1 = Milliliters of standard $AgNO_3$ solution added in titrating the sample prepared in Step 7.1.

V_2 = Milliliters of standard $AgNO_3$ solution added in titrating the sample prepared in Step 7.3.

N = Normality of standard $AgNO_3$ solution.

S = Milliliters of original sample in the 50 mL test sample prepared in Step 7.1.

71,000 = 2 x 35,500 mg Cl^-/equivalent, since $V_1 \sim 2V_2$.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection. Refer to Chapter One for specific quality control guidelines.

8.2 Analyze a standard reference material to ensure that correct procedures are being followed and that all standard reagents have been prepared properly.

8.3 Employ a minimum of one blank per analytical batch or twenty samples, whichever is more frequent, to determine if contamination has occurred.

8.4 Run one matrix spike and matrix duplicate every analytical batch or twenty samples, whichever is more frequent. Matrix spikes and duplicates are brought through the whole sample preparation and analytical process.

9.0 METHOD PERFORMANCE

9.1 These data are based on 32 data points obtained by five laboratories who each analyzed four used crankcase oils and three fuel oil blends with crankcase in duplicate. The samples were combusted using Method 5050. A data point represents one duplicate analysis of a sample. Three data points were judged to be outliers and were not included in these results.

9.1.1 Precision. The precision of the method as determined by the statistical examination of interlaboratory test results is as follows:

Repeatability - The difference between successive results obtained by the same operator with the same apparatus under constant operating

conditions on identical test material would exceed, in the long run, in the normal and correct operation of the test method, the following values only in 1 case in 20 (see Table 1):

$$Repeatability = 0.36\ x^*$$

*where x is the average of two results in µg/g.

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would exceed, in the long run, the following values only in 1 case in 20:

$$Reproducibility = 0.71\ x^*$$

*where x is the average of two results in µg/g.

9.1.2 Bias. The bias of this method varies with concentration, as shown in Table 2:

Bias = Amount found - Amount expected

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

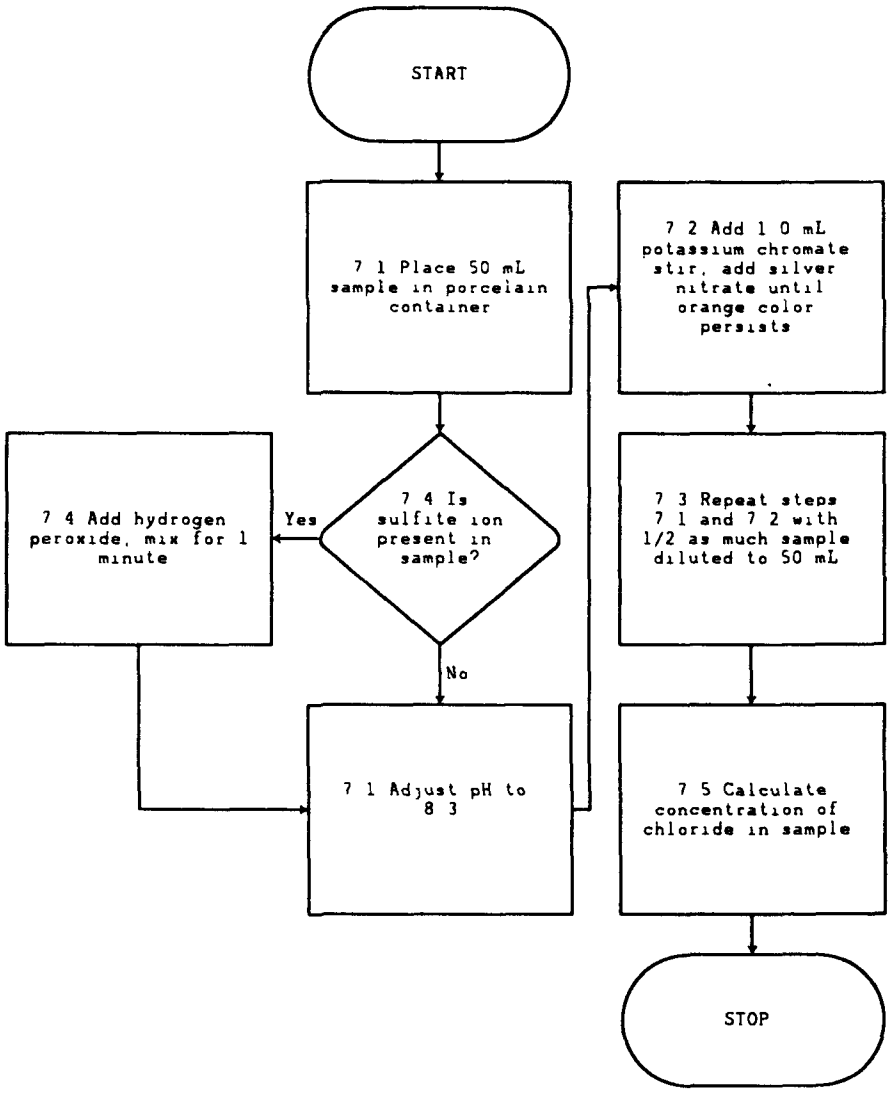
3. Gaskill, A.; Estes, E. D.; Hardison, D. L.; and Myers, L. E. "Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels," Prepared for U.S. Environmental Protection Agency, Office of Solid Waste. EPA Contract No. 68-01-7075, WA 80. July 1988.

TABLE 1.
REPEATABILITY AND REPRODUCIBILITY FOR CHLORINE IN USED OILS BY BOMB OXIDATION AND SILVER NITRATE TITRATION

Average value (μg/g)	Repeatability (μg/g)	Reproducibility (μg/g)
500	180	355
1,000	360	710
1,500	540	1,065
2,000	720	1,420
2,500	900	1,775
3,000	1,080	2,130

TABLE 2.
RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS BY BOMB OXIDATION AND SILVER NITRATE TITRATION

Amount expected (μg/g)	Amount found (μg/g)	Bias, (μg/g)	Percent bias
320	645	325	+102
480	665	185	+39
920	855	-65	-7
1,498	1,515	17	+1
1,527	1,369	-158	-10
3,029	2,570	-460	-15
3,045	2,683	-362	-12


START
7 1 Place 50 mL sample in porcelain container
7 2 Add 1 0 mL potassium chromate stir, add silver nitrate until orange color persists
7 4 Is sulfite ion present in sample?
Yes
7 4 Add hydrogen peroxide, mix for 1 minute
No
7 3 Repeat steps 7 1 and 7 2 with 1/2 as much sample diluted to 50 mL
7 1 Adjust pH to 8 3
7 5 Calculate concentration of chloride in sample
STOP

METHOD 1310

EXTRACTION PROCEDURE (EP) TOXICITY TEST METHOD AND STRUCTURAL INTEGRITY TEST

1.0 SCOPE AND APPLICATION

1.1 This method is employed to determine whether a waste exhibits the characteristic of Extraction Procedure Toxicity (see Chapter 7, Step 7.4 for interim guidance).

1.2 The procedure may also be used to simulate the leaching which a waste will undergo if disposed of in a sanitary landfill. Method 1310 is applicable to liquid, solid, and multiphase samples.

2.0 SUMMARY OF METHOD

2.1 If a representative sample of the waste contains > 0.5% solids, the solid phase of the sample is ground to pass a 9.5 mm sieve and extracted with deionized water which is maintained at a pH of 5 $\pm$ 0.2, with acetic acid. Wastes that contain < 0.5% solids are not subjected to extraction but are directly analyzed. Monolithic wastes which can be formed into a cylinder 3.3 cm (dia) x 7.1 cm, or from which such a cylinder can be formed which is representative of the waste, may be evaluated using the Structural Integrity Procedure instead of being ground to pass a 9.5-mm sieve.

3.0 INTERFERENCES

3.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.0 APPARATUS AND MATERIALS

4.1 Extractor - For purposes of this test, an acceptable extractor is one that will impart sufficient agitation to the mixture to (1) prevent stratification of the sample and extraction fluid and (2) ensure that all sample surfaces are continuously brought into contact with well-mixed extraction fluid. Examples of suitable extractors are shown in Figures 1-3 of this method and are available from: Associated Designs & Manufacturing Co., Alexandria, Virginia; Glas-Col Apparatus Co., Terre Haute, Indiana; Millipore, Bedford, Massachusetts; and Rexnard, Milwaukee, Wisconsin.

4.2 pH meter or pH controller - Accurate to 0.05 pH units with temperature compensation.

4.3 Filter holder - Capable of supporting a 0.45-um filter membrane and of withstanding the pressure needed to accomplish separation. Suitable filter holders range from simple vacuum units to relatively complex systems that can exert up to 5.3 kg/cm^3 (75 psi) of pressure. The type of filter holder used depends upon the properties of the mixture to be filtered. Filter holders known to EPA and deemed suitable for use are listed in Table 1.

4.4 Filter membrane - Filter membrane suitable for conducting the required filtration shall be fabricated from a material that (1) is not physically changed by the waste material to be filtered and (2) does not absorb or leach the chemical species for which a waste's EP extract will be analyzed. Table 2 lists filter media known to the agency to be suitable for solid waste testing.

4.4.1 In cases of doubt about physical effects on the filter, contact the filter manufacturer to determine if the membrane or the prefilter is adversely affected by the particular waste. If no information is available, submerge the filter in the waste's liquid phase. A filter that undergoes visible physical change after 48 hours (i.e. curls, dissolves, shrinks, or swells) is unsuitable for use.

4.4.2 To test for absorbtion or leaching by the filter:

4.4.2.1 Prepare a standard solution of the chemical species of interest.

4.4.2.2 Analyze the standard for its concentration of the chemical species.

4.4.2.3 Filter the standard and reanalyze. If the concentration of the filtrate differs from that of the original standard, then the filter membrane leaches or absorbs one or more of the chemical species and is not usable in this test method.

4.5 Structural integrity tester - A device meeting the specifications shown in Figure 4 and having a 3.18-cm (1.25-in) diameter hammer weighing 0.33 kg (0.73 lb) with a free fall of 15.24 cm (6 in) shall be used. This device is available from Associated Design and Manufacturing Company, Alexandria, VA 22314, as Part No. 125, or it may be fabricated to meet these specifications.

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 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Acetic acid (0.5N), CH_3COOH. This can be made by diluting concentrated glacial acetic acid (17.5N) by adding 57 mL glacial acetic acid to 1,000 mL of water and diluting to 2 liters. The glacial acetic acid should be of high purity and monitored for impurities.

5.4 Analytical standards should be prepared according to the applicable analytical methods.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Preservatives must not be added to samples.

6.3 Samples can be refrigerated if it is determined that refrigeration will not affect the integrity of the sample.

7.0 PROCEDURE

7.1 If the waste does not contain any free liquid, go to Step 7.9. If the sample is liquid or multiphase, continue as follows. Weigh filter membrane and prefilter to $\pm$ 0.01 g. Handle membrane and prefilters with blunt curved-tip forceps or vacuum tweezers, or by applying suction with a pipet.

7.2 Assemble filter holder, membranes, and prefilters following the manufacturer's instructions. Place the 0.45-um membrane on the support screen and add prefilters in ascending order of pore size. Do not prewet filter membrane.

7.3 Weigh out a representative subsample of the waste (100 g minimum).

7.4 Allow slurries to stand, to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration.

7.5 Wet the filter with a small portion of the liquid phase from the waste or from the extraction mixture. Transfer the remaining material to the filter holder and apply vacuum or gentle pressure (10-15 psi) until all liquid passes through the filter. Stop filtration when air or pressurizing gas moves through the membrane. If this point is not reached under vacuum or gentle pressure, slowly increase the pressure in 10-psi increments to 75 psi. Halt filtration when liquid flow stops. This liquid will constitute part or all of the extract (refer to Step 7.16). The liquid should be refrigerated until time of analysis.

NOTE: Oil samples or samples containing oil are treated in exactly the same way as any other sample. The liquid portion of the sample is filtered and treated as part of the EP extract. If the liquid portion of the sample will not pass through the filter (usually the case with heavy oils or greases), it should be carried through the EP extraction as a solid.

7.6 Remove the solid phase and filter media and, while not allowing them to dry, weigh to $\pm$ 0.01 g. The wet weight of the residue is determined by calculating the weight difference between the weight of the filters (Step 7.1) and the weight of the solid phase and the filter media.

7.7 The waste will be handled differently from this point on, depending on whether it contains more or less than 0.5% solids. If the sample appears to have < 0.5% solids, determine the percent solids exactly (see Note below) by the following procedure:

7.7.1 Dry the filter and residue at 80°C until two successive weighings yield the same value.

7.7.2 Calculate the percent solids, using the following equation:

$$\% \text{ solids} = \frac{\text{weight of filtered solid and filters - tared weight of filters}}{\text{initial weight of waste material}} \times 100$$

NOTE: This procedure is used only to determine whether the solid must be extracted or whether it can be discarded unextracted. It is not used in calculating the amount of water or acid to use in the extraction step. Do not extract solid material that has been dried at 80°C. A new sample will have to be used for extraction if a percent solids determination is performed.

7.8 If the solid constitutes < 0.5% of the waste, discard the solid and proceed immediately to Step 7.17, treating the liquid phase as the extract.

7.9 The solid material obtained from Step 7.5 and all materials that do not contain free liquids should be evaluated for particle size. If the solid material has a surface area per g of material $\geq$ 3.1 cm^2 or passes through a 9.5-mm (0.375-in.) standard sieve, the operator should proceed to Step 7.11. If the surface area is smaller or the particle size larger than specified above, the solid material is prepared for extraction by crushing, cutting, or grinding the material so that it passes through a 9.5-mm (0.375-in.) sieve or, if the material is in a single piece, by subjecting the material to the "Structural Integrity Procedure" described in Step 7.10.

7.10 Structural Integrity Procedure (SIP)

7.10.1 Cut a 3.3-cm diameter by 7.1-cm long cylinder from the waste material. If the waste has been treated using a fixation process, the waste may be cast in the form of a cylinder and allowed to cure for 30 days prior to testing.

7.10.2 Place waste into sample holder and assemble the tester. Raise the hammer to its maximum height and drop. Repeat 14 additional times.

7.10.3 Remove solid material from tester and scrape off any particles adhering to sample holder. Weigh the waste to the nearest 0.01 g and transfer it to the extractor.

7.11 If the sample contains > 0.5% solids, use the wet weight of the solid phase (obtained in Step 7.6) to calculate the amount of liquid and acid to employ for extraction by using the following equation:

$$W = W_f - W_t$$

where :

W = Wet weight in g of solid to be charged to extractor.

W_f = Wet weight in g of filtered solids and filter media.

W_t = Weight in g of tared filters.

If the waste does not contain any free liquids, 100 g of the material will be subjected to the extraction procedure.

7.12 Place the appropriate amount of material (refer to Step 7.11) into the extractor and add 16 times its weight with water.

7.13 After the solid material and water are placed in the extractor, the operator should begin agitation and measure the pH of the solution in the extractor. If the pH is > 5.0, the pH of the solution should be decreased to 5.0 $\pm$ 0.2 by adding 0.5N acetic acid. If the pH is $\leq$ 5.0, no acetic acid should be added. The pH of the solution should be monitored, as described below, during the course of the extraction, and, if the pH rises above 5.2, 0.5N acetic acid should be added to bring the pH down to 5.0 $\pm$ 0.2. However, in no event shall the aggregate amount of acid added to the solution exceed 4 mL of acid per g of solid. The mixture should be agitated for 24 hours and maintained at 20-40°C (68-104°F) during this time. It is recommended that the operator monitor and adjust the pH during the course of the extraction with a device such as the Type 45-A pH Controller, manufactured by Chemtrix, Inc., Hillsboro, Oregon 97123, or its equivalent, in conjunction with a metering pump and reservoir of 0.5N acetic acid. If such a system is not available, the following manual procedure shall be employed.

7.13.1 A pH meter should be calibrated in accordance with the manufacturer's specifications.

7.13.2 The pH of the solution should be checked, and, if necessary, 0.5 N acetic acid should be manually added to the extractor until the pH reaches 5.0 $\pm$ 0.2. The pH of the solution should be adjusted at 15-, 30-, and 60-minute intervals, moving to the next longer interval if the pH does not have to be adjusted > 0.5 pH units.

7.13.3 The adjustment procedure should be continued for at least 6 hours.

7.13.4 If, at the end of the 24-hour extraction period, the pH of the solution is not below 5.2 and the maximum amount of acid (4 mL per g of solids) has not been added, the pH should be adjusted to 5.0 $\pm$ 0.2 and the extraction continued for an additional 4 hours, during which the pH should be adjusted at 1-hour intervals.

7.14 At the end of the extraction period, water should be added to the extractor in an amount determined by the following equation:

$$V = (20)(W) - 16(W) - A$$

where:

V = mL water to be added.

W = Weight in g of solid charged to extractor.

A = mL of 0.5N acetic acid added during extraction.

7.15 The material in the extractor should be separated into its component liquid and solid phases in the following manner:

7.15.1 Allow slurries to stand to permit the solid phase to settle (wastes that are slow to settle may be centrifuged prior to filtration) and set up the filter apparatus (refer to Steps 4.3 and 4.4).

7.15.2 Wet the filter with a small portion of the liquid phase from the waste or from the extraction mixture. Transfer the remaining material to the filter holder and apply vacuum or gentle pressure (10-15 psi) until all liquid passes through the filter. Stop filtration when air or pressurizing gas moves through the membrane. If this point is not reached under vacuum or gentle pressure, slowly increase the pressure in 10-psi increments to 75 psi. Halt filtration when liquid flow stops.

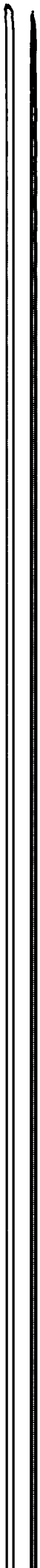
7.16 The liquids resulting from Steps 7.5 and 7.15 should be combined. This combined liquid (or waste itself, if it has < 0.5% solids, as noted in Step 7.8) is the extract and should be analyzed for the presence of any of the contaminants specified in 40 CFR Part 261.24 using the analytical procedures as designated in Step 7.17.

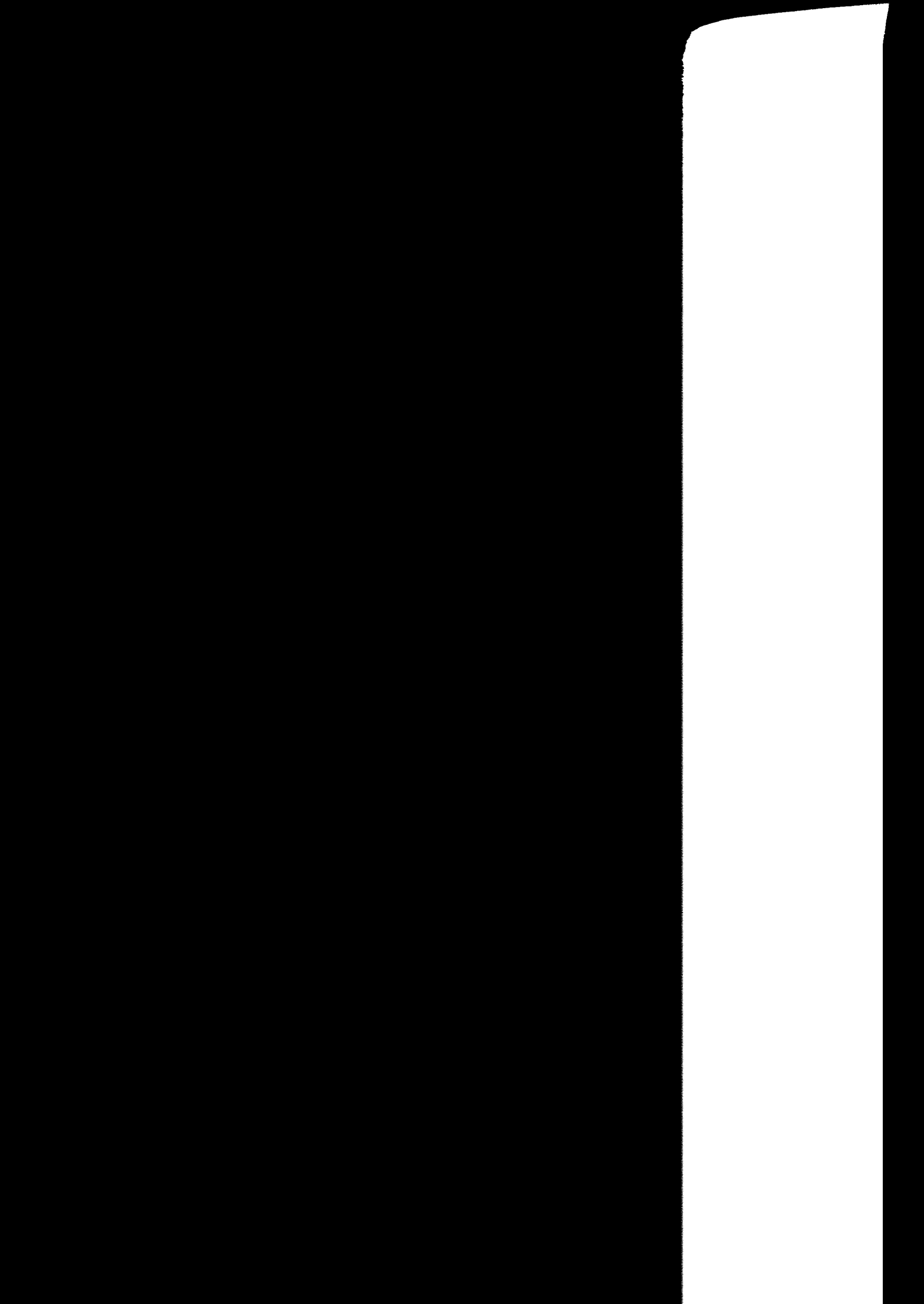
7.17 The extract is then prepared and analyzed using the appropriate analytical methods described in Chapters Three and Four of this manual.

NOTE: If the EP extract includes two phases, concentration of contaminants is determined by using a simple weighted average. For example: An EP extract contains 50 mL of oil and 1,000 mL of an aqueous phase. Contaminant concentrations are determined for each phase. The final contamination concentration is taken to be:

$$\frac{(50)(\text{contaminant conc. in oil}) + (1{,}000)(\text{contaminant conc. of aqueous phase})}{1050}$$

7.18 The extract concentrations are compared with the maximum contamination limits listed in 40 CFR Part 261.24. If the extract concentrations are greater than or equal to the respective values, the waste then is considered to exhibit the characteristic of Extraction Procedure Toxicity.





8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.3 All quality control measures described in Chapter One and in the referenced analytical methods should be followed.

9.0 METHOD PERFORMANCE

9.1 The data tabulated in Table 3 were obtained from records of state and contractor laboratories and are intended to show the precision of the entire method (1310 plus analysis method).

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

3. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. EPA-APPROVED FILTER HOLDERS

Manufacturer	Size	Model No.	Comments
Vacuum Filters			
Nalgene	500 mL	44-0045	Disposable plastic unit, including prefilter, filter pads, and reservoir; can be used when solution is to be analyzed for inorganic constituents.
Nuclepore	47 mm	410400	
Millipore	47 mm	XX10 047 00	
Pressure Filters			
Nuclepore	142 mm	425900	
Micro Filtration Systems	142 mm	302300	
Millipore	142 mm	YT30 142 HW	

METHOD 1330

EXTRACTION PROCEDURE FOR OILY WASTES

1.0 SCOPE AND APPLICATION

1.1 Method 1330 is used to determine the mobile metal concentration (MMC) in oily wastes.

1.2 Method 1330 is applicable to API separator sludges, rag oils, slop oil emulsions, and other oil wastes derived from petroleum refining.

2.0 SUMMARY OF METHOD

2.1 The sample is separated into solid and liquid components by filtration.

2.2 The solid phase is placed in a Soxhlet extractor, charged with tetrahydrofuran, and extracted. The THF is removed, the extractor is then charged with toluene, and the sample is reextracted.

2.3 The EP method (Method 1310) is run on the dry solid residue.

2.4 The original liquid, combined extracts, and EP leachate are analyzed for the EP metals.

3.0 INTERFERENCES

3.1 Matrix interferences will be coextracted from the sample. The extent of these interferences will vary considerably from waste to waste, depending on the nature and diversity of the particular refinery waste being analyzed.

4.0 APPARATUS AND MATERIALS

4.1 Soxhlet extraction apparatus.

4.2 Vacuum pump or other source of vacuum.

4.3 Buchner funnel 12.

4.4 Electric heating mantle.

4.5 Paper extraction thimble.

4.6 Filter paper.

4.7 Muslin cloth disks.

4.8 Evaporative flask - 250-mL.

4.9 Balance - Analytical, capable of weighing to $\pm$ 0.5 mg.

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 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Tetrahydrofuran, C_4H_8O.

5.4 Toluene, $C_6H_5CH_3$.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Samples must be collected in glass containers having a total volume of at least 150 mL. No solid material should interfere with sealing the sample container.

6.2 Sampling devices should be wiped clean with paper towels or absorbent cloth, rinsed with a small amount of hexane followed by acetone rinse, and dried between samples. Alternatively, samples can be taken with disposable sampling devices in beakers.

7.0 PROCEDURE

7.1 Separate the sample (minimum 100 g) into its solid and liquid components. The liquid component is defined as that portion of the sample which passes through a 0.45 um filter media under a pressure differential of 75 psi.

7.2 Determine the quantity of liquid (mL) and the concentration of the toxicants of concern in the liquid phase (mg/L).

7.3 Place the solid phase into a Soxhlet extractor, charge the concentration flask with 300 mL tetrahydrofuran, and extract for 3 hours.

7.4 Remove the flask containing tetrahydrofuran and replace it with one containing 300 mL toluene.

7.5 Extract the solid a second time, for 3 hours, with the toluene.

7.6 Combine the tetrahydrofuran and toluene extracts.

7.7 Analyze the combined extracts for the toxicants of concern.

7.8 Determine the quantity of liquid (mL) and the concentration of the toxicants of concern in the combined extracts (mg/L).

7.9 Take the solid material remaining in the Soxhlet thimble and dry it at 100°C for 30 minutes.

7.10 Run the EP (Method 1310) on the dried solid.

7.11 Calculate the mobile metal concentration (MMC) in mg/L using the following formula:

$$MMC = 1{,}000 \times \frac{(Q_1 + Q_2 + Q_3)}{(L_1 + L_2 + L_3)}$$

where:

Q_1 = Mass of toxicant in initial liquid phase of sample (amount of liquid x concentration of toxicant) (mg).

Q_2 = Mass of toxicant in combined organic extracts of sample (amount of liquid x concentration of toxicant) (mg).

Q_3 = Mass of toxicant in EP extract of solid (amount of extract x concentration of toxicant) (mg).

L_1 = Volume of initial liquid (mL).

L_2 = Volume of liquid in EP (mL) = 20 x [weight of dried solid from Step 7.8 (g)].

L_3 = Volume of liquid in THF and toluene extract (mL).

8.0 QUALITY CONTROL

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

8.2 Refer to Chapter One for specific quality control procedures.

9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

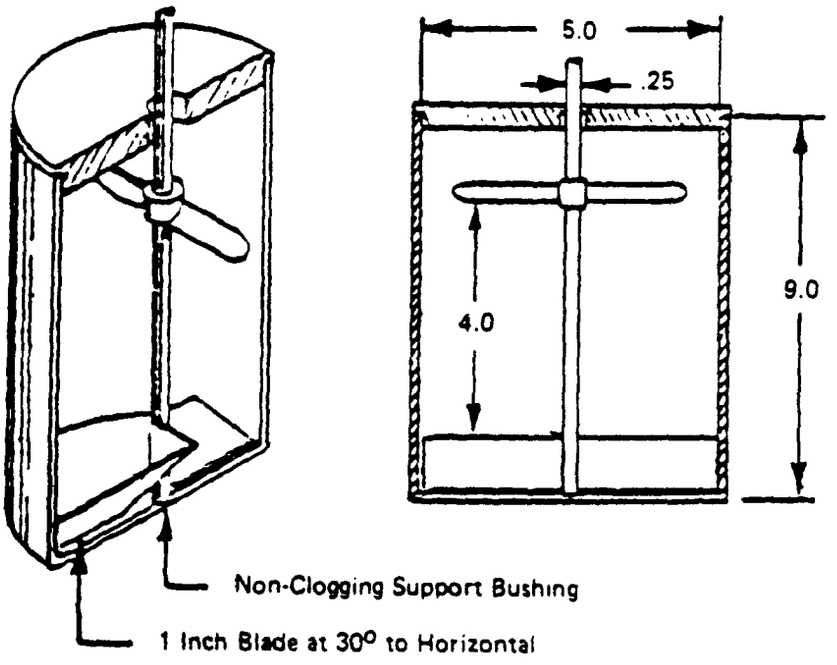


Figure 1. Extractor.

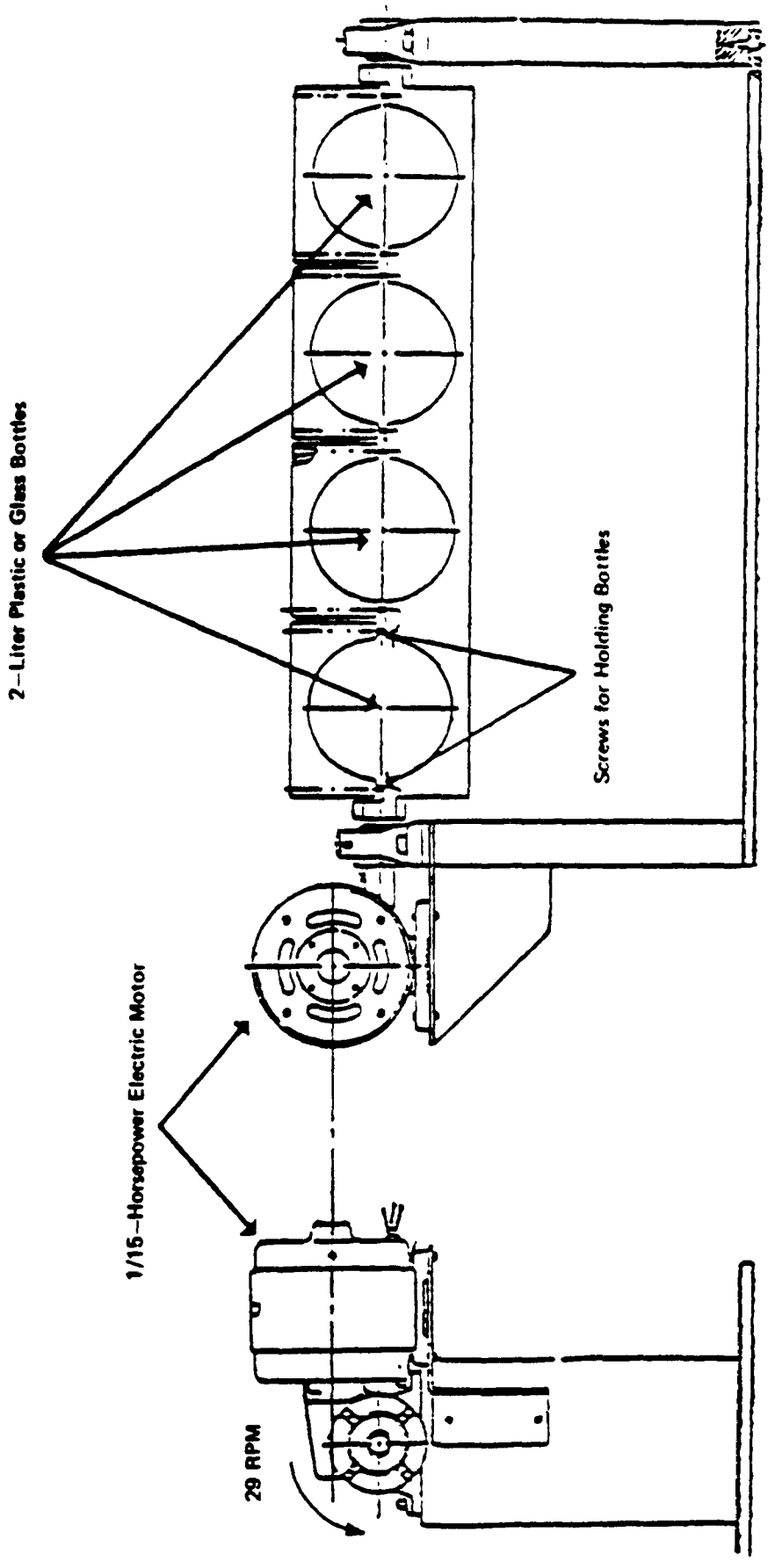


Figure 2. Rotary Extractor.

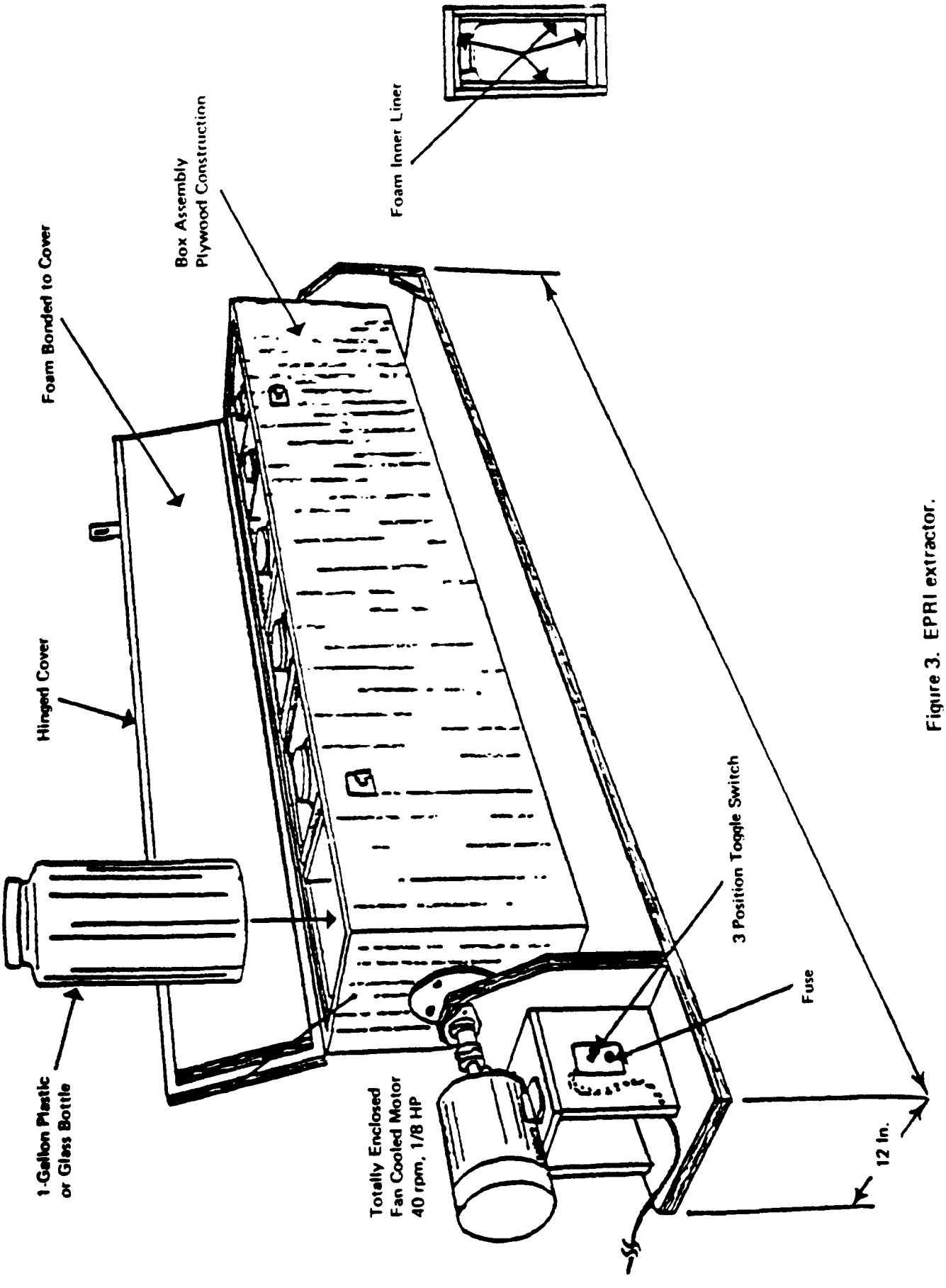
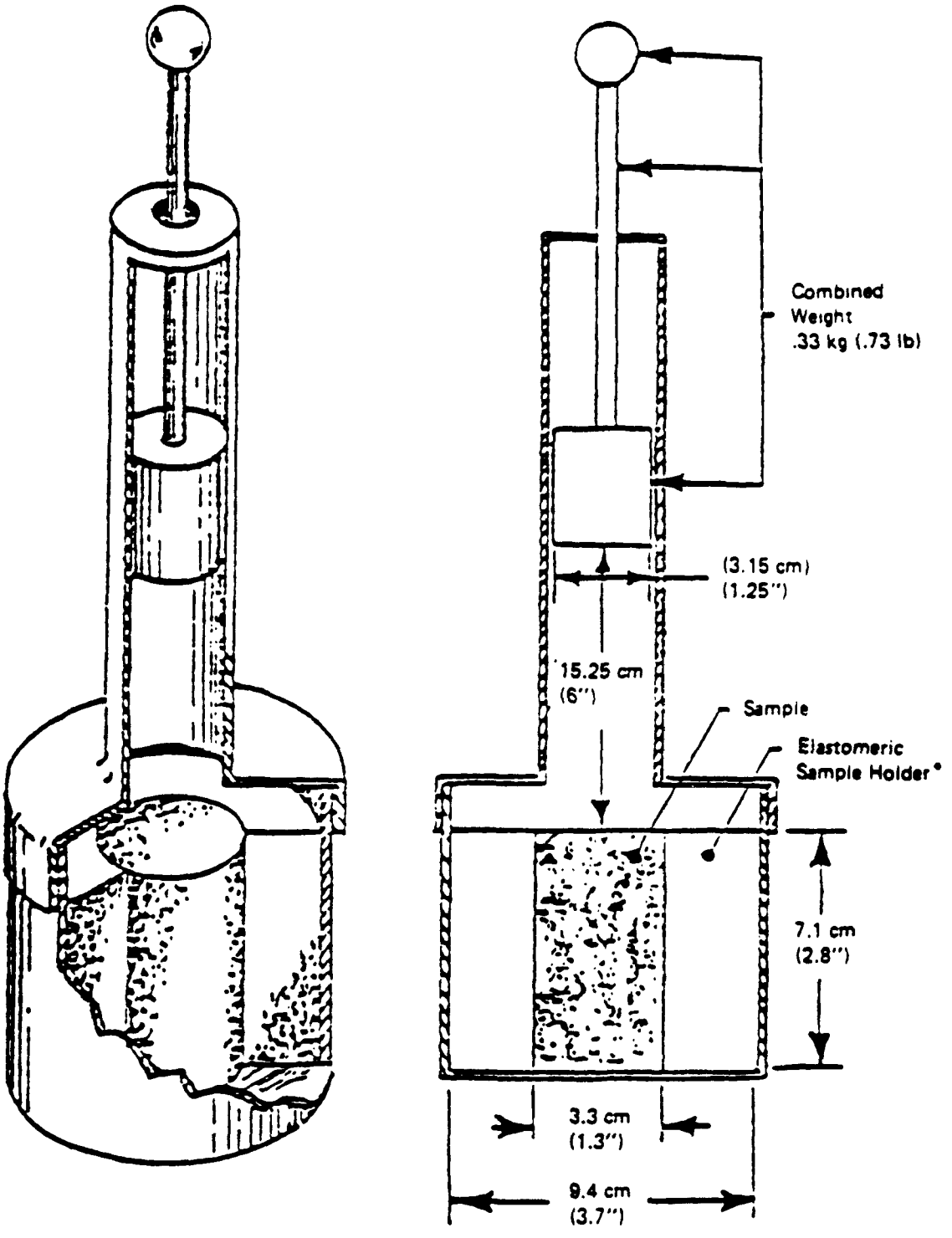


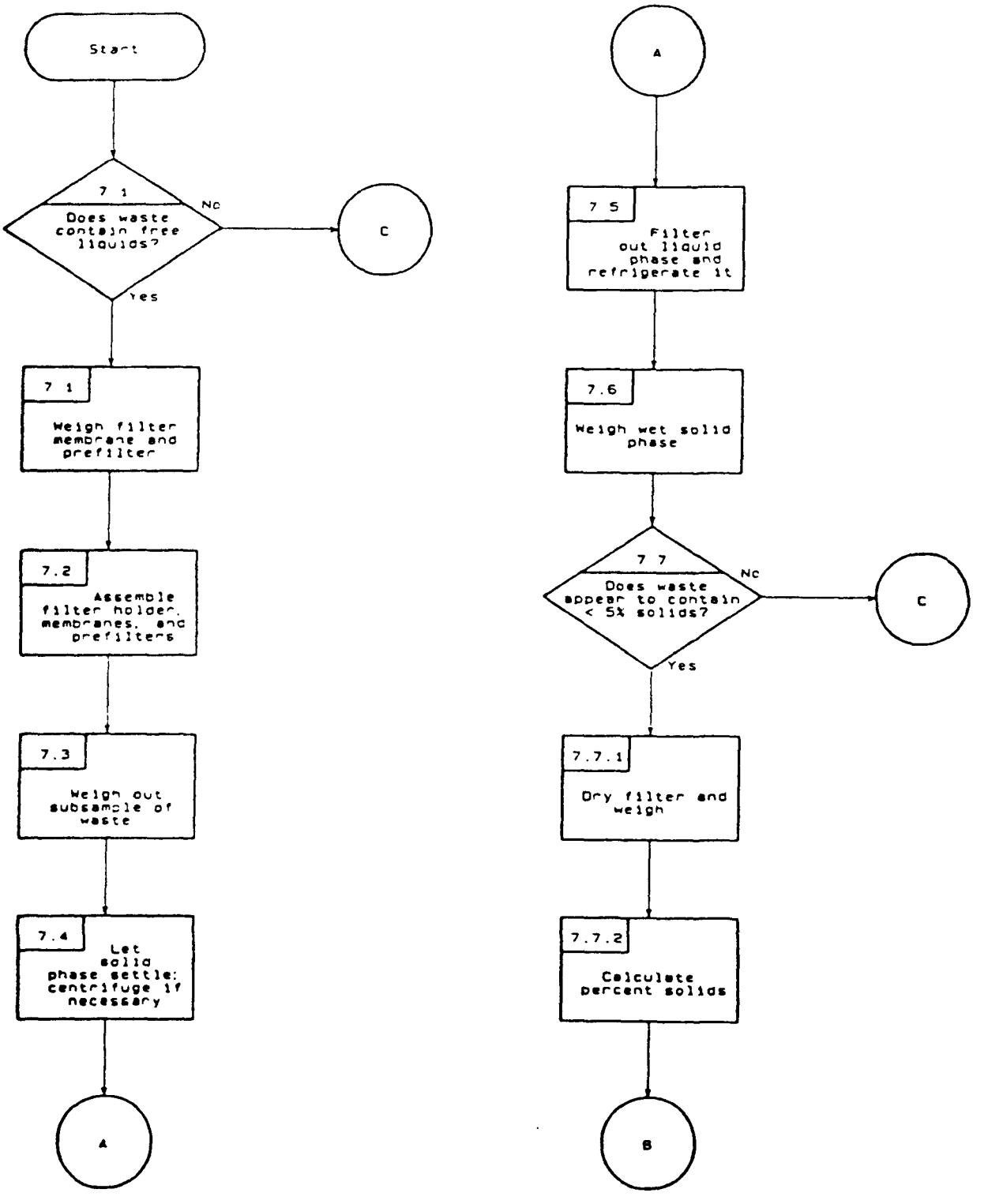
Figure 3. EPRI extractor.



* Elastomeric sample holder fabricated of material firm enough to support the sample.

Figure 4. Compaction tester.

METHOD 1330
EXTRACTION PROCEDURE FOR OIL WASTE



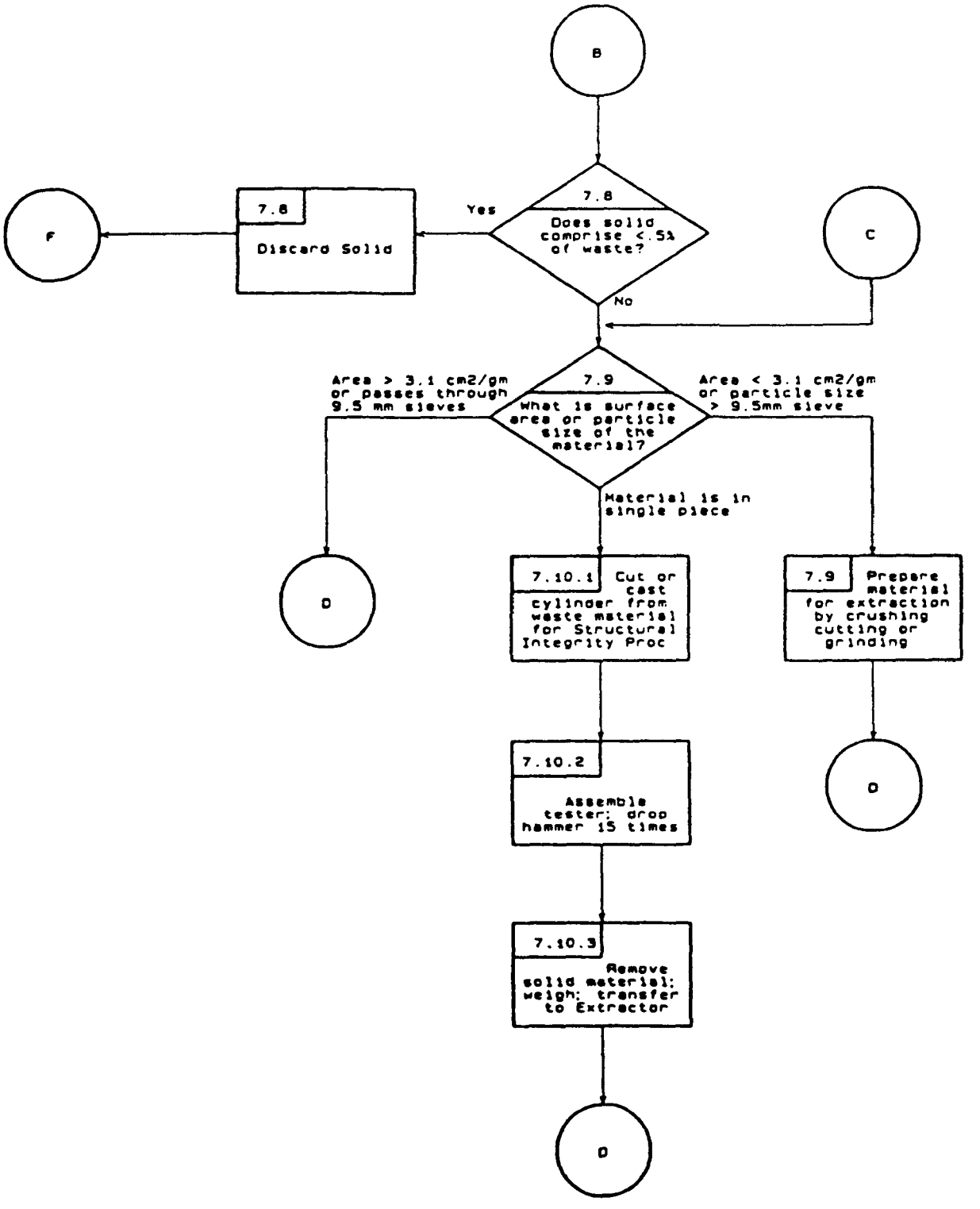

B
7.8
Does solid comprise <.5% of waste?
Yes
No
7.8
Discard Solid
F
C
7.9
What is surface area or particle size of the material?
Area > 3.1 cm2/gm or passes through 9.5 mm sieves
Area < 3.1 cm2/gm or particle size > 9.5mm sieve
Material is in single piece
D
7.10.1 Cut or cast cylinder from waste material for Structural Integrity Proc
7.9 Prepare material for extraction by crushing cutting or grinding
7.10.2
Assemble tester; drop hammer 15 times
D
7.10.3
Remove solid material; weigh; transfer to Extractor
D

TABLE 2. EPA-APPROVED FILTRATION MEDIA

Supplier	Filter to be used for aqueous systems	Filter to be used for organic systems
Coarse prefilter		
Gelman	61631, 61635	61631, 61635
Nuclepore	210907, 211707	210907, 211707
Millipore	AP25 035 00, AP25 127 50	AP25 035 00, AP25 127 50
Medium prefilters		
Nuclepore	210905, 211705	210905, 211705
Millipore	AP20 035 00, AP20 124 50	AP20 035 00, AP20 124 50
Fine prefilters		
Gelman	64798, 64803	64798, 64803
Nuclepore	210903, 211703	210903, 211703
Millipore	AP15 035 00, AP15 124 50	AP15 035 00, AP15 124 50
Fine filters (0.45 um)		
Gelman	60173, 60177	60540 or 66149, 60544 or 66151
Pall	NX04750, NX14225	
Nuclepore	142218	142218[a]
Millipore	HAWP 047 00, HAWP 142 50	FHUP 047 00, FHLP 142 50
Selas	83485-02, 83486-02	83485-02, 83486-02

[a]Susceptible to decomposition by certain polar organic solvents.

TABLE 3. PRECISIONS OF EXTRACTION-ANALYSIS PROCEDURES FOR SEVERAL ELEMENTS

Element	Sample Matrix	Analysis Method	Laboratory Replicates
Arsenic	1. Auto fluff	7060	1.8, 1.5 ug/L
	2. Barrel sludge	7060	0.9, 2.6 ug/L
	3. Lumber treatment company sediment	7060	28, 42 mg/L
Barium	1. Lead smelting emission control dust	6010	0.12, 0.12 mg/L
	2. Auto fluff	7081	791, 780 ug/L
	3. Barrel sludge	7081	422, 380 ug/L
Cadmium	1. Lead smelting emission control dust	3010/7130	120, 120 mg/L
	2. Wastewater treatment sludge from electroplating	3010/7130	360, 290 mg/L
	3. Auto fluff	7131	470, 610 ug/L
	4. Barrel sludge	7131	1100, 890 ug/L
	5. Oil refinery tertiary pond sludge	7131	3.2, 1.9 ug/L
Chromium	1. Wastewater treatment sludge from electroplating	3010/7190	1.1, 1.2 mg/L
	2. Paint primer	7191	61, 43 ug/L
	3. Paint primer filter	7191	--
	4. Lumber treatment company sediment	7191	0.81, 0.89 mg/L
	5. Oil refinery tertiary pond sludge	7191	--
Mercury	1. Barrel sludge	7470	0.15, 0.09 ug/L
	2. Wastewater treatment sludge from electroplating	7470	1.4, 0.4 ug/L
	3. Lead smelting emission control dust	7470	0.4, 0.4 ug/L

TABLE 3 (Continued)

Element	Sample Matrix	Analysis Method	Laboratory Replicates
Lead	1. Lead smelting emission control dust	3010/7420	940, 920 mg/L
	2. Auto fluff	7421	1540, 1490 ug/L
	3. Incinerator ash	7421	1000, 974 ug/L
	4. Barrel sludge	7421	2550, 2800 ug/L
	5. Oil refinery tertiary pond sludge	7421	31, 29 ug/L
Nickel	1. Sludge	7521	2260, 1720 ug/L
	2. Wastewater treatment sludge from electroplating	3010/7520	130, 140 mg/L
Chromium(VI)	1. Wastewater treatment sludge from electroplating	7196	18, 19 ug/L

FIGURE 1.
EXTRACTOR

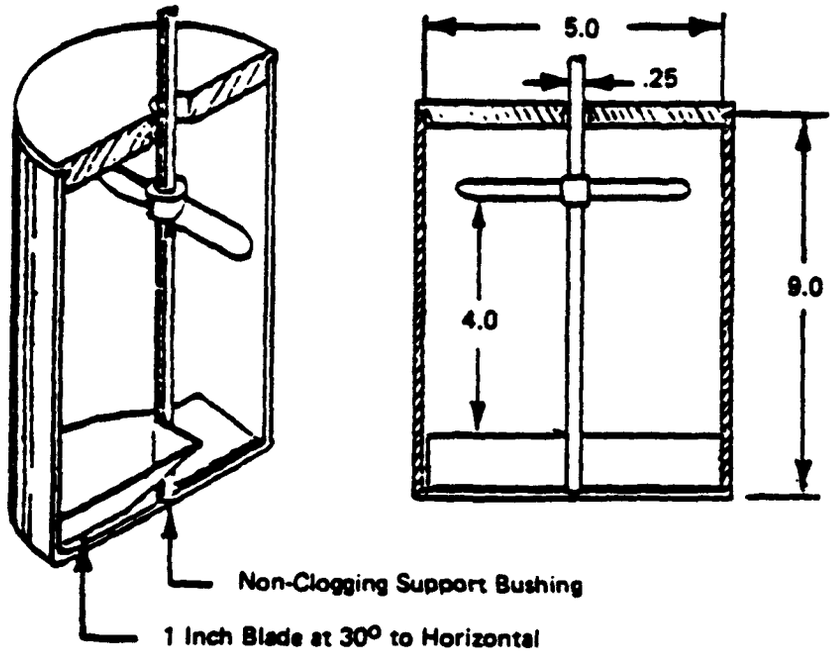


FIGURE 2.
ROTARY EXTRACTOR

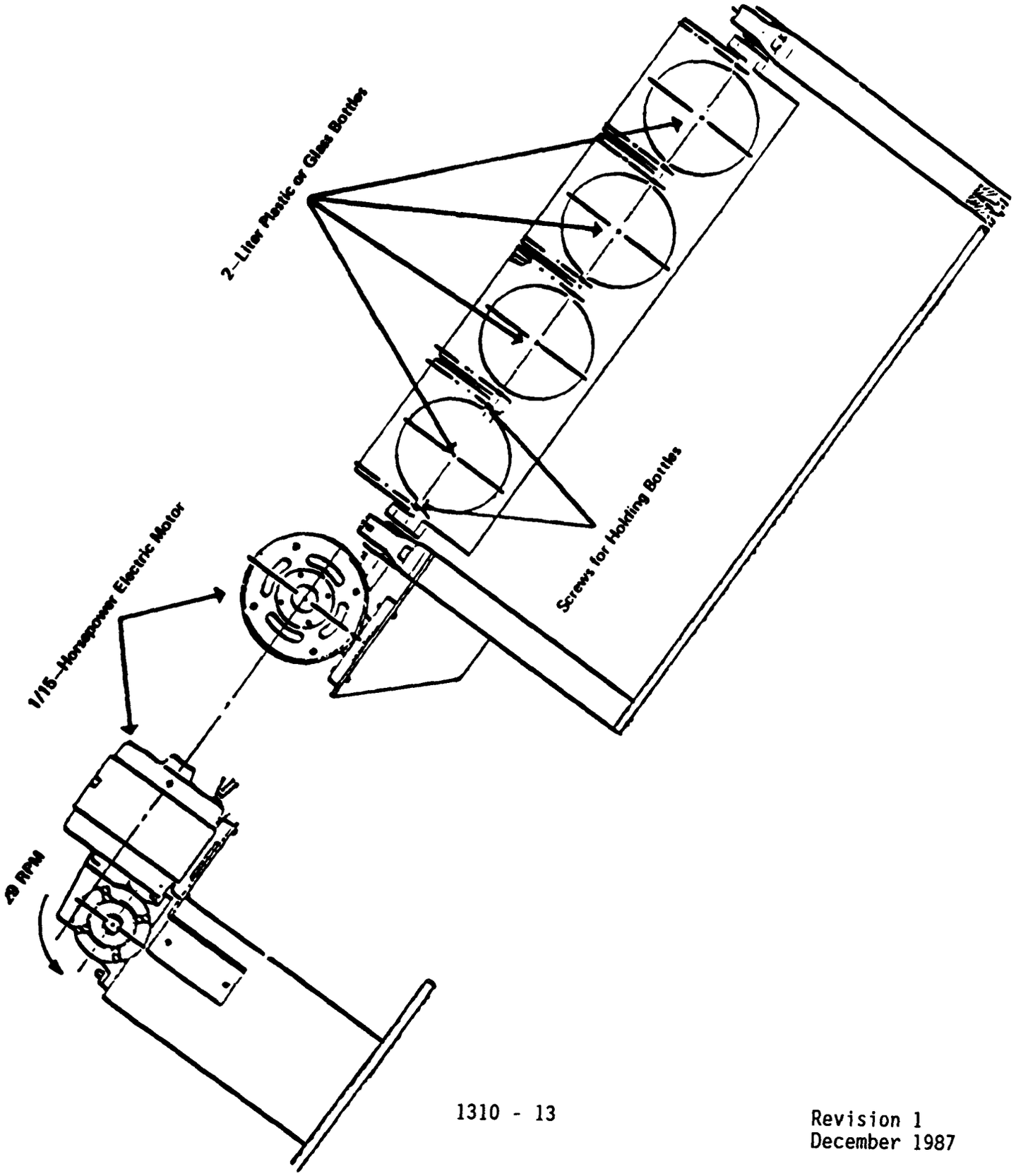


FIGURE 3.
EPRI EXTRACTOR

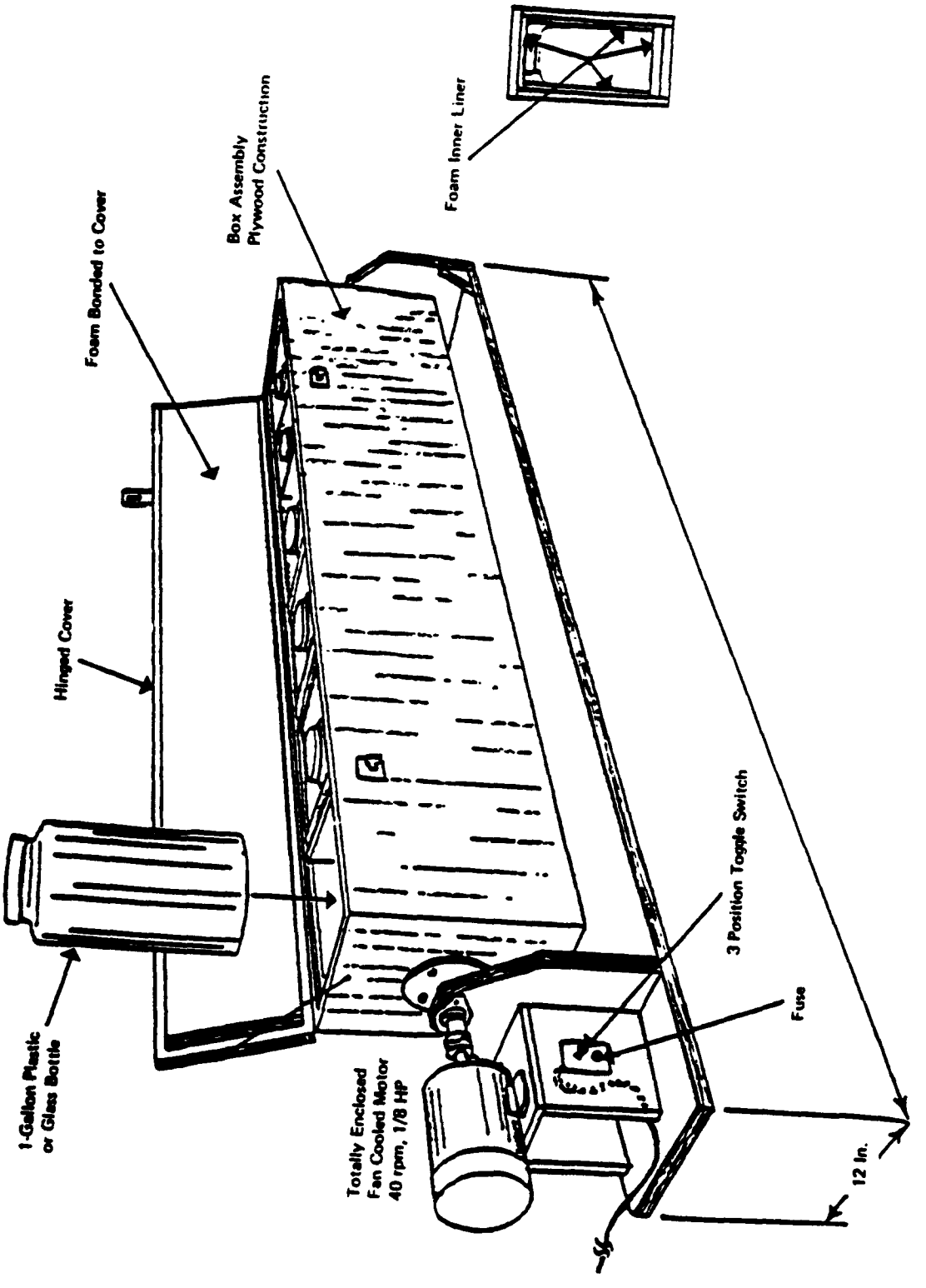
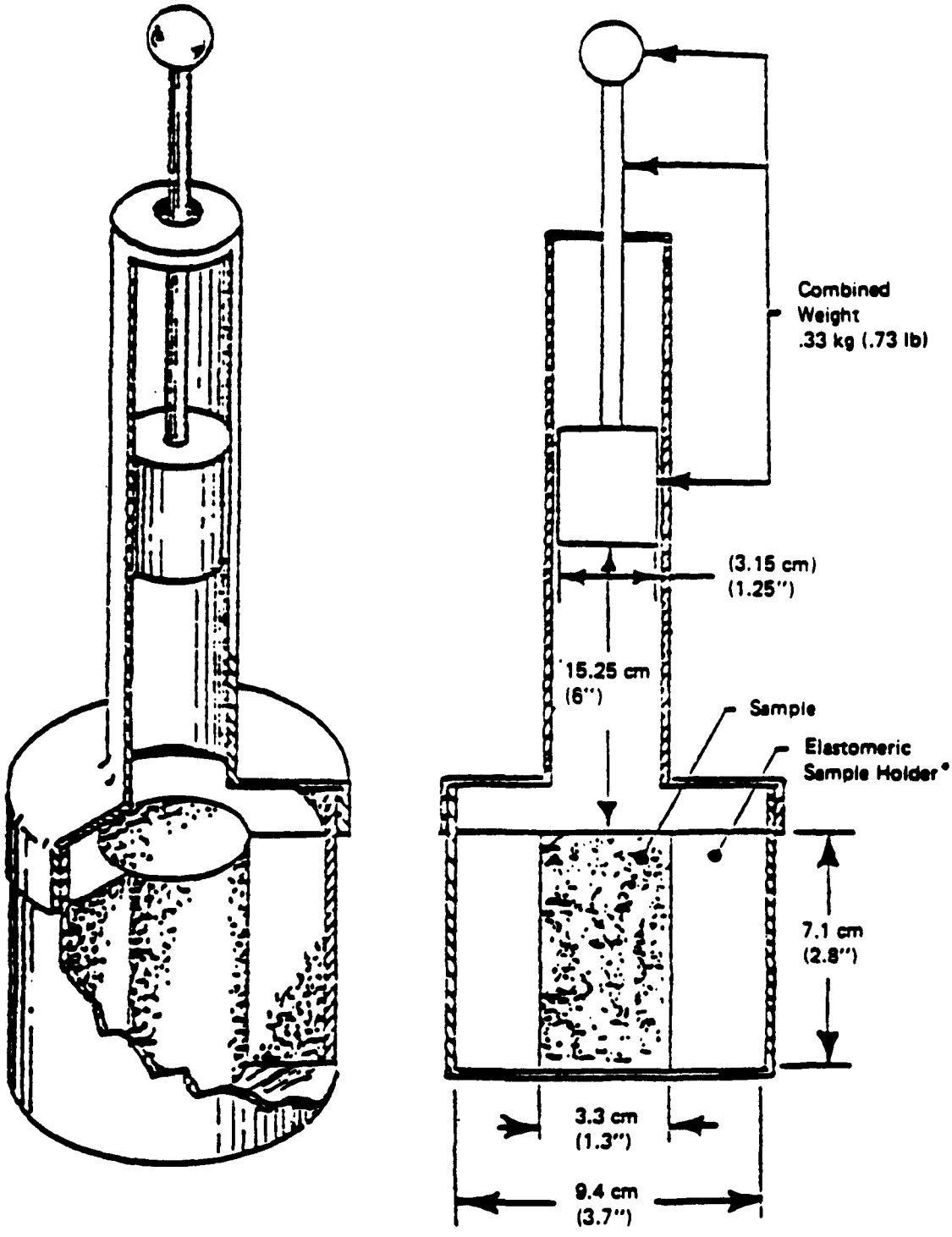
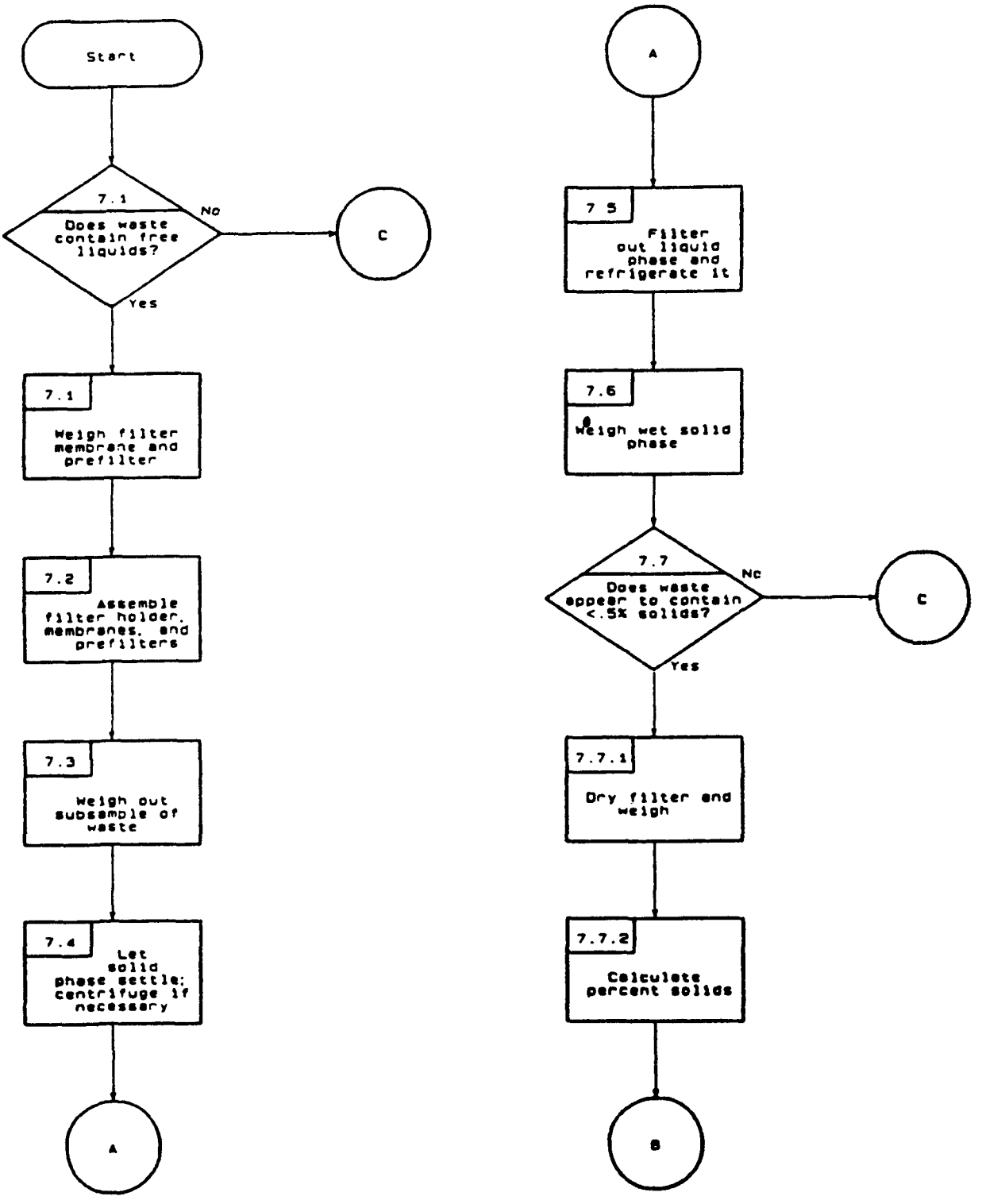


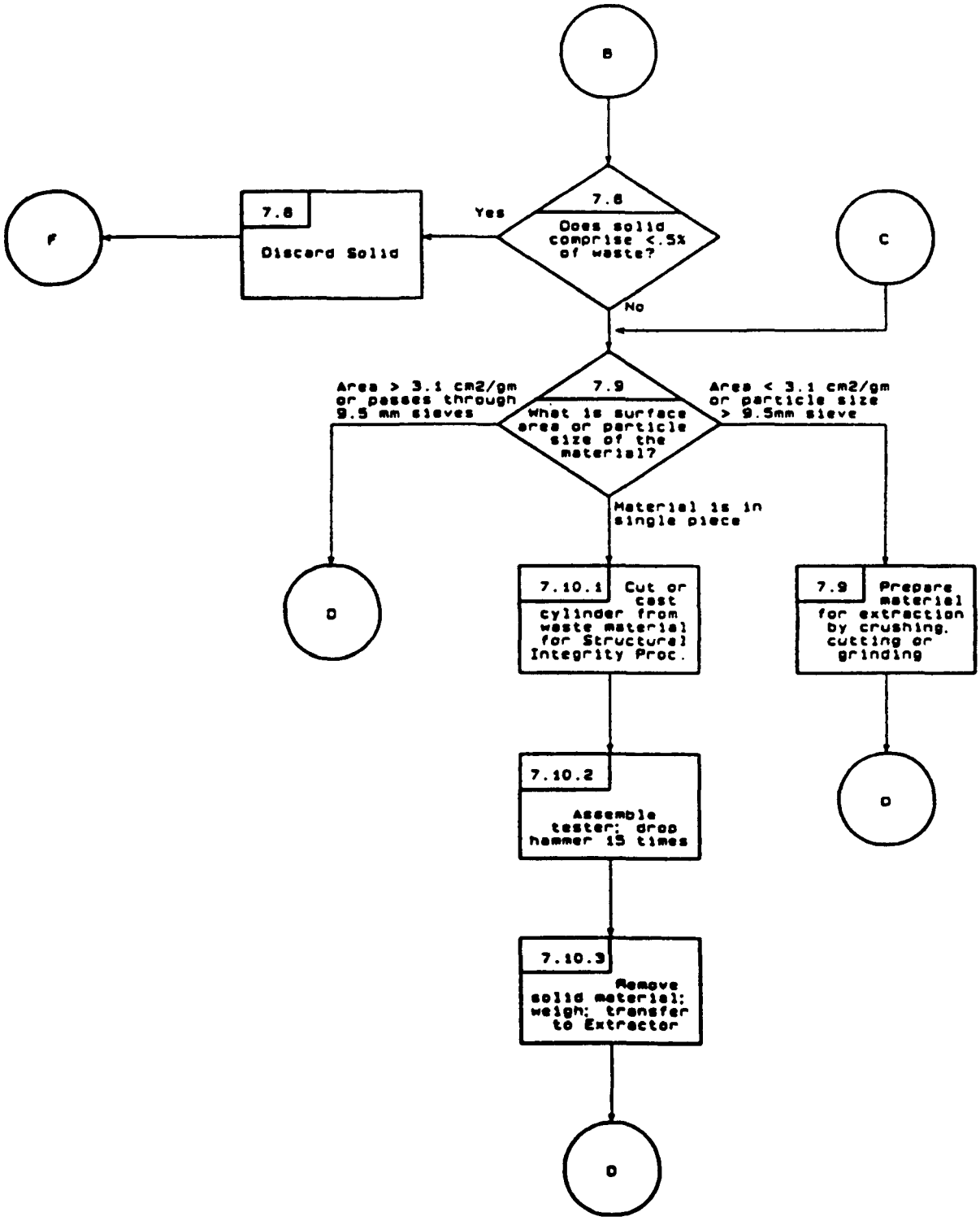
FIGURE 4.
COMPACTION TESTER

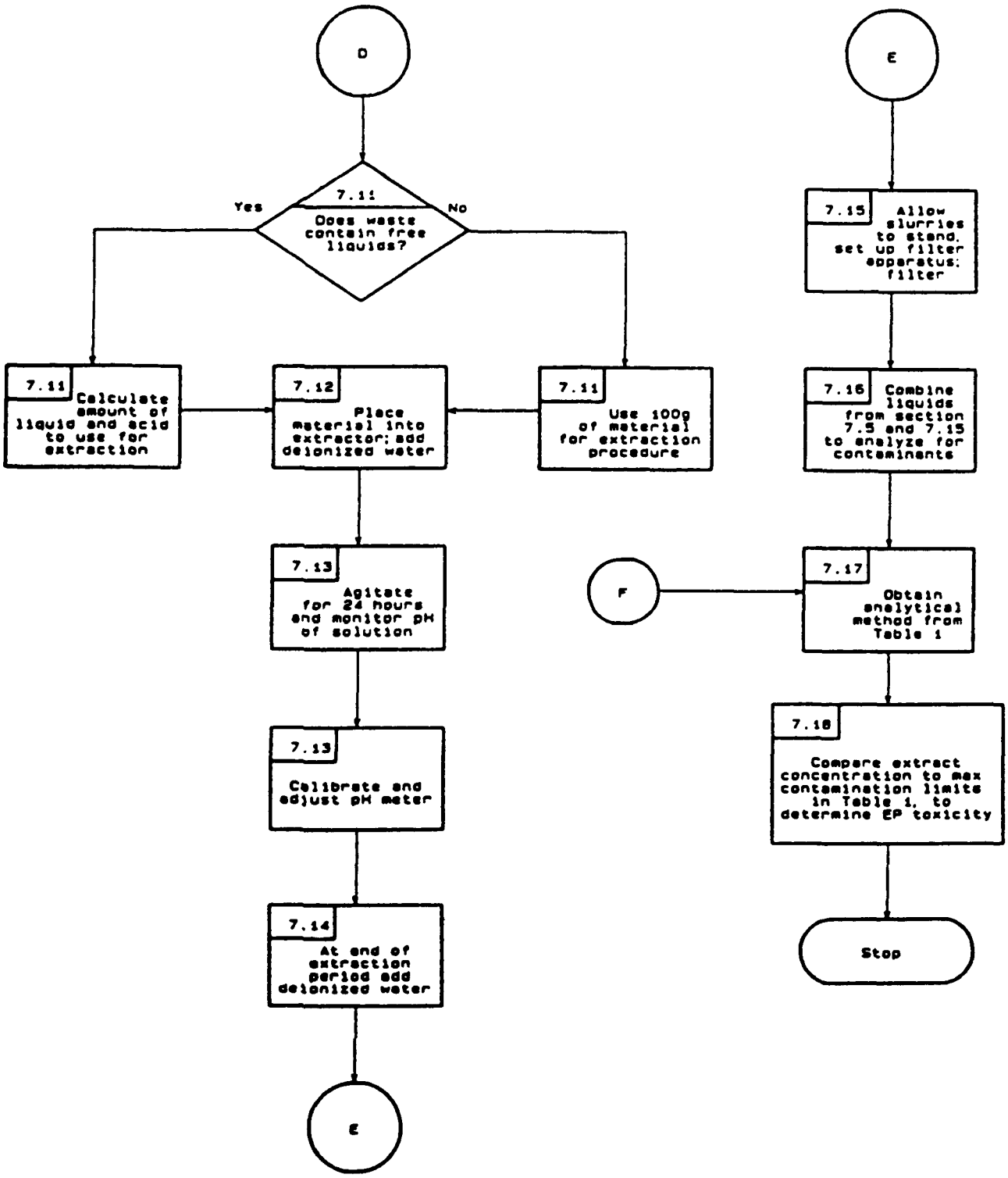


* Elastomeric sample holder fabricated of material firm enough to support the sample.

METHOD 1310
EXTRACTION PROCEDURE (EP) TOXICITY TEST METHOD AND STRUCTURAL INTEGRITY TEST




B
7.8
Does solid comprise <.5% of waste?
Yes
No
F
7.8
Discard Solid
C
7.9
What is surface area or particle size of the material?
Area > 3.1 cm2/gm or passes through 9.5 mm sieves
Area < 3.1 cm2/gm or particle size > 9.5mm sieve
Material is in single piece
D
7.10.1 Cut or cast cylinder from waste material for Structural Integrity Proc.
7.9 Prepare material for extraction by crushing, cutting or grinding
D
7.10.2
Assemble tester; drop hammer 15 times
7.10.3
Remove solid material; weigh; transfer to Extractor
D


D
7.11
Does waste contain free liquids?
Yes
No
7.11
Calculate amount of liquid and acid to use for extraction
7.12
Place material into extractor; add deionized water
7.11
Use 100g of material for extraction procedure
7.13
Agitate for 24 hours and monitor pH of solution
7.13
Calibrate and adjust pH meter
7.14
At end of extraction period add deionized water
E
E
7.15
Allow slurries to stand, set up filter apparatus; filter
7.16
Combine liquids from section 7.5 and 7.15 to analyze for contaminants
F
7.17
Obtain analytical method from Table 1
7.18
Compare extract concentration to max contamination limits in Table 1, to determine EP toxicity
Stop

METHOD 1312

SYNTHETIC PRECIPITATION LEACHING PROCEDURE

1.0 SCOPE AND APPLICATION

1.1 Method 1312 is designed to determine the mobility of both organic and inorganic analytes present in samples of soils and wastes.

2.0 SUMMARY OF METHOD

2.1 For liquid samples (i.e., those containing less than 0.5 % dry solid material), the sample, after filtration through a 0.6 to 0.8 μm glass fiber filter, is defined as the 1312 extract.

2.2 For samples containing greater than 0.5 % solids, the liquid phase, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the region of the country where the sample site is located if the sample is a soil. If the sample is a waste or wastewater, the extraction fluid employed is a pH 4.2 solution. A special extractor vessel is used when testing for volatile analytes (see Table 1 for a list of volatile compounds). Following extraction, the liquid extract is separated from the sample by 0.6 to 0.8 μm glass fiber filter.

2.3 If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3.0 INTERFERENCES

3.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.0 APPARATUS AND MATERIALS

4.1 Agitation apparatus: The agitation apparatus must be capable of rotating the extraction vessel in an end-over-end fashion (see Figure 1) at 30 $\pm$ 2 rpm. Suitable devices known to EPA are identified in Table 2.

4.2 Extraction Vessels

4.2.1 Zero Headspace Extraction Vessel (ZHE). This device is for use only when the sample is being tested for the mobility of volatile analytes (i.e., those listed in Table 1). The ZHE (depicted in Figure 2) allows for liquid/solid separation within the device and effectively precludes headspace. This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without opening the vessel (see Step 4.3.1). These vessels shall have an internal volume of

500-600 mL and be equipped to accommodate a 90-110 mm filter. The devices contain VITON®[1] O-rings which should be replaced frequently. Suitable ZHE devices known to EPA are identified in Table 3.

For the ZHE to be acceptable for use, the piston within the ZHE should be able to be moved with approximately 15 psi or less. If it takes more pressure to move the piston, the O-rings in the device should be replaced. If this does not solve the problem, the ZHE is unacceptable for 1312 analyses and the manufacturer should be contacted.

The ZHE should be checked for leaks after every extraction. If the device contains a built-in pressure gauge, pressurize the device to 50 psi, allow it to stand unattended for 1 hour, and recheck the pressure. If the device does not have a built-in pressure gauge, pressurize the device to 50 psi, submerge it in water, and check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Retest the device. If leakage problems cannot be solved, the manufacturer should be contacted.

Some ZHEs use gas pressure to actuate the ZHE piston, while others use mechanical pressure (see Table 3). Whereas the volatiles procedure (see Step 7.3) refers to pounds-per-square-inch (psi), for the mechanically actuated piston, the pressure applied is measured in torque-inch-pounds. Refer to the manufacturer's instructions as to the proper conversion.

4.2.2 Bottle Extraction Vessel. When the sample is being evaluated using the nonvolatile extraction, a jar with sufficient capacity to hold the sample and the extraction fluid is needed. Headspace is allowed in this vessel.

The extraction bottles may be constructed from various materials, depending on the analytes to be analyzed and the nature of the waste (see Step 4.3.3). It is recommended that borosilicate glass bottles be used instead of other types of glass, especially when inorganics are of concern. Plastic bottles, other than polytetrafluoroethylene, shall not be used if organics are to be investigated. Bottles are available from a number of laboratory suppliers. When this type of extraction vessel is used, the filtration device discussed in Step 4.3.2 is used for initial liquid/solid separation and final extract filtration.

4.3 Filtration Devices: It is recommended that all filtrations be performed in a hood.

4.3.1 Zero-Headspace Extraction Vessel (ZHE): When the sample is evaluated for volatiles, the zero-headspace extraction vessel described in Step 4.2.1 is used for filtration. The device shall be capable of supporting and keeping in place the glass fiber filter and be able to withstand the pressure needed to accomplish separation (50 psi).

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[1]VITON® is a trademark of Du Pont.

NOTE: When it is suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.

4.3.2 Filter Holder: When the sample is evaluated for other than volatile analytes, a filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation may be used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures of up to 50 psi or more. The type of filter holder used depends on the properties of the material to be filtered (see Step 4.3.3). These devices shall have a minimum internal volume of 300 mL and be equipped to accommodate a minimum filter size of 47 mm (filter holders having an internal capacity of 1.5 L or greater, and equipped to accommodate a 142 mm diameter filter, are recommended). Vacuum filtration can only be used for wastes with low solids content (<10 %) and for highly granular, liquid-containing wastes. All other types of wastes should be filtered using positive pressure filtration. Suitable filter holders known to EPA are shown in Table 4.

4.3.3 Materials of Construction: Extraction vessels and filtration devices shall be made of inert materials which will not leach or absorb sample components. Glass, polytetrafluoroethylene (PTFE), or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components. Devices made of high-density polyethylene (HDPE), polypropylene (PP), or polyvinyl chloride (PVC) may be used only when evaluating the mobility of metals. Borosilicate glass bottles are recommended for use over other types of glass bottles, especially when inorganics are analytes of concern.

4.4 Filters: Filters shall be made of borosilicate glass fiber, shall contain no binder materials, and shall have an effective pore size of 0.6 to 0.8-μm or equivalent. Filters known to EPA which meet these specifications are identified in Table 5. Pre-filters must not be used. When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with 1N nitric acid followed by three consecutive rinses with deionized distilled water (a minimum of 1-L per rinse is recommended). Glass fiber filters are fragile and should be handled with care.

4.5 pH Meters: The meter should be accurate to $\pm$ 0.05 units at 25°C.

4.6 ZHE Extract Collection Devices: TEDLAR®[2] bags or glass, stainless steel or PTFE gas-tight syringes are used to collect the initial liquid phase and the final extract when using the ZHE device. These devices listed are recommended for use under the following conditions:

4.6.1 If a waste contains an aqueous liquid phase or if a waste does not contain a significant amount of nonaqueous liquid (i.e., <1 % of total waste), the TEDLAR® bag or a 600 mL syringe should be used to collect and combine the initial liquid and solid extract.

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[2]TEDLAR® is a registered trademark of Du Pont.

4.6.2 If a waste contains a significant amount of nonaqueous liquid in the initial liquid phase (i.e., >1 % of total waste), the syringe or the TEDLAR® bag may be used for both the initial solid/liquid separation and the final extract filtration. However, analysts should use one or the other, not both.

4.6.3 If the waste contains no initial liquid phase (is 100 % solid) or has no significant solid phase (is 100 % liquid), either the TEDLAR® bag or the syringe may be used. If the syringe is used, discard the first 5 mL of liquid expressed from the device. The remaining aliquots are used for analysis.

4.7 ZHE Extraction Fluid Transfer Devices: Any device capable of transferring the extraction fluid into the ZHE without changing the nature of the extraction fluid is acceptable (e.g., a positive displacement or peristaltic pump, a gas-tight syringe, pressure filtration unit (see Step 4.3.2), or other ZHE device).

4.8 Laboratory Balance: Any laboratory balance accurate to within ± 0.01 grams may be used (all weight measurements are to be within ± 0.1 grams).

4.9 Beaker or Erlenmeyer flask, glass, 500 mL.

4.10 Watchglass, appropriate diameter to cover beaker or Erlenmeyer flask.

4.11 Magnetic stirrer.

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 Reagent Water. Reagent water is defined as water in which an interferant is not observed at or above the method's detection limit of the analyte(s) of interest. For nonvolatile extractions, ASTM Type II water or equivalent meets the definition of reagent water. For volatile extractions, it is recommended that reagent water be generated by any of the following methods. Reagent water should be monitored periodically for impurities.

5.2.1 Reagent water for volatile extractions may be generated by passing tap water through a carbon filter bed containing about 500 grams of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.2.2 A water purification system (Millipore Super-Q or equivalent) may also be used to generate reagent water for volatile extractions.

5.2.3 Reagent water for volatile extractions may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the water temperature at 90 ± 5 degrees C, bubble a contaminant-free inert gas (e.g. nitrogen) through the water for 1 hour. While still hot, transfer the water to a narrow mouth screw-cap bottle under zero-headspace and seal with a Teflon-lined septum and cap.

5.3 Sulfuric acid/nitric acid (60/40 weight percent mixture) H_2SO_4/HNO_3. Cautiously mix 60 g of concentrated sulfuric acid with 40 g of concentrated nitric acid.

5.4 Extraction fluids.

5.4.1 Extraction fluid #1: This fluid is made by adding the 60/40 weight percent mixture of sulfuric and nitric acids to reagent water (Step 5.2) until the pH is 4.20 ± 0.05. The fluid is used to determine the leachability of soil from a site that is east of the Mississippi River, and the leachability of wastes and wastewaters.

NOTE: Solutions are unbuffered and exact pH may not be attained.

5.4.2 Extraction fluid #2: This fluid is made by adding the 60/40 weight percent mixture of sulfuric and nitric acids to reagent water (Step 5.2) until the pH is 5.00 ± 0.05. The fluid is used to determine the leachability of soil from a site that is west of the Mississippi River.

5.4.3 Extraction fluid #3: This fluid is reagent water (Step 5.2) and is used to determine cyanide and volatiles leachability.

NOTE: These extraction fluids should be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the above specifications, the fluid shall be discarded and fresh extraction fluid prepared.

5.5 Analytical standards shall be prepared according to the appropriate analytical method.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples shall be collected using an appropriate sampling plan.

6.2 There may be requirements on the minimal size of the field sample depending upon the physical state or states of the waste and the analytes of concern. An aliquot is needed for the preliminary evaluations of the percent solids and the particle size. An aliquot may be needed to conduct the nonvolatile analyte extraction procedure (see Step 1.4 concerning the use of this extract for volatile organics). If volatile organics are of concern, another aliquot may be needed. Quality control measures may require additional aliquots. Further, it is always wise to collect more sample just in case something goes wrong with the initial attempt to conduct the test.

6.3 Preservatives shall not be added to samples before extraction.

6.4 Samples may be refrigerated unless refrigeration results in irreversible physical change to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

6.5 When the sample is to be evaluated for volatile analytes, care shall be taken to minimize the loss of volatiles. Samples shall be collected and stored in a manner intended to prevent the loss of volatile analytes (e.g., samples should be collected in Teflon-lined septum capped vials and stored at 4°C. Samples should be opened only immediately prior to extraction).

6.6 1312 extracts should be prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH < 2, unless precipitation occurs (see Step 7.2.14 if precipitation occurs). Extracts should be preserved for other analytes according to the guidance given in the individual analysis methods. Extracts or portions of extracts for organic analyte determinations shall not be allowed to come into contact with the atmosphere (i.e., no headspace) to prevent losses. See Section 8.0 (Quality Control) for acceptable sample and extract holding times.

7.0 PROCEDURE

7.1 Preliminary Evaluations

Perform preliminary 1312 evaluations on a minimum 100 gram aliquot of sample. This aliquot may not actually undergo 1312 extraction. These preliminary evaluations include: (1) determination of the percent solids (Step 7.1.1); (2) determination of whether the waste contains insignificant solids and is, therefore, its own extract after filtration (Step 7.1.2); and (3) determination of whether the solid portion of the waste requires particle size reduction (Section 7.1.3).

7.1.1 Preliminary determination of percent solids: Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure, as described below.

7.1.1.1 If the sample will obviously yield no free liquid when subjected to pressure filtration (i.e., is 100% solids), weigh out a representative subsample (100 g minimum) and proceed to Step 7.1.3.

7.1.1.2 If the sample is liquid or multiphasic, liquid/solid separation to make a preliminary determination of percent solids is required. This involves the filtration device discussed in Step 4.3.2, and is outlined in Steps 7.1.1.3 through 7.1.1.9.

7.1.1.3 Pre-weigh the filter and the container that will receive the filtrate.

7.1.1.4 Assemble filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure.

7.1.1.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight.

7.1.1.6 Allow slurries to stand to permit the solid phase to settle. Samples that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.1.1.7 Quantitatively transfer the sample to the filter holder (liquid and solid phases). Spread the sample evenly over the surface of the filter. If filtration of the waste at 4°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering.

NOTE: If sample material (>1 % of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 7.1.1.5 to determine the weight of the sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within any 2-minute period), stop the filtration.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.1.1.8 The material in the filter holder is defined as the solid phase of the sample, and the filtrate is defined as the liquid phase.

NOTE: Some samples, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid, but even after applying vacuum or pressure filtration, as outlined in Step 7.1.1.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.1.1.9 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (see Step 7.1.1.3) from the total weight of the filtrate-filled container. Determine the weight of the solid phase of the sample by subtracting the weight of the liquid phase from the weight of the total sample, as determined in Step 7.1.1.5 or 7.1.1.7.

Record the weight of the liquid and solid phases. Calculate the percent solids as follows:

$$\text{Percent solids} = \frac{\text{Weight of solid (Step 7.1.1.9)}}{\text{Total weight of waste (Step 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2 If the percent solids determined in Step 7.1.1.9 is equal to or greater than 0.5%, then proceed either to Step 7.1.3 to determine whether the solid material requires particle size reduction or to Step 7.1.2.1 if it is noticed that a small amount of the filtrate is entrained in wetting of the filter. If the percent solids determined in Step 7.1.1.9 is less than 0.5%, then proceed to Step 7.2.9 if the nonvolatile 1312 analysis is to be performed, and to Section 7.3 with a fresh portion of the waste if the volatile 1312 analysis is to be performed.

7.1.2.1 Remove the solid phase and filter from the filtration apparatus.

7.1.2.2 Dry the filter and solid phase at 100 $\pm$ 20°C until two successive weighings yield the same value within $\pm$ 1 %. Record the final weight.

Note: Caution should be taken to ensure that the subject solid will not flash upon heating. It is recommended that the drying oven be vented to a hood or other appropriate device.

7.1.2.3 Calculate the percent dry solids as follows:

$$\text{Percent dry solids} = \frac{\text{(Weight of dry sample + filter) - tared weight of filter}}{\text{Initial weight of sample (Step 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2.4 If the percent dry solids is less than 0.5%, then proceed to Step 7.2.9 if the nonvolatile 1312 analysis is to be performed, and to Step 7.3 if the volatile 1312 analysis is to be performed. If the percent dry solids is greater than or equal to 0.5%, and if the nonvolatile 1312 analysis is to be performed, return to the beginning of this Section (7.1) and, with a fresh portion of sample, determine whether particle size reduction is necessary (Step 7.1.3).

7.1.3 Determination of whether the sample requires particle-size reduction (particle-size is reduced during this step): Using the solid portion of the sample, evaluate the solid for particle size. Particle-size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1 cm^2, or is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5 mm (0.375 inch) standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the sample for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above. If the solids are prepared for organic volatiles extraction, special precautions must be taken (see Step 7.3.6).

Note: Surface area criteria are meant for filamentous (e.g., paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended. For materials that do not obviously meet the criteria, sample-specific methods would need to be developed and employed to measure the surface area. Such methodology is currently not available.

7.1.4 Determination of appropriate extraction fluid:

7.1.4.1 For soils, if the sample is from a site that is east of the Mississippi River, extraction fluid #1 should be used. If the sample is from a site that is west of the Mississippi River, extraction fluid #2 should be used.

7.1.4.2 For wastes and wastewater, extraction fluid #1 should be used.

7.1.4.3 For cyanide-containing wastes and/or soils, extraction fluid #3 (reagent water) must be used because leaching of cyanide-containing samples under acidic conditions may result in the formation of hydrogen cyanide gas.

7.1.5 If the aliquot of the sample used for the preliminary evaluation (Steps 7.1.1 - 7.1.4) was determined to be 100% solid at Step 7.1.1.1, then it can be used for the Section 7.2 extraction (assuming at least 100 grams remain), and the Section 7.3 extraction (assuming at least 25 grams remain). If the aliquot was subjected to the procedure in Step 7.1.1.7, then another aliquot shall be used for the volatile extraction procedure in Section 7.3. The aliquot of the waste subjected to the procedure in Step 7.1.1.7 might be appropriate for use for the Section 7.2 extraction if an adequate amount of solid (as determined by Step 7.1.1.9) was obtained. The amount of solid necessary is dependent upon whether a sufficient amount of extract will be produced to support the analyses. If an adequate amount of solid remains, proceed to Step 7.2.10 of the nonvolatile 1312 extraction.

7.2 Procedure when Volatiles are not Involved

A minimum sample size of 100 grams (solid and liquid phases) is recommended. In some cases, a larger sample size may be appropriate, depending on the solids content of the waste sample (percent solids, See Step 7.1.1),

whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of 1312 extract will be sufficient to support all of the analyses required. If the amount of extract generated by a single 1312 extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

7.2.1 If the sample will obviously yield no liquid when subjected to pressure filtration (i.e., is 100 % solid, see Step 7.1.1), weigh out a subsample of the sample (100 gram minimum) and proceed to Step 7.2.9.

7.2.2 If the sample is liquid or multiphasic, liquid/solid separation is required. This involves the filtration device described in Step 4.3.2 and is outlined in Steps 7.2.3 to 7.2.8.

7.2.3 Pre-weigh the container that will receive the filtrate.

7.2.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (see Step 4.4).

Note: Acid washed filters may be used for all nonvolatile extractions even when metals are not of concern.

7.2.5 Weigh out a subsample of the sample (100 gram minimum) and record the weight. If the waste contains <0.5 % dry solids (Step 7.1.2), the liquid portion of the waste, after filtration, is defined as the 1312 extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required of the 1312 extract. For wastes containing >0.5 % dry solids (Steps 7.1.1 or 7.1.2), use the percent solids information obtained in Step 7.1.1 to determine the optimum sample size (100 gram minimum) for filtration. Enough solids should be generated by filtration to support the analyses to be performed on the 1312 extract.

7.2.6 Allow slurries to stand to permit the solid phase to settle. Samples that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the sample is centrifuged, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.2.7 Quantitatively transfer the sample (liquid and solid phases) to the filter holder (see Step 4.3.2). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering.

NOTE: If waste material (>1 % of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 7.2.5, to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point if not reached under 10 psi, and if no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10-psi increments to maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psi increment. When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within a 2-minute period), stop the filtration.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.2.8 The material in the filter holder is defined as the solid phase of the sample, and the filtrate is defined as the liquid phase. Weigh the filtrate. The liquid phase may now be either analyzed (see Steps 7.2.12) or stored at 4°C until time of analysis.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material which appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Step 7.2.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid, and is carried through the extraction as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.2.9 If the sample contains <0.5% dry solids (see Step 7.1.2), proceed to Step 7.2.13. If the sample contains >0.5 % dry solids (see Step 7.1.1 or 7.1.2), and if particle-size reduction of the solid was needed in Step 7.1.3, proceed to Step 7.2.10. If the sample as received passes a 9.5 mm sieve, quantitatively transfer the solid material into the extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to Step 7.2.11.

7.2.10 Prepare the solid portion of the sample for extraction by crushing, cutting, or grinding the waste to a surface area or particle-size as described in Step 7.1.3. When the surface area or particle-size has been appropriately altered, quantitatively transfer the solid material into an extractor bottle. Include the filter used to separate the initial liquid from the solid phase.

NOTE: Sieving of the waste is not normally required. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended. If

sieving is necessary, a Teflon-coated sieve should be used to avoid contamination of the sample.

7.2.11 Determine the amount of extraction fluid to add to the extractor vessel as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \%\ \text{solids (Step 7.1.1)} \times \text{weight of waste filtered (Step 7.2.5 or 7.2.7)}}{100}$$

Slowly add this amount of appropriate extraction fluid (see Step 7.1.4) to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal), secure in rotary extractor device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction takes place) shall be maintained at 23 ± 2°C during the extraction period.

NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of sample (e.g., limed or calcium carbonate-containing sample may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

7.2.12 Following the 18 ± 2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter, as outlined in Step 7.2.7. For final filtration of the 1312 extract, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filter(s) shall be acid-washed (see Step 4.4) if evaluating the mobility of metals.

7.2.13 Prepare the 1312 extract as follows:

7.2.13.1 If the sample contained no initial liquid phase, the filtered liquid material obtained from Step 7.2.12 is defined as the 1312 extract. Proceed to Step 7.2.14.

7.2.13.2 If compatible (e.g., multiple phases will not result on combination), combine the filtered liquid resulting from Step 7.2.12 with the initial liquid phase of the sample obtained in Step 7.2.7. This combined liquid is defined as the 1312 extract. Proceed to Step 7.2.14.

7.2.13.3 If the initial liquid phase of the waste, as obtained from Step 7.2.7, is not or may not be compatible with the filtered liquid resulting from Step 7.2.12, do not combine these liquids. Analyze these liquids, collectively defined as the 1312 extract, and combine the results mathematically, as described in Step 7.2.14.

7.2.14 Following collection of the 1312 extract, the pH of the extract should be recorded. Immediately aliquot and preserve the extract

for analysis. Metals aliquots must be acidified with nitric acid to pH < 2. If precipitation is observed upon addition of nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metals analyses shall not be acidified and the extract shall be analyzed as soon as possible. All other aliquots must be stored under refrigeration (4°C) until analyzed. The 1312 extract shall be prepared and analyzed according to appropriate analytical methods. 1312 extracts to be analyzed for metals shall be acid digested except in those instances where digestion causes loss of metallic analytes. If an analysis of the undigested extract shows that the concentration of any regulated metallic analyte exceeds the regulatory level, then the waste is hazardous and digestion of the extract is not necessary. However, data on undigested extracts alone cannot be used to demonstrate that the waste is not hazardous. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to $\pm$ 0.5 %), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)\ (C_1) + (V_2)\ (C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phase (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.2.15 Compare the analyte concentrations in the 1312 extract with the levels identified in the appropriate regulations. Refer to Section 8.0 for quality assurance requirements.

7.3 Procedure when Volatiles are Involved

Use the ZHE device to obtain 1312 extract for analysis of volatile compounds only. Extract resulting from the use of the ZHE shall not be used to evaluate the mobility of non-volatile analytes (e.g., metals, pesticides, etc.).

The ZHE device has approximately a 500 mL internal capacity. The ZHE can thus accommodate a maximum of 25 grams of solid (defined as that fraction of a sample from which no additional liquid may be forced out by an applied pressure of 50 psi), due to the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase.

Charge the ZHE with sample only once and do not open the device until the final extract (of the solid) has been collected. Repeated filling of the ZHE to obtain 25 grams of solid is not permitted.

Do not allow the sample, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary. Any

manipulation of these materials should be done when cold (4°C) to minimize loss of volatiles.

7.3.1 Pre-weigh the (evacuated) filtrate collection container (see Step 4.6) and set aside. If using a TEDLAR® bag, express all liquid from the ZHE device into the bag, whether for the initial or final liquid/solid separation, and take an aliquot from the liquid in the bag for analysis. The containers listed in Step 4.6 are recommended for use under the conditions stated in Steps 4.6.1-4.6.3.

7.3.2 Place the ZHE piston within the body of the ZHE (it may be helpful first to moisten the piston O-rings slightly with extraction fluid). Adjust the piston within the ZHE body to a height that will minimize the distance the piston will have to move once the ZHE is charged with sample (based upon sample size requirements determined from Step 7.3, Step 7.1.1 and/or 7.1.2). Secure the gas inlet/outlet flange (bottom flange) onto the ZHE body in accordance with the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set liquid inlet/outlet flange (top flange) aside.

7.3.3 If the sample is 100% solid (see Step 7.1.1), weigh out a subsample (25 gram maximum) of the waste, record weight, and proceed to Step 7.3.5.

7.3.4 If the sample contains <0.5% dry solids (Step 7.1.2), the liquid portion of waste, after filtration, is defined as the 1312 extract. Filter enough of the sample so that the amount of filtered liquid will support all of the volatile analyses required. For samples containing $\geq$0.5% dry solids (Steps 7.1.1 and/or 7.1.2), use the percent solids information obtained in Step 7.1.1 to determine the optimum sample size to charge into the ZHE. The recommended sample size is as follows:

7.3.4.1 For samples containing <5% solids (see Step 7.1.1), weigh out a 500 gram subsample of waste and record the weight.

7.3.4.2 For wastes containing >5% solids (see Step 7.1.1), determine the amount of waste to charge into the ZHE as follows:

$$\text{Weight of waste to charge ZHE} = \frac{25}{\text{percent solids (Step 7.1.1)}} \times 100$$

Weigh out a subsample of the waste of the appropriate size and record the weight.

7.3.5 If particle-size reduction of the solid portion of the sample was required in Step 7.1.3, proceed to Step 7.3.6. If particle-size reduction was not required in Step 7.1.3, proceed to Step 7.3.7.

7.3.6 Prepare the sample for extraction by crushing, cutting, or grinding the solid portion of the waste to a surface area or particle size

as described in Step 7.1.3.1. Wastes and appropriate reduction equipment should be refrigerated, if possible, to 4°C prior to particle-size reduction. The means used to effect particle-size reduction must not generate heat in and of itself. If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be avoided to the extent possible.

NOTE: Sieving of the waste is not recommended due to the possibility that volatiles may be lost. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended.

When the surface area or particle-size has been appropriately altered, proceed to Step 7.3.7.

7.3.7 Waste slurries need not be allowed to stand to permit the solid phase to settle. Do not centrifuge samples prior to filtration.

7.3.8 Quantitatively transfer the entire sample (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens into the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom). Do not attach the extraction collection device to the top plate.

Note: If sample material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the ZHE, determine the weight of this residue and subtract it from the sample weight determined in Step 7.3.4 to determine the weight of the waste sample that will be filtered.

Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1-10 psi (or more if necessary) to force all headspace slowly out of the ZHE device into a hood. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If filtration of the waste at 4°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering. If the waste is 100 % solid (see Step 7.1.1), slowly increase the pressure to a maximum of 50 psi to force most of the headspace out of the device and proceed to Step 7.3.12.

7.3.9 Attach the evacuated pre-weighed filtrate collection container to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1-10 psi to force the liquid phase of the sample into the filtrate collection container. If no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10-psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psi increment.

When liquid flow has ceased such that continued pressure filtration at 50 psi does not result in any additional filtrate within a 2-minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the filtrate collection container.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.3.10 The material in the ZHE is defined as the solid phase of the sample and the filtrate is defined as the liquid phase.

NOTE: Some samples, such as oily wastes and some paint wastes, will obviously contain some material which appears to be a liquid. Even after applying pressure filtration, this material will not filter. If this is the case, the material within the filtration device is defined as a solid, and is carried through the 1312 extraction as a solid.

If the original waste contained <0.5 % dry solids (see Step 7.1.2), this filtrate is defined as the 1312 extract and is analyzed directly. Proceed to Step 7.3.15.

7.3.11 The liquid phase may now be either analyzed immediately (see Steps 7.3.13 through 7.3.15) or stored at 4°C under minimal headspace conditions until time of analysis. Determine the weight of extraction fluid #3 to add to the ZHE as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \%\ \text{solids (Step 7.1.1)} \times \text{weight of waste filtered (Step 7.3.4 or 7.3.8)}}{100}$$

7.3.12 The following steps detail how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction fluid #3 is used in all cases (see Step 5.7).

7.3.12.1 With the ZHE in the vertical position, attach a line from the extraction fluid reservoir to the liquid inlet/outlet valve. The line used shall contain fresh extraction fluid and should be preflushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping or similar means) into the ZHE. Continue pumping extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device.

7.3.12.2 After the extraction fluid has been added, immediately close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Manually rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the

vertical position with the liquid inlet/outlet valve on top. Pressurize the ZHE to 5-10 psi (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. This bleeding shall be done quickly and shall be stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE with 5-10 psi and check all ZHE fittings to ensure that they are closed.

7.3.12.3 Place the ZHE in the rotary extractor apparatus (if it is not already there) and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction occurs) shall be maintained at 23 ± 2°C during agitation.

7.3.13 Following the 18 ± 2 hour agitation period, check the pressure behind the ZHE piston by quickly opening and closing the gas inlet/outlet valve and noting the escape of gas. If the pressure has not been maintained (i.e., no gas release observed), the ZHE is leaking. Check the ZHE for leaking as specified in Step 4.2.1, and perform the extraction again with a new sample of waste. If the pressure within the device has been maintained, the material in the extractor vessel is once again separated into its component liquid and solid phases. If the waste contained an initial liquid phase, the liquid may be filtered directly into the same filtrate collection container (i.e., TEDLAR® bag) holding the initial liquid phase of the waste. A separate filtrate collection container must be used if combining would create multiple phases, or there is not enough volume left within the filtrate collection container. Filter through the glass fiber filter, using the ZHE device as discussed in Step 7.3.9. All extracts shall be filtered and collected if the TEDLAR® bag is used, if the extract is multiphasic, or if the waste contained an initial liquid phase (see Steps 4.6 and 7.3.1).

NOTE: An in-line glass fiber filter may be used to filter the material within the ZHE if it is suspected that the glass fiber filter has been ruptured

7.3.14 If the original sample contained no initial liquid phase, the filtered liquid material obtained from Step 7.3.13 is defined as the 1312 extract. If the sample contained an initial liquid phase, the filtered liquid material obtained from Step 7.3.13 and the initial liquid phase (Step 7.3.9) are collectively defined as the 1312 extract.

7.3.15 Following collection of the 1312 extract, immediately prepare the extract for analysis and store with minimal headspace at 4°C until analyzed. Analyze the 1312 extract according to the appropriate analytical methods. If the individual phases are to be analyzed separately (i.e., are not miscible), determine the volume of the individual phases (to 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume- weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)\ (C_1) + (V_2)\ (C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phases (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.3.16 Compare the analyte concentrations in the 1312 extract with the levels identified in the appropriate regulations. Refer to Section 8.0 for quality assurance requirements.

8.0 QUALITY CONTROL

8.1 A minimum of one blank (using the same extraction fluid as used for the samples) for every 20 extractions that have been conducted in an extraction vessel.

8.2 A matrix spike shall be performed for each waste type (e.g., wastewater treatment sludge, contaminated soil, etc.) unless the result exceeds the regulatory level and the data is being used solely to demonstrate that the waste property exceeds the regulatory level. A minimum of one matrix spike must be analyzed for each analytical batch. As a minimum, follow the matrix spike addition guidance provided in each analytical method.

8.2.1 Matrix spikes are to be added after filtration of the 1312 extract and before preservation. Matrix spikes should not be added prior to 1312 extraction of the sample.

8.2.2 In most cases, matrix spike levels should be added at a concentration equivalent to the corresponding regulatory level. If the analyte concentration is less than one half the regulatory level, the spike concentration may be as low as one half of the analyte concentration, but may not be less than five times the method detection limit. In order to avoid differences in matrix effects, the matrix spikes must be added to the same nominal volume of 1312 extract as that which was analyzed for the unspiked sample.

8.2.3 The purpose of the matrix spike is to monitor the performance of the analytical methods used, and to determine whether matrix interferences exist. Use of other internal calibration methods, modification of the analytical methods, or use of alternate analytical methods may be needed to accurately measure the analyte concentration in the 1312 extract when the recovery of the matrix spike is below the expected analytical method performance.

8.2.4 Matrix spike recoveries are calculated by the following formula:

$$\%R \text{ (\% Recovery)} = 100 \, (X_s - X_u) / K$$

where:

X_s = measured value for the spiked sample
X_u = measured value for the unspiked sample, and
K = known value of the spike in the sample.

K = known value of the spike in the sample.

8.3 All quality control measures described in the appropriate analytical methods shall be followed.

8.4 The use of internal calibration quantitation methods shall be employed for a metallic contaminant if: (1) Recovery of the contaminant from the 1312 extract is not at least 50% and the concentration does not exceed the appropriate regulatory level, and (2) The concentration of the contaminant measured in the extract is within 20% of the appropriate regulatory level.

8.4.1. The method of standard additions shall be employed as the internal calibration quantitation method for each metallic contaminant.

8.4.2 The method of standard additions requires preparing calibration standards in the sample matrix rather than reagent water or blank solution. It requires taking four identical aliquots of the solution and adding known amounts of standard to three of these aliquots. The forth aliquot is the unknown. Preferably, the first addition should be prepared so that the resulting concentration is approximately 50% of the expected concentration of the sample. The second and third additions should be prepared so that the concentrations are approximately 100% and 150% of the expected concentration of the sample. All four aliquots are maintained at the same final volume by adding reagent water or a blank solution, and may need dilution adjustment to maintain the signals in the linear range of the instrument technique. All four aliquots are analyzed.

8.4.3 Prepare a plot, or subject data to linear regression, of instrument signals or external-calibration-derived concentrations as the dependant variable (y-axis) versus concentrations of the additions of standards as the independent variable (x-axis). Solve for the intercept of the abscissa (the independent variable, x-axis) which is the concentration in the unknown.

8.4.4 Alternately, subtract the instrumental signal or external-calibration-derived concentration of the unknown (unspiked) sample from the instrumental signals or external-calibration-derived concentrations of the standard additions. Plot or subject to linear regression of the corrected instrument signals or external-calibration-derived concentrations as the dependant variable versus the independent variable. Derive concentrations for the unknowns using the internal calibration curve as if it were an external calibration curve.

8.5 Samples must undergo 1312 extraction within the following time periods:

SAMPLE MAXIMUM HOLDING TIMES (days)

	From: Field Collection To: 1312 extraction	From: 1312 extraction To: Preparative extraction	From: Preparative extraction To: determinative analysis	Total Elapsed Time
Volatiles	14	NA	14	28
Semi-volatiles	14	7	40	61
Mercury	28	NA	28	56
Metals, except mercury	180	NA	180	360
NA = Not Applicable				

If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding the holding time is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory level.

9.0 METHOD PERFORMANCE

9.1 Precision results for semi-volatiles and metals: An eastern soil with high organic content and a western soil with low organic content were used for the semi-volatile and metal leaching experiments. Both types of soil were analyzed prior to contaminant spiking. The results are shown in Table 6. The concentrations of contaminants leached from the soils were consistently reproducible, as shown by the low relative standard deviations (RSDs) of the recoveries (generally less than 10 % for most of the compounds).

9.2 Precision results for volatiles: Four different soils were spiked and tested for the extraction of volatiles. Soils One and Two were from western and eastern Superfund sites. Soils Three and Four were mixtures of a western soil with low organic content and two different municipal sludges. The results are shown in Table 7. Extract concentrations of volatile organics from the eastern soil were lower than from the western soil. Replicate leachings of Soils Three and Four showed lower precision than the leachates from the Superfund soils.

10.0 REFERENCES

1.0 Environmental Monitoring Systems Laboratory, "Performance Testing of Method 1312; QA Support for RCRA Testing: Project Report". EPA/600/4-89/022. EPA Contract 68-03-3249 to Lockheed Engineering and Sciences Company, June 1989.

2.0 Research Triangle Institute, "Interlaboratory Comparison of Methods 1310, 1311, and 1312 for Lead in Soil". U.S. EPA Contract 68-01-7075, November 1988.

Table 1. Volatile Analytes[1]

Compound	CAS No.
Acetone	67-64-1
Benzene	71-43-2
n-Butyl alcohol	71-36-3
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroform	67-66-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethylene	75-35-4
Ethyl acetate	141-78-6
Ethyl benzene	100-41-4
Ethyl ether	60-29-7
Isobutanol	78-83-1
Methanol	67-56-1
Methylene chloride	75-09-2
Methyl ethyl ketone	78-93-3
Methyl isobutyl ketone	108-10-1
Tetrachloroethylene	127-18-4
Toluene	108-88-3
1,1,1,-Trichloroethane	71-55-6
Trichloroethylene	79-01-6
Trichlorofluoromethane	75-69-4
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1
Vinyl chloride	75-01-4
Xylene	1330-20-7

[1] When testing for any or all of these analytes, the zero-headspace extractor vessel shall be used instead of the bottle extractor.

Table 2. Suitable Rotary Agitation Apparatus[1]

Company	Location	Model No.
Analytical Testing and Consulting Services, Inc.	Warrington, PA (215) 343-4490	4-vessel extractor (DC20S); 8-vessel extractor (DC20); 12-vessel extractor (DC20B)
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	2-vessel (3740-2); 4-vessel (3740-4); 6-vessel (3740-6); 8-vessel (3740-8); 12-vessel (3740-12); 24-vessel (3740-24)
Environmental Machine and Design, Inc.	Lynchburg, VA (804) 845-6424	8-vessel (08-00-00) 4-vessel (04-00-00)
IRA Machine Shop and Laboratory	Santurce, PR (809) 752-4004	8-vessel (011001)
Lars Lande Manufacturing	Whitmore Lake, MI (313) 449-4116	10-vessel (10VRE) 5-vessel (5VRE)
Millipore Corp.	Bedford, MA (800) 225-3384	4-ZHE or 4 1-liter bottle extractor (YT300RAHW)

[1] Any device that rotates the extraction vessel in an end-over-end fashion at 30 ±2 rpm is acceptable.

Table 3. Suitable Zero-Headspace Extractor Vessels[1]

Company	Location	Model No.
Analytical Testing & Consulting Services, Inc.	Warrington, PA (215) 343-4490	C102, Mechanical Pressure Device
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	3745-ZHE, Gas Pressure Device
Lars Lande Manufacturing[2]	Whitmore Lake, MI (313) 449-4116	ZHE-11, Gas Pressure Device
Millipore Corporation	Bedford, MA (800) 225-3384	YT30090HW, Gas Pressure Device
Environmental Machine and Design, Inc.	Lynchburg, VA (804) 845-6424	VOLA-TOX1, Gas Pressure Device

[1] Any device that meets the specifications listed in Step 4.2.1 of the method is suitable.

[2] This device uses a 110 mm filter.

Table 4. Suitable Filter Holders[1]

Company	Location	Model/ Catalogue #	Size
Nucleopore Corporation	Pleasanton, CA (800) 882-7711	425910 410400	142 mm 47 mm
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	302400 311400	142 mm 47 mm
Millipore Corporation	Bedford, MA (800) 225-3384	YT30142HW XX1004700	142 mm 47 mm

[1] Any device capable of separating the liquid from the solid phase of the waste is suitable, providing that it is chemically compatible with the waste and the constituents to be analyzed. Plastic devices (not listed above) may be used when only inorganic analytes are of concern. The 142 mm size filter holder is recommended.

Table 5. Suitable Filter Media[1]

Company	Location	Model	Pore Size (μm)
Millipore Corporation	Bedford, MA (800) 225-3384	AP40	0.7
Nucleopore Corporation	Pleasanton, CA (415) 463-2530	211625	0.7
Whatman Laboratory Products, Inc.	Clifton, NJ (201) 773-5800	GFF	0.7
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	GF75	0.7

[1] Any filter that meets the specifications in Step 4.4 of the Method is suitable.

TABLE 6 - METHOD 1312 PRECISION RESULTS FOR SEMI-VOLATILES AND METALS

		Eastern Soil (pH 4.2)		Western Soil (pH 5.0)	
	Amount Spiked (μg)	Amount Recovered* (μg)	% RSD	Amount Recovered* (μg)	% RSD
FORTIFIED ANALYTES					
bis(2-chloroethyl)-ether	1040	834	12.5	616	14.2
2-Chlorophenol	1620	1010	6.8	525	54.9
1,4-Dichlorobenzene	2000	344	12.3	272	34.6
1,2-Dichlorobenzene	8920	1010	8.0	1520	28.4
2-Methylphenol	3940	1860	7.7	1130	32.6
Nitrobenzene	1010	812	10.0	457	21.3
2,4-Dimethylphenol	1460	200	18.4	18	87.6
Hexachlorobutadiene	6300	95	12.9	280	22.8
Acenaphthene	3640	210	8.1	310**	7.7
2,4-Dinitrophenol	1300	896**	6.1	23**	15.7
2,4-Dinitrotoluene	1900	1150	5.4	585	54.4
Hexachlorobenzene	1840	3.7	12.0	10	173.2
gamma BHC (Lindane)	7440	230	16.3	1240	55.2
beta BHC	640	35	13.3	65.3	51.7
METALS					
Lead	5000	70	4.3	10	51.7
Cadmium	1000	387	2.3	91	71.3

* = Triplicate analyses.
** = Duplicate analyses; one value was rejected as an outlier at the 90% confidence level using the Dixon Q test.

TABLE 7 - METHOD 1312 PRECISION RESULTS FOR VOLATILES

Compound Name	Soil No. 1 (Western) Avg. %Rec.*	%RSD	Soil No. 2 (Eastern) Avg. %Rec.*	%RSD	Soil No. 3 (Western and Sludge) Avg. %Rec.**	%RSD	Soil No. 4 (Western and Sludge) Avg. %Rec.***	%RSD
Acetone	44.0	12.4	43.8	2.25	116.0	11.5	21.3	71.4
Acrylonitrile	52.5	68.4	50.5	70.0	49.3	44.9	51.8	4.6
Benzene	47.8	8.29	34.8	16.3	49.8	36.7	33.4	41.1
n-Butyl Alcohol (1-Butanol)	55.5	2.91	49.2	14.6	65.5	37.2	73.0	13.9
Carbon disulfide	21.4	16.4	12.9	49.5	36.5	51.5	21.3	31.5
Carbon tetrachloride	40.6	18.6	22.3	29.1	36.2	41.4	24.0	34.0
Chlorobenzene	64.4	6.76	41.5	13.1	44.2	32.0	33.0	24.9
Chloroform	61.3	8.04	54.8	16.4	61.8	29.1	45.8	38.6
1,2-Dichloroethane	73.4	4.59	68.7	11.3	58.3	33.3	41.2	37.8
1,1-Dichloroethane	31.4	14.5	22.9	39.3	32.0	54.4	16.8	26.4
Ethyl acetate	76.4	9.65	75.4	4.02	23.0	119.8	11.0	115.5
Ethylbenzene	56.2	9.22	23.2	11.5	37.5	36.1	27.2	28.6
Ethyl ether	48.0	16.4	55.1	9.72	37.3	31.2	42.0	17.6
Isobutanol (4-Methyl -1-propanol)	0.0	ND	0.0	ND	61.8	37.7	76.0	12.2
Methylene chloride	47.5	30.3	42.2	42.9	52.0	37.4	37.3	16.6
Methyl ethyl ketone (2-Butanone)	56.7	5.94	61.9	3.94	73.7	31.3	40.6	39.0
Methyl isobutyl ketone	81.1	10.3	88.9	2.99	58.3	32.6	39.8	40.3
1,1,1,2-Tetrachloroethane	69.0	6.73	41.1	11.3	50.8	31.5	36.8	23.8
1,1,2,2-Tetrachloroethane	85.3	7.04	58.9	4.15	64.0	25.7	53.6	15.8
Tetrachloroethene	45.1	12.7	15.2	17.4	26.2	44.0	18.6	24.2
Toluene	59.2	8.06	49.3	10.5	45.7	35.2	31.4	37.2
1,1,1-Trichloroethane	47.2	16.0	33.8	22.8	40.7	40.6	26.2	38.8
1,1,2-Trichloroethane	76.2	5.72	67.3	8.43	61.7	28.0	46.4	25.4
Trichloroethene	54.5	11.1	39.4	19.5	38.8	40.9	25.6	34.1
Trichlorofluoromethane	20.7	24.5	12.6	60.1	28.5	34.0	19.8	33.9
1,1,2-Trichlorotrifluoroethane	18.1	26.7	6.95	58.0	21.5	67.8	15.3	24.8
Vinyl chloride	10.2	20.3	7.17	72.8	25.0	61.0	11.8	25.4

* Triplicate analyses
** Six replicate analyses
*** Five replicate analyses

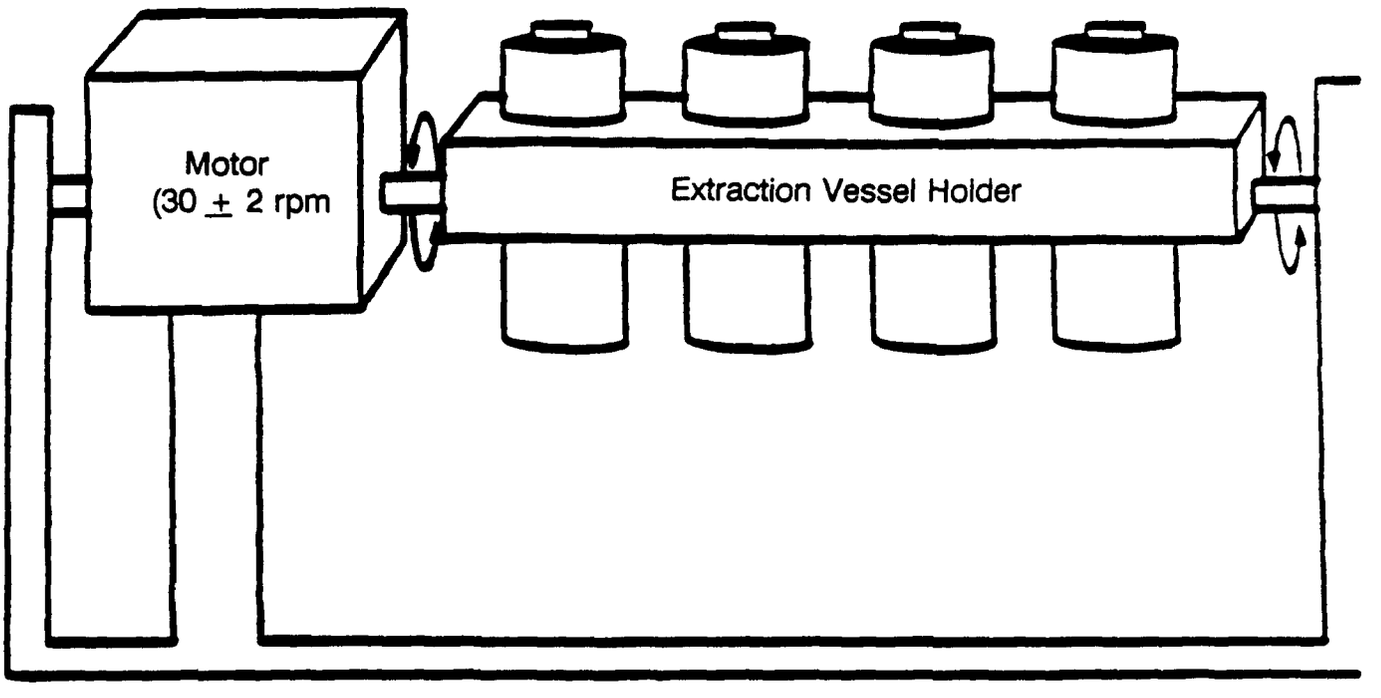


Figure 1. Rotary Agitation Apparatus

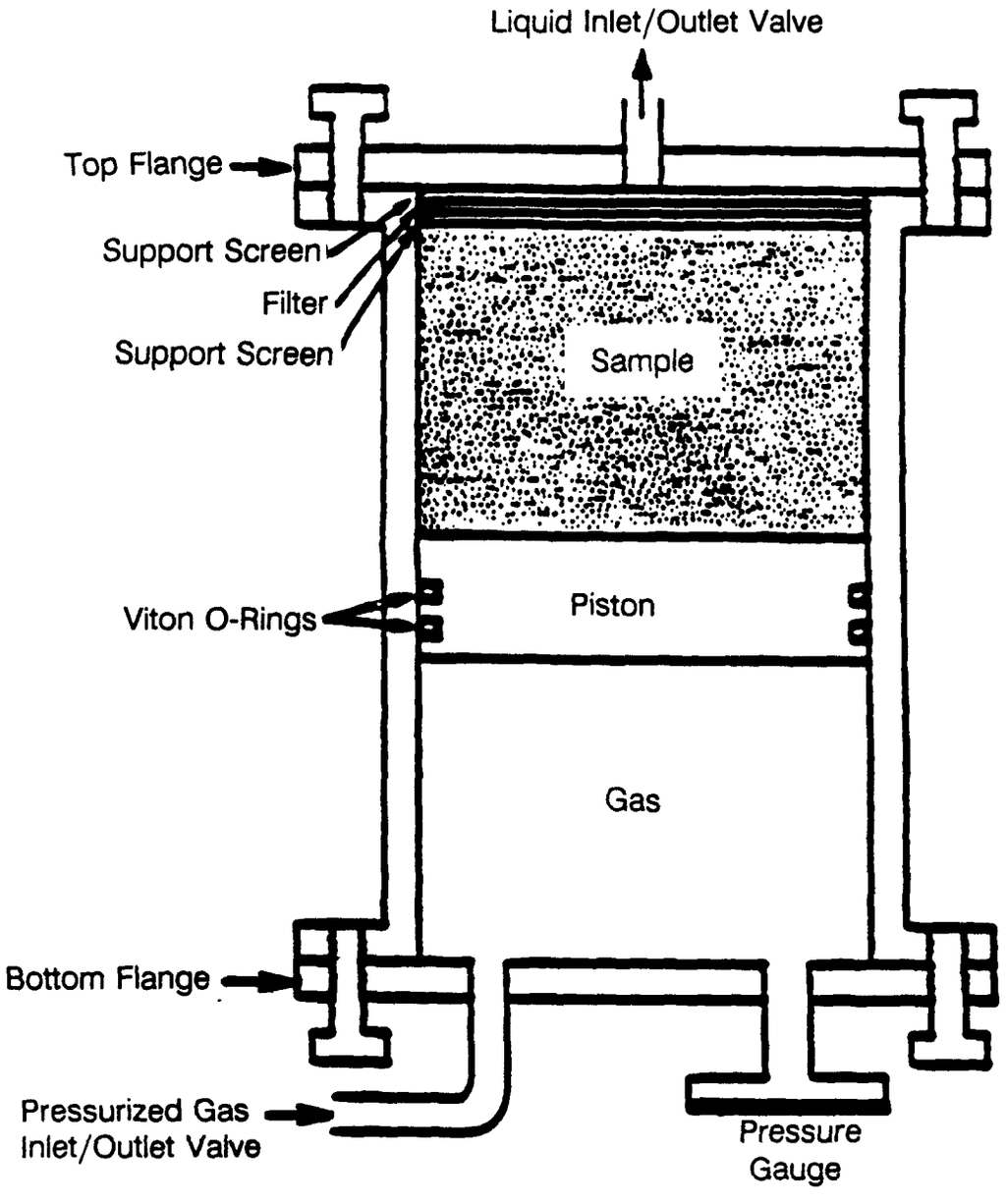
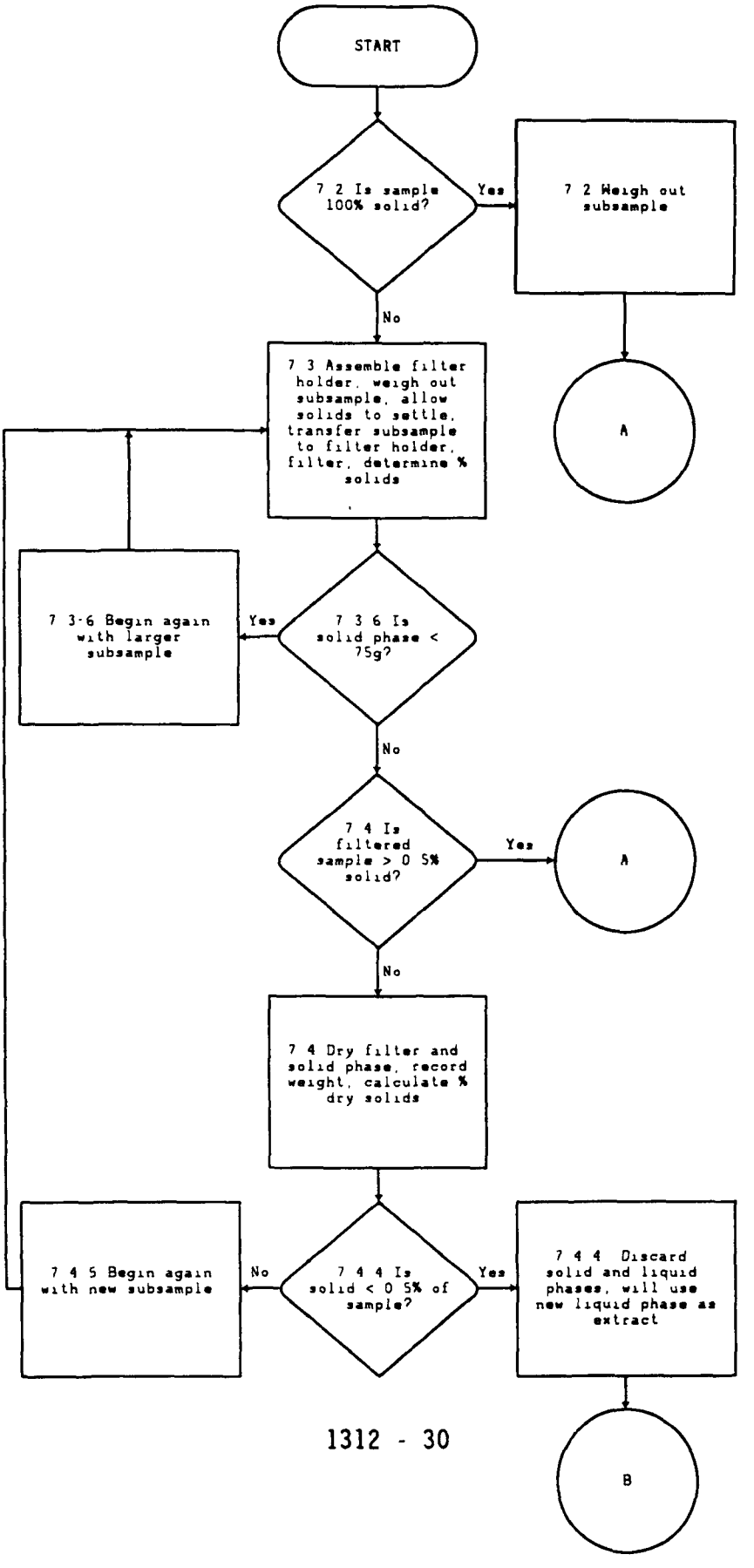


Figure 2. Zero-Headspace Extractor (ZHE)

METHOD 1312

SYNTHETIC PRECIPITATION LEACHING PROCEDURE



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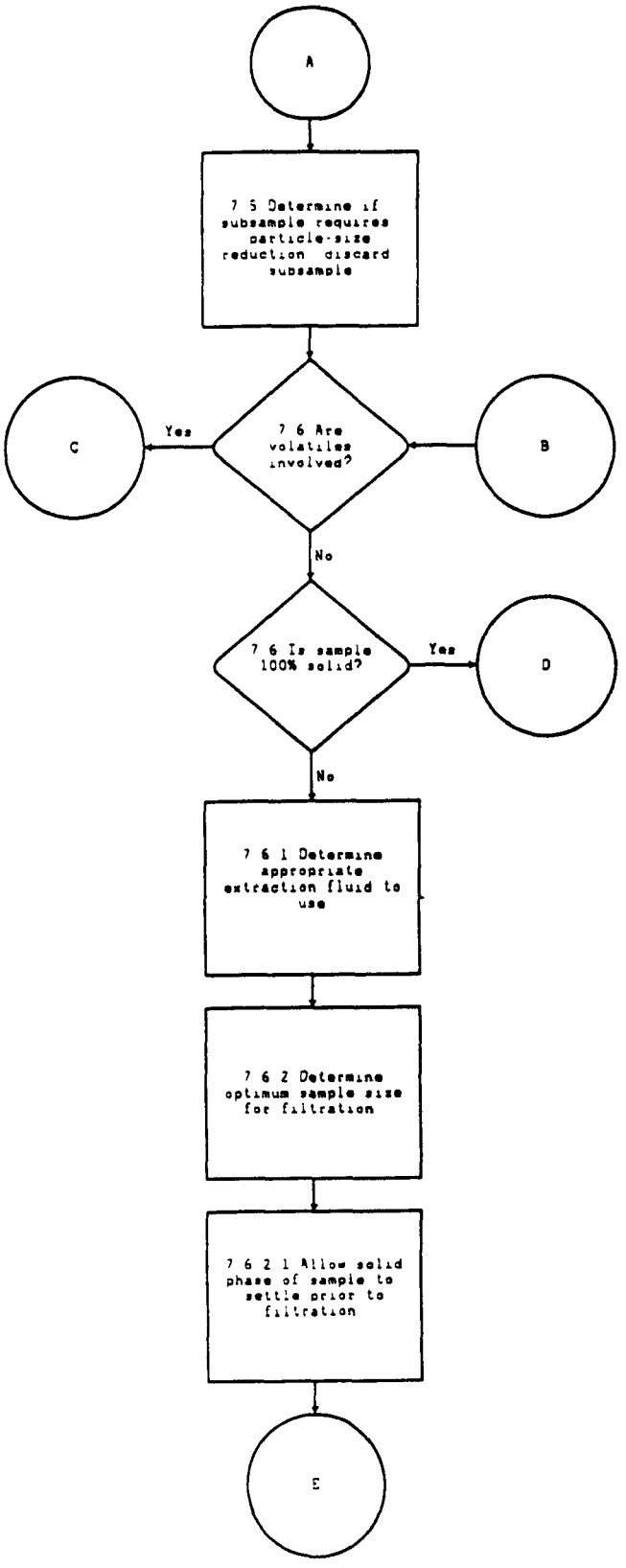

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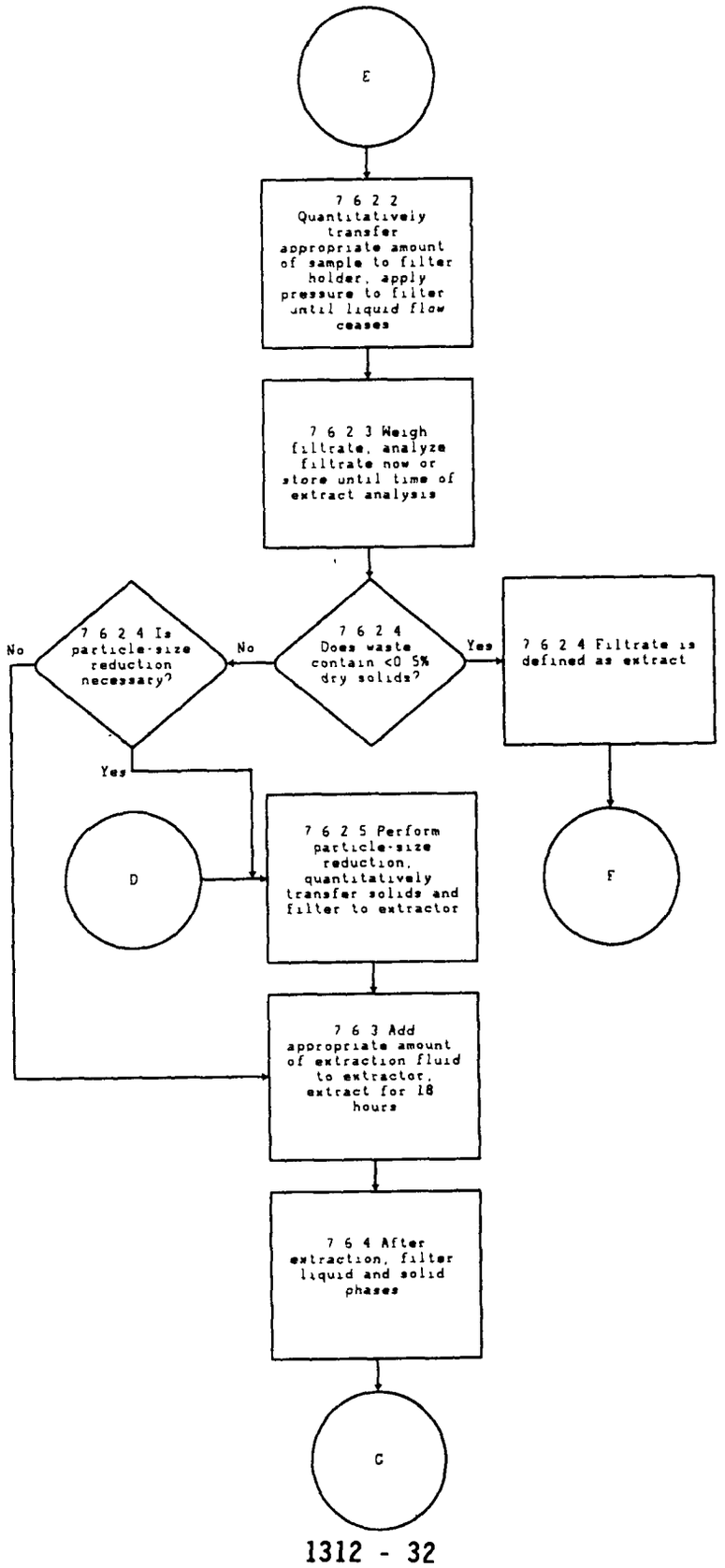

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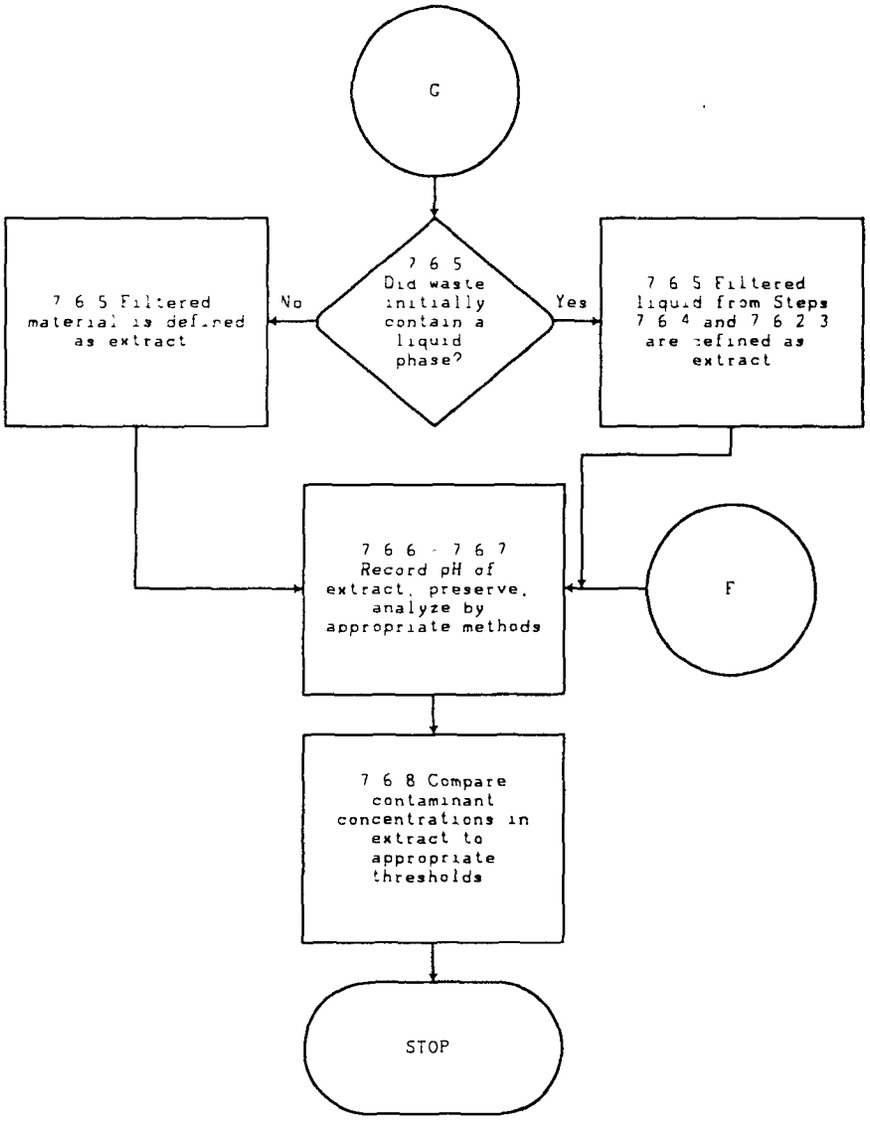

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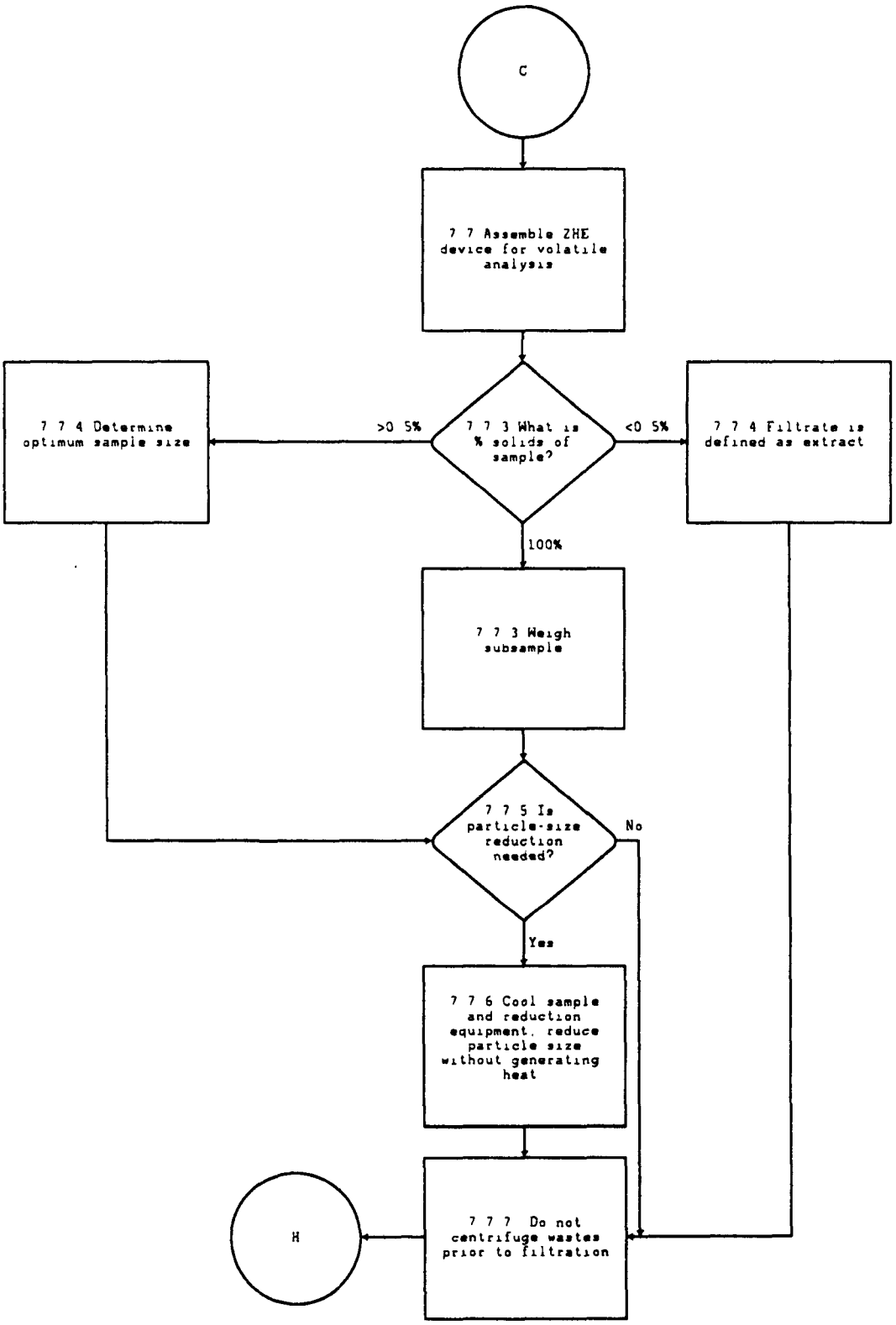

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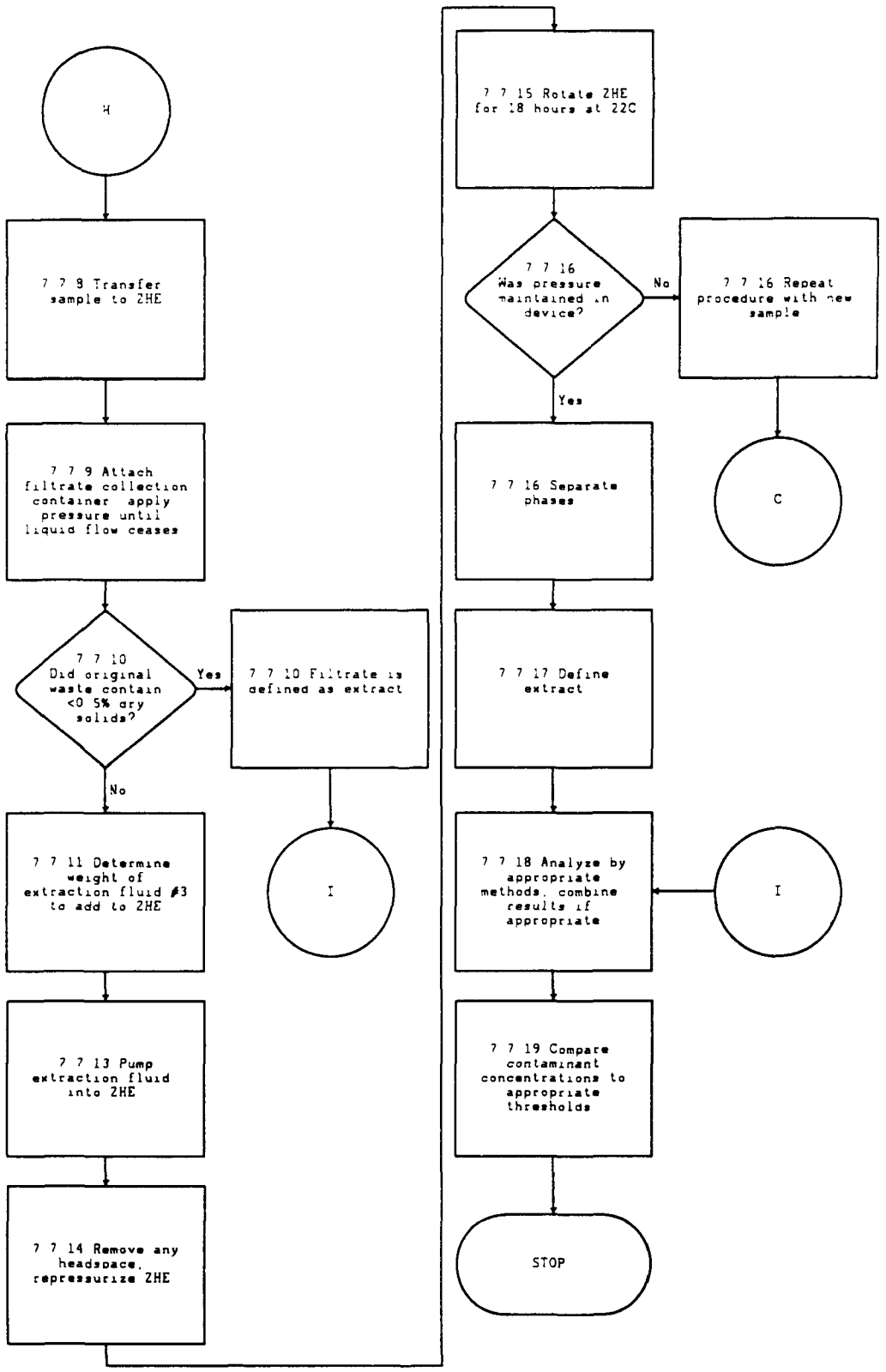


METHOD 9045B

SOIL AND WASTE pH

1.0 SCOPE AND APPLICATION

1.1 Method 9045 is an electrometric procedure for measuring pH in soils and waste samples. Wastes may be solids, sludges, or non-aqueous liquids. If water is present, it must constitute less than 20% of the total volume of the sample.

2.0 SUMMARY OF METHOD

2.1 The sample is mixed with reagent water, and the pH of the resulting aqueous solution is measured.

3.0 INTERFERENCES

3.1 Samples with very low or very high pH may give incorrect readings on the meter. For samples with a true pH of >10, the measured pH may be incorrectly low. This error can be minimized by using a low-sodium-error electrode. Strong acid solutions, with a true pH of <1, may give incorrectly high pH measurements.

3.2 Temperature fluctuations will cause measurement errors.

3.3 Errors will occur when the electrodes become coated. If an electrode becomes coated with an oily material that will not rinse free, the electrode can either (1) be cleaned with an ultrasonic bath, or (2) be washed with detergent, rinsed several times with water, placed in 1:10 HCl so that the lower third of the electrode is submerged, and then thoroughly rinsed with water.

4.0 APPARATUS AND MATERIALS

4.1 pH Meter with means for temperature compensation.

4.2 Electrodes:

4.2.1 Calomel electrode.

4.2.2 Glass electrode.

4.2.3 A combination electrode can be employed instead of calomel or glass.

4.3 Beaker: 50-mL.

4.4 Thermometer.

4.5 Analytical balance: capable of weighing 0.1 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 Reagent water. All reference to water in this method refer to reagent water, as defined in Chapter One.

5.3 Primary standard buffer salts are available from the National Institute of Standards and Technology (NIST) and should be used in situations where extreme accuracy is necessary. Preparation of reference solutions from these salts requires some special precautions and handling, such as low-conductivity dilution water, drying ovens, and carbon-dioxide-free purge gas. These solutions should be replaced at least once each month.

5.4 Secondary standard buffers may be prepared from NIST salts or purchased as solutions from commercial vendors. These commercially available solutions, which have been validated by comparison with NIST standards, are recommended for routine use.

6.0 SAMPLE PRESERVATION AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Samples should be analyzed as soon as possible.

7.0 PROCEDURE

7.1 Calibration:

7.1.1 Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.

7.1.2 Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart. Repeat adjustments on successive portions of the two buffer solutions until readings are within 0.05 pH units of the buffer solution value.

7.2 Sample preparation and pH measurement of soils:

7.2.1 To 20 g of soil in a 50-mL beaker, add 20 mL of reagent water and stir the suspension several times during the next 30 minutes.

7.2.2 Let the soil suspension stand for about 1 hour to allow most of the suspended clay to settle out from the suspension or filter off the aqueous phase for pH measurement.

7.2.3 Adjust the electrodes in the clamps of the electrode holder so that, upon lowering the electrodes into the beaker, the glass electrode will be immersed just deep enough into the clear supernatant solution to establish a good electrical contact through the ground-glass joint or the fiber-capillary hole. Insert the electrodes into the sample solution in this manner. For combination electrodes, immerse just below the suspension.

7.2.4 If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values must be corrected.

7.2.5 Report the results as "soil pH measured in water at __°C" where __°C is the temperature at which the test was conducted.

7.3 Sample preparation and pH measurement of waste materials:

7.3.1 To 20 g of waste sample in a 50-mL beaker, add 20 mL of reagent water and stir the suspension several times during the next 30 minutes.

7.3.2 Let the waste suspension stand for about 15 minutes to allow most of the suspended waste to settle out from the suspension or filter off aqueous phase for pH measurement.

NOTE: If the waste is hydroscopic and absorbs all the reagent water, begin the experiment again using 20 g of waste and 40 mL of reagent water.

NOTE: If the supernatant is multiphasic, decant the oily phase and measure the pH of the aqueous phase. The electrode may need to be cleaned (Step 3.3) if it becomes coated with an oily material.

7.3.3 Adjust the electrodes in the clamps of the electrode holder so that, upon lowering the electrodes into the beaker, the glass electrode will be immersed just deep enough into the clear supernatant to establish good electrical contact through the ground-glass joint or the fiber-capillary hole. Insert the electrode into the sample solution in this manner. For combination electrodes, immerse just below the suspension.

7.3.4 If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values must be corrected.

7.3.5 Report the results as "waste pH measured in water at __°C" where __°C is the temperature at which the test was conducted.

8.0 QUALITY CONTROL

8.1 Duplicate samples and check standards should be analyzed with each analytical batch.

8.2 Electrodes must be thoroughly rinsed between samples.

9.0 METHOD PERFORMANCE

9.1 No data provided.

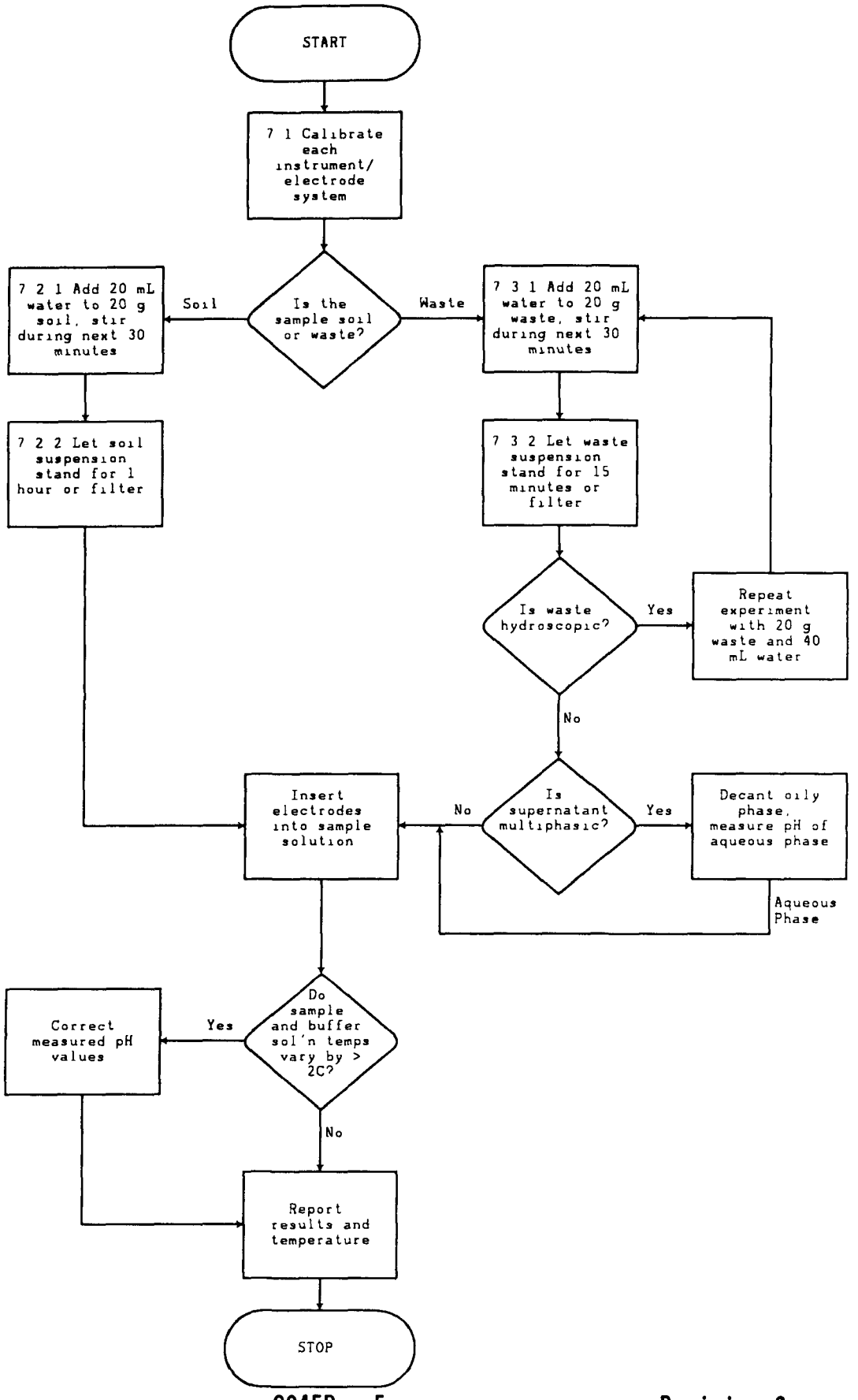
10.0 REFERENCES

1. Black, Charles Allen; Methods of Soil Analysis; American Society of Agronomy: Madison, WI, 1973.

2. National Institute of Standards and Technology, Standard Reference Material Catalog, 1986-87, Special Publication 260.

METHOD 9045B

SOIL AND WASTE pH



ERRATA FOR SW-846 PROPOSED UPDATE II METHOD 9040A

THIS PACKET CONTAINS AN OFFICIAL ERRATA SHEET FOR METHOD 9040A, PROPOSED UPDATE II, OF *TEST METHODS FOR EVALUATING SOLID WASTE, PHYSICAL/CHEMICAL METHODS, SW-846, 3RD EDITION*

Incorporate this errata for Proposed Update II Method 9040A by either:

1. **Placing the errata sheet at the beginning of the method, or**

2. **Manually editing the method to show the text change.**

If you have any problems including this errata in your copy of the Proposed Update II for SW-846, please telephone the Methods Information Communication Exchange (MICE) at (703) 821-4789.

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ERRATA FOR PROPOSED UPDATE II METHOD 9040A

In Step 7.1.2., replace the following text:

> (For corrosivity characterization, the calibration of the pH meter should include a buffer of pH 2 for acidic wastes and a pH 12 buffer for caustic wastes; also for corrosivity characterization, the sample must be measured at 25°C $\pm$ 1°C if the pH of the waste is above 12.0.)

with:

> (For corrosivity characterization, the calibration of the pH meter should include a buffer of pH 2 for acidic wastes and a pH 12 buffer for caustic wastes.)

METHOD 9096

LIQUID RELEASE TEST (LRT) PROCEDURE

1.0 SCOPE AND APPLICATION

1.1 The Liquid Release Test (LRT) is a laboratory test designed to determine whether or not liquids will be released from sorbents when they are subjected to overburden pressures in a landfill.

1.2 Any liquid-loaded sorbent that fails the EPA Paint Filter Free Liquids Test (PFT) (SW-846 Method 9095), may be assumed to release liquids in this test. Analysts should ensure that the material in question will pass the PFT before performing the LRT.

2.0 SUMMARY OF METHOD

2.1 A representative sample of the liquid-loaded sorbent, standing 10 cm high in the device, is placed between twin stainless steel screens and two stainless-steel grids, in a device capable of simulating landfill overburden pressures. An absorptive filter paper is placed on the side of each stainless-steel grid opposite the sample (i.e., the stainless-steel screen separates the sample and the filter paper, while the stainless-steel grid provides a small air gap to prevent wicking of liquid from the sample onto the filter paper). A compressive force of 50 psi is applied to the top of the sample. Release of liquid is indicated when a visible wet spot is observed on either filter paper.

3.0 INTERFERENCES

3.1 When testing sorbents are loaded with volatile liquids (e.g., solvents), any released liquid migrating to the filter paper may rapidly evaporate. For this reason, filter papers should be examined immediately after the test has been conducted.

3.2 It is necessary to thoroughly clean and dry the stainless-steel screens prior to testing to prevent false positive or false negative results. Material caught in screen holes may impede liquid transmission through the screen causing false negative results. A stiff bristled brush, like those used to clean testing sieves, may be used to dislodge material from holes in the screens. The screens should be ultrasonically cleaned with a laboratory detergent, rinsed with deionized water, rinsed with acetone, and thoroughly dried.

When sorbents containing oily substances are tested, it may be necessary to use solvents (e.g., methanol or methylene chloride) to remove any oily residue from the screens and from the sample holder surfaces.

3.3 When placing the 76 mm screen on top of the loaded sample it is important to ensure that no sorbent is present on top of the screen to contact the filter paper and cause false positive results. In addition, some sorbent residue may adhere to container sidewalls and contact the filter as the sample compresses under load, causing wet spots on the edges of the filter. This type of false positive may be avoided by carefully centering the 76 mm filter paper in the device prior to initiating the test.

3.4 Visual examination of the sample may indicate that a release is certain (e.g., free standing liquid or a sample that flows like a liquid), raising concern over unnecessary clean-up of the LRT device. An optional 5 minute Pre-Test, described in Appendix A of this procedure, may be used to determine whether or not an LRT must be performed.

4.0 APPARATUS AND MATERIALS

4.1 LRT Device (LRTD): A device capable of applying 50 psi of pressure continuously to the top of a confined, cylindrical sample (see Figure 1). The pressure is applied by a piston on the top of the sample. All device components contacting the sample (i.e., sample-holder, screens, and piston) should be resistant to attack by substances being tested. The LRTD consists of two basic components, described below.

4.1.1 Sample holder: A rigid-wall cylinder, with a bottom plate, capable of holding a 10 cm high by 76 mm diameter sample.

4.1.2 Pressure Application Device: In the LRTD (Figure 1), pressure is applied to the sample by a pressure rod pushing against a piston that lies directly over the sample. The rod may be pushed against the piston at a set pressure using pneumatic, mechanical, or hydraulic pressure. Pneumatic pressure application devices should be equipped with a pressure gauge accurate to within $\pm$ 1 psi, to indicate when the desired pressure has been attained and whether or not it is adequately maintained during the test. Other types of pressure application devices (e.g., mechanical or hydraulic) may be used if they can apply the specified pressure continuously over the ten minute testing time. The pressure application device must be calibrated by the manufacturer, using a load cell or similar device placed under the piston, to ensure that 50 $\pm$ 1 psi is applied to the top of the sample. The pressure application device should be sufficiently rugged to deliver consistent pressure to the sample with repeated use.

4.2 Stainless-Steel Screens: To separate the sample from the filter, thereby preventing false positive results from particles falling on the filter paper. The screens are made of stainless steel and have hole diameters of 0.012 inches with 2025 holes per square inch. Two diameters of screens are used: a larger (90 mm) screen beneath the sample and a smaller (76 mm) screen that is placed on top of the sample in the sample-holding cylinder.

4.3 Stainless-Steel Grids: To provide an air gap between the stainless-steel screen and filter paper, preventing false positive results from capillary action. The grids are made of 1/32" diameter, woven, stainless steel wire cut to two diameters, 90 mm and 76 mm.

4.4 Filter Papers: To detect released liquid. Two sizes, one 90 mm and one 76 mm, are placed on the side of the screen opposite the sample. The 76 mm diameter filter paper has the outer 6 mm cut away except 3 conical points used for centering the paper (see Figure 2). Blue, seed-germination filter paper manufactured by Schleicher and Schuell (Catalog Number 33900) is suitable. Other colored, absorptive papers may be used as long as they provide sufficient wet/dry contrast for the operator to clearly see a wet spot.

4.5 Spatula: To assist in loading and removing the sample.

4.6 Rubber or wooden mallet: To tap the sides of the device to settle and level the sample.

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 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Acetone.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 All samples should be collected using a sampling plan that addresses the considerations discussed in "Test Methods for Evaluating Solid Wastes (SW-846)." The sampling plan should be designed to detect and sample any pockets of liquids that may be present in a container (i.e., in the bottom or top of the container).

6.2 Preservatives should not be added to samples.

6.3 Samples should be tested as soon as possible after collection, but in no case after more than three days after collection. If samples must be stored, they can be stored in sealed containers and maintained under dark, cool conditions (temperature ranging between 35° and 72° F). Samples should not be frozen.

7.0 PROCEDURE

The procedure below was developed for the original LRTD, manufactured by Associated Design and Manufacturing Company (ADM). Procedures for other LRTDs, along with evidence for equivalency to the ADM device, should be supplied by the manufacturer.

7.1 Disassemble the LRTD and make sure that all parts are clean and dry.

7.2 Invert the sample-holding cylinder and place the large stainless-steel screen, the large stainless-steel grid, then a 90 mm filter paper on the cylinder base (bottom-plate side).

7.3 Secure the bottom plate (plate with a hole in the center and four holes located on the outer circumference) to the flange on the bottom of the sample-holding cylinder using four knob screws.

7.4 Turn the sample holder assembly to the right-side-up position (bottom-plate-side down). Fill the sample holder with a representative sample until the sample height measures 10 cm (up to the etched line in the cylinder).

7.5 Tap the sides of the sample holder with a rubber or wooden mallet to remove air pockets and to settle and level the sample.

7.6 Repeat filling, and tapping until a sample height of 10 cm is maintained after tapping.

7.7 Smooth the top of the sample with a spatula to create a horizontal surface.

7.8 Place the small stainless-steel screen, then the small stainless-steel grid on top of the sample.

NOTE: Prior to placing the stainless-steel grid on top of the screen, make sure that no sorbent material is on the grid side of the stainless-steel screen.

7.9 Place the 76 mm filter paper on top of the small stainless-steel grid, making sure the filter paper is centered in the device.

7.10 Using the piston handle (screwed into the top of the piston) lower the piston into the sample holder until it sits on top of the filter paper. Unscrew and remove the handle.

7.11 Place the loaded sample holder into position on the baseplate and lock into place with two toggle clamps.

7.12 Place the pressure application device on top of the sample-holder. Rotate the device to lock it into place and insert the safety key.

7.13 Connect air lines.

7.14 Initiate rod movement and pressure application by pulling the air-valve lever toward the operator and note time on data sheet. The pressure gauge at the top of the pressure application device should read as specified in the factory calibration record for the particular device. If not, adjust regulator to attain the specified pressure.

NOTE: After pressure application, the air lines can be disconnected, the toggle clamps can be released, and the LRTD can be set aside for 10 minutes while other LRTDs are pressurized. LRTD pressures should be checked every 3 minutes to ensure that the specified pressure is being maintained. If the specified pressure is not being maintained to within $\pm$ psi, the LRTD must be reconnected to the air lines and pressure applied throughout the 10 minute test.

7.15 After 10 minutes place the LRTD on the baseplate, reconnect air lines and toggle clamps, and turn off pressure (retract the rod) by pushing the air-valve lever away from the operator. Note time on data sheet.

7.16 When the air gauge reaches 0 psi, disconnect the air lines and remove the pressure-application device by removing the safety key, rotating the device, and lifting it away from the sample holder.

7.17 Screw the piston handle into the top of the piston.

7.18 Lift out the piston.

7.19 Remove the filter paper and immediately examine it for wet spots (wet area on the filter paper). The presence of a wet spot(s) indicates a positive test (i.e., liquid release). Note results on data sheet.

7.20 Release toggle clamps and remove sample holder from baseplate. Invert sample holder onto suitable surface and remove the knob screws holding the bottom plate.

7.21 Remove the bottom plate and immediately examine the filter paper for wet spots as described in Step 7.19. Note results on data sheet. Wet spot(s) on either filter indicates a positive test.

8.0 QUALITY CONTROL

8.1 Duplicate samples should be analyzed every twenty samples or every analytical batch, whichever is more frequent.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are not available at this time.

10.0 REFERENCES

1. Hoffman, P., G. Kingsbury, B. Lesnik, M. Meyers, "Background Document for the Liquid Release Test (LRT) Procedure"; document submitted to the Environmental Protection Agency by Research Triangle Institute: Research Triangle Park, NC under Contract No. 68-01-7075, Work Assignment 76 and Contract No. 68-WO-0032, Work Assignment 12.

APPENDIX A

1.0 SCOPE AND APPLICATION

1.1 The LRT Pre-Test is an optional, 5 minute laboratory test designed to determine whether or not liquids will be definitely released from sorbents before applying the LRT. This test is performed to prevent unnecessary cleanup and possible damage to the LRT device.

1.2 This test is purely optional and completely up to the discretion of the operator as to when it should be used.

2.0 SUMMARY OF METHOD

A representative sample will be loaded into a glass grid that is placed on a glass plate already stained with 2 dyes (one water soluble and one oil soluble). A second glass plate will be placed on top and a 2 lb. weight placed on top for 5 minutes. At the end of 5 minutes the base of the glass grid is examined for any dye running along the edges, this would indicate a liquid release.

3.0 INTERFERENCES

A liquid release can be detected at lower Liquid Loading Levels with extremely clean glassware. The glass plates and glass grid should be cleaned with a laboratory detergent, rinsed with Deionized water, rinsed with acetone, and thoroughly dried.

4.0 APPARATUS AND MATERIALS

4.1 Glass Plate: 2 glass plates measuring 7.5 cm x 7.5 cm.

4.2 Glass Grid: See Figure 3.

4.3 Paint Brush: Two small paint brushes for applying dyes.

4.4 Spatula: To assist in loading the sample.

4.5 Weight: 2.7 kg weight to apply pressure to the sample.

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 Methylene Blue dye in methanol.

5.3 Anthraquinone dye in toluene.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

See LRT Procedure.

7.0 PROCEDURE

7.1 Paint one strip, approximately 1 cm wide, of methylene blue dye across the center of a clean and dry glass plate (see Figure 4). The dye is allowed to dry.

7.2 Paint one strip, approximately 1 cm wide, of anthraquinone dye across the center of the same glass plate (see Figure 4). This strip should be adjacent to and parallel with the methylene blue strip. The dye is allowed to dry.

7.3 Place the glass grid in the center of the dye-painted glass plate.

7.4 Place a small amount of sample into the glass-grid holes, pressing down gently until the holes are filled to slightly above the grid top.

7.5 Place a second, clean and dry, glass plate on top of the sample and grid.

7.6 Place a 2.7 kg weight on top of the glass for 5 minutes.

7.7 After 5 minutes remove the weight and examine the base of the grid extending beyond the sample holes for any indication of dyed liquid. The entire assembly may be turned upside down for observation. Any indication of liquid constitutes a release and the LRT does not need to be performed.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are not available at this time.

10.0 REFERENCES

1. Research Triangle Institute. "Background Document for the Liquid Release Test: Single Laboratory Evaluation and 1988 Collaborative Study". Submitted to the Environmental Protection Agency under Contract No. 68-01-7075, Work Assignment 76 and Contract No. 68-WO-0032, Work Assignment 12. September 18, 1991.

FIGURE 1.
LRT DEVICE

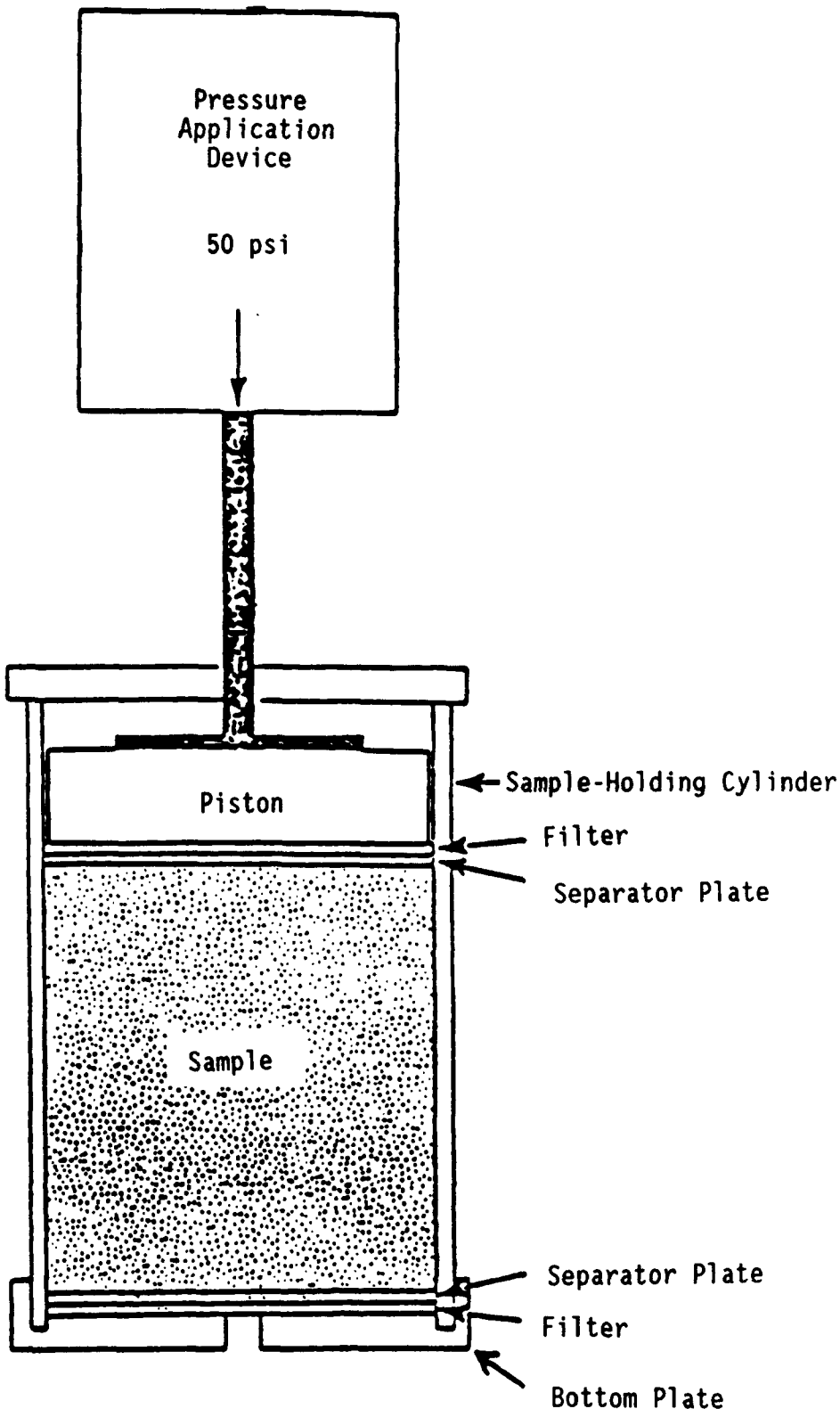


FIGURE 2.
76 MM DIAMETER FILTER PAPER

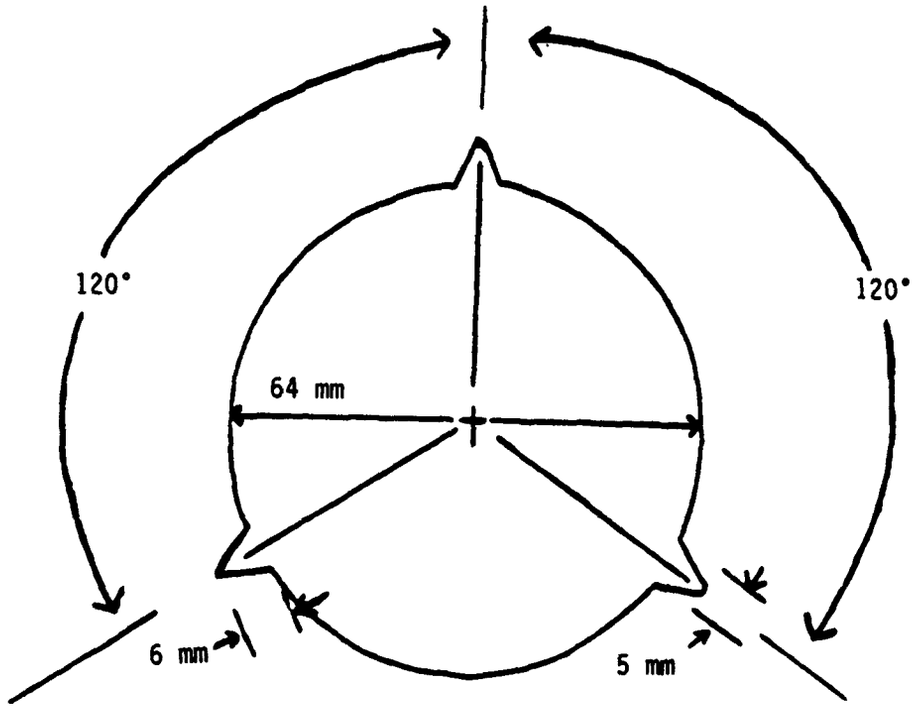


FIGURE 3.
GLASS GRID SPECIFICATIONS.

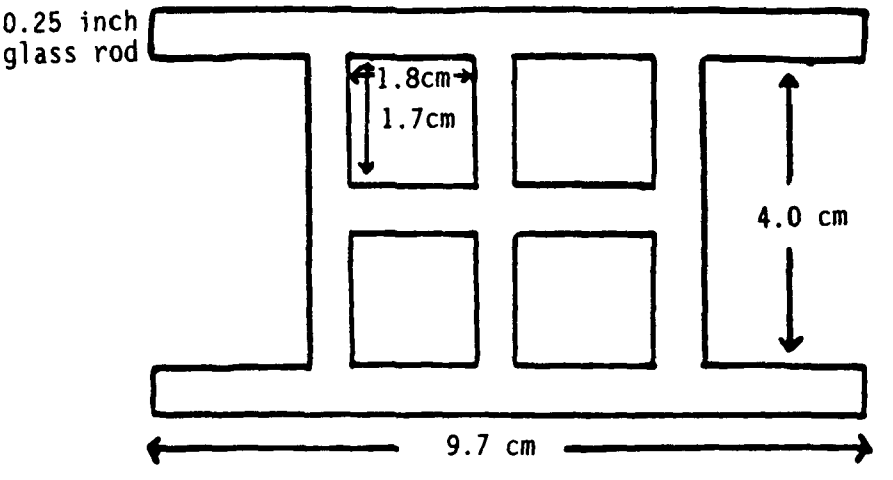
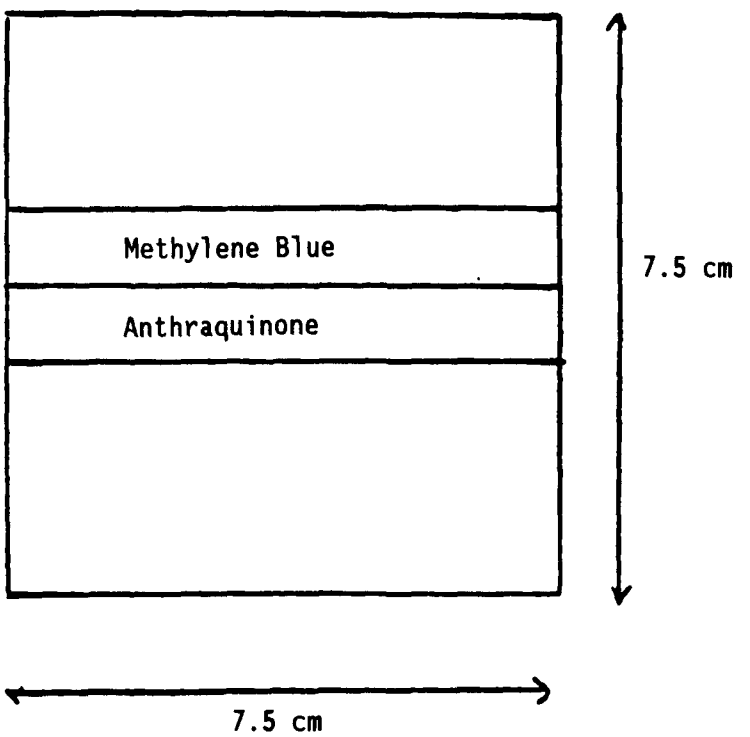
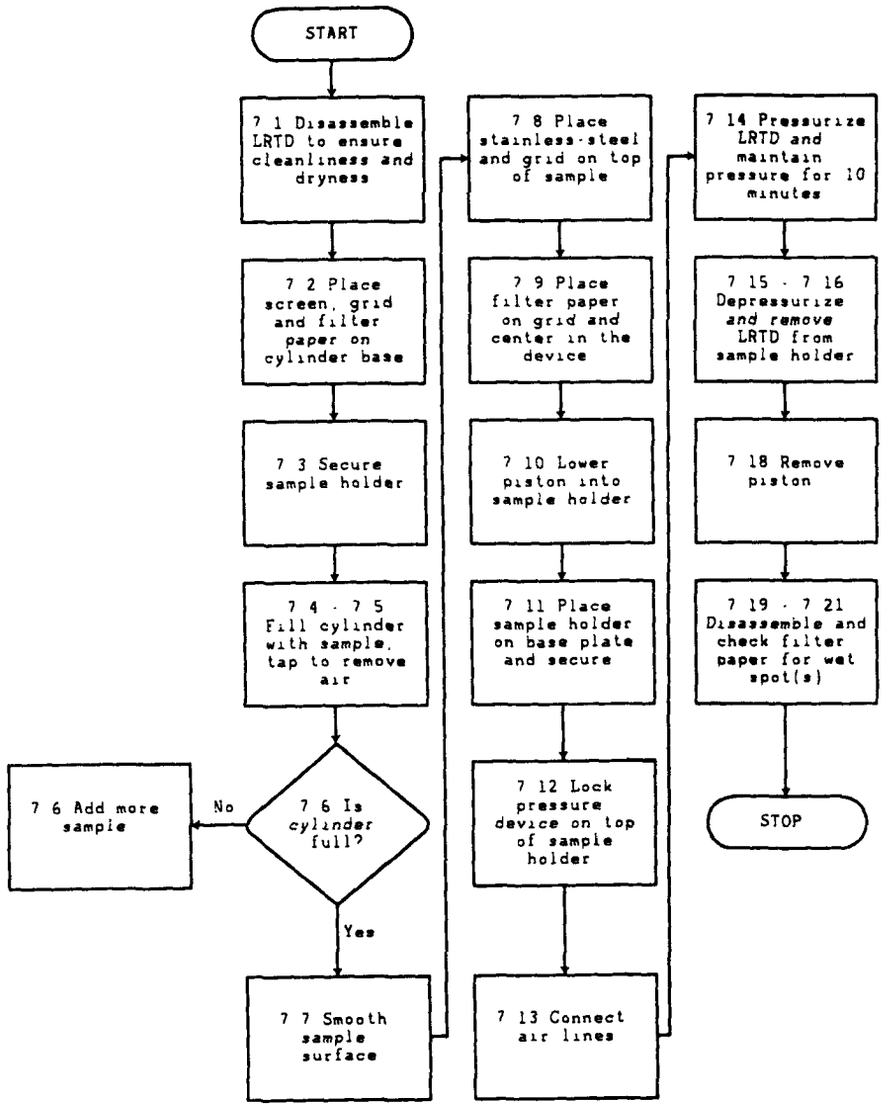


FIGURE 4.
POSITIONING OF DYE ON GLASS PLATE




START
7 1 Disassemble LRTD to ensure cleanliness and dryness
7 2 Place screen, grid and filter paper on cylinder base
7 3 Secure sample holder
7 4 - 7 5 Fill cylinder with sample, tap to remove air
7 6 Is cylinder full?
No
7 6 Add more sample
Yes
7 7 Smooth sample surface
7 8 Place stainless-steel and grid on top of sample
7 9 Place filter paper on grid and center in the device
7 10 Lower piston into sample holder
7 11 Place sample holder on base plate and secure
7 12 Lock pressure device on top of sample holder
7 13 Connect air lines
7 14 Pressurize LRTD and maintain pressure for 10 minutes
7 15 - 7 16 Depressurize and remove LRTD from sample holder
7 18 Remove piston
7 19 - 7 21 Disassemble and check filter paper for wet spot(s)
STOP

METHOD 9040A

pH ELECTROMETRIC MEASUREMENT

1.0 SCOPE AND APPLICATION

1.1 Method 9040 is used to measure the pH of aqueous wastes and those multiphase wastes where the aqueous phase constitutes at least 20% of the total volume of the waste.

1.2 The corrosivity of concentrated acids and bases, or of concentrated acids and bases mixed with inert substances, cannot be measured. The pH measurement requires some water content.

2.0 SUMMARY

2.1 The pH of the sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode. The measuring device is calibrated using a series of standard solutions of known pH.

3.0 INTERFERENCES

3.1 The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants, or high salinity.

3.2 Sodium error at pH levels >10 can be reduced or eliminated by using a low-sodium-error electrode.

3.3 Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing, followed by rinsing with distilled water. An additional treatment with hydrochloric acid (1:10) may be necessary to remove any remaining film.

3.4 Temperature effects on the electrometric determination of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference can be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. The second source of temperature effects is the change of pH due to changes in the sample as the temperature changes. This error is sample-dependent and cannot be controlled. It should, therefore, be noted by reporting both the pH and temperature at the time of analysis.

4.0 APPARATUS AND MATERIALS

4.1 pH meter: Laboratory or field model. Many instruments are commercially available with various specifications and optional equipment.

4.2 Glass electrode.

4.3 Reference electrode: A silver-silver chloride or other reference electrode of constant potential may be used.

NOTE: Combination electrodes incorporating both measuring and referenced functions are convenient to use and are available with solid, gel-type filling materials that require minimal maintenance.

4.4 Magnetic stirrer and Teflon-coated stirring bar.

4.5 Thermometer or temperature sensor for automatic compensation.

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 Primary standard buffer salts are available from the National Institute of Standards and Technology (NIST) and should be used in situations where extreme accuracy is necessary. Preparation of reference solutions from these salts requires some special precautions and handling, such as low-conductivity dilution water, drying ovens, and carbon-dioxide-free purge gas. These solutions should be replaced at least once each month.

5.3 Secondary standard buffers may be prepared from NIST salts or purchased as solutions from commercial vendors. These commercially available solutions have been validated by comparison with NIST standards and are recommended for routine use.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Samples should be analyzed as soon as possible.

7.0 PROCEDURE

7.1 Calibration:

7.1.1 Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.

7.1.2 Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart. (For corrosivity characterization, the calibration of the pH meter should include a buffer of pH 2 for acidic wastes and a pH 12 buffer for caustic wastes; also for

corrosivity characterization, the sample must be measured at 25°C ± 1°C if the pH of the waste is above 12.0.) Various instrument designs may involve use of a dial (to "balance" or "standardize") or a slope adjustment, as outlined in the manufacturer's instructions. Repeat adjustments on successive portions of the two buffer solutions until readings are within 0.05 pH units of the buffer solution value.

7.2 Place the sample or buffer solution in a clean glass beaker using a sufficient volume to cover the sensing elements of the electrodes and to give adequate clearance for the magnetic stirring bar. If field measurements are being made, the electrodes may be immersed directly into the sample stream to an adequate depth and moved in a manner to ensure sufficient sample movement across the electrode-sensing element as indicated by drift-free readings (<0.1 pH).

7.3 If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values must be corrected. Instruments are equipped with automatic or manual compensators that electronically adjust for temperature differences. Refer to manufacturer's instructions.

7.4 Thoroughly rinse and gently wipe the electrodes prior to measuring pH of samples. Immerse the electrodes into the sample beaker or sample stream and gently stir at a constant rate to provide homogeneity and suspension of solids. Note and record sample pH and temperature. Repeat measurement on successive volumes of sample until values differ by <0.1 pH units. Two or three volume changes are usually sufficient.

8.0 QUALITY CONTROL

8.1 Duplicate samples and check standards should be analyzed with each analytical batch.

8.2 Electrodes must be thoroughly rinsed between samples.

9.0 METHOD PERFORMANCE

9.1 Forty-four analysts in twenty laboratories analyzed six synthetic water samples containing exact increments of hydrogen-hydroxyl ions, with the following results:

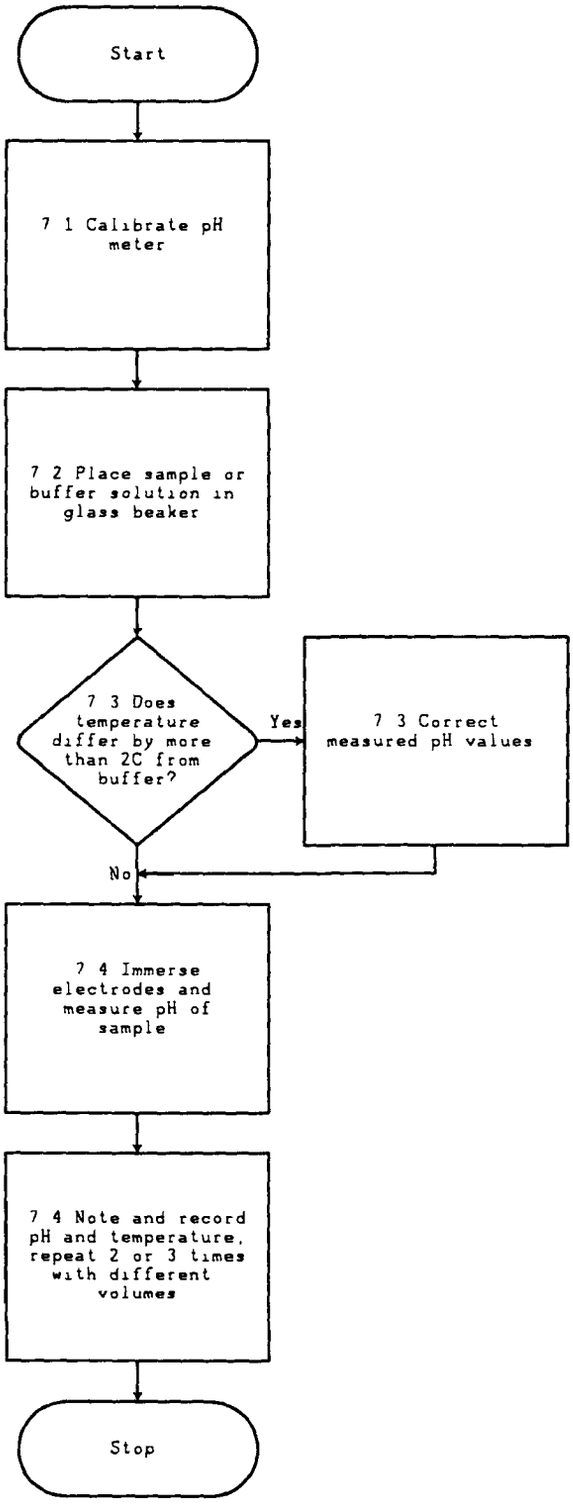
		Accuracy as	
	Standard Deviation	Bias	Bias
pH Units	pH Units	%	pH Units
3.5	0.10	-0.29	-0.01
3.5	0.11	-0.00	
7.1	0.20	+1.01	+0.07
7.2	0.18	-0.03	-0.002
8.0	0.13	-0.12	-0.01
8.0	0.12	+0.16	+0.01

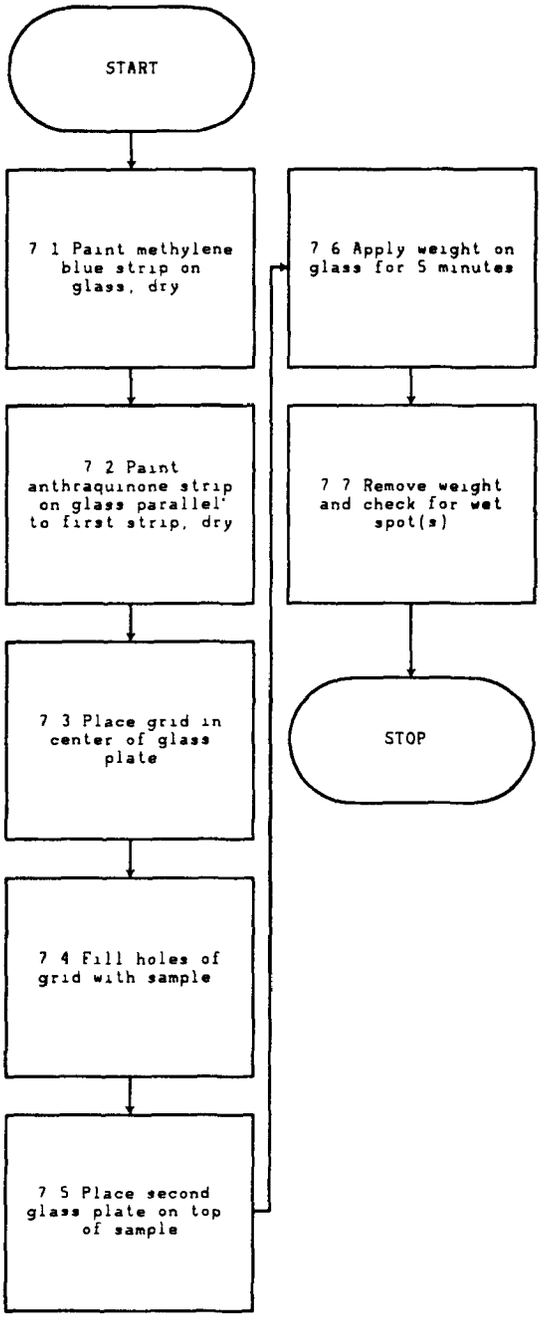
10.0 REFERENCES

1. National Institute of Standards and Technology, Standard Reference Material Catalog 1986-87, Special Publication 260.

METHOD 9040A

pH ELECTROMETRIC MEASUREMENT




START
7 1 Paint methylene blue strip on glass, dry
7 2 Paint anthraquinone strip on glass parallel to first strip, dry
7 3 Place grid in center of glass plate
7 4 Fill holes of grid with sample
7 5 Place second glass plate on top of sample
7 6 Apply weight on glass for 5 minutes
7 7 Remove weight and check for wet spot(s)
STOP