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Methods for the Determination of Organic Compounds in Drinking Water

Supplement III

(WITH ERRATA SHEETS)

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METHODS FOR THE DETERMINATION OF ORGANIC COMPOUNDS IN DRINKING WATER

SUPPLEMENT III

(WITH ERRATA SHEETS)

NATIONAL EXPOSURE RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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ERRATA

Methods for the Determination of Organic Compounds in Drinking Water
Supplement III, EPA/600-R-95/131

they are certified by the manufacturer or by an independent source.

7.17.2 Transfer the stock standard solutions into 15-mL TFE-fluorocarbon-sealed screw cap amber vials. Store at 4°C or less when not in use.

7.17.3 Stock standard solutions should be replaced after 2 months or sooner if comparison with laboratory fortified blanks, or QC samples indicate a problem.

7.17.4 Primary Dilution Standards -- Prepare two sets of standards according to the sets labeled A and B in Table 1. For each set, add approximately 25 mL of methanol to a 50 mL volumetric flask. Add aliquots of each stock standard in the range of approximately 20 to 400 µL and dilute to volume with methanol. Individual analyte concentrations will then be in the range of 0.4 to 8 µg/mL (for a 1.0 mg/mL stock). The minimum concentration would be appropriate for an analyte with strong electron capture detector (ECD) response, e.g. pentachlorophenol. The maximum concentration is for an analyte with weak response, e.g., 2,4-DB. The concentrations given in Table 2 reflect the relative volumes of stock standards used for the primary dilution standards used in generating the method validation data. Use these relative values to determine the aliquot volumes of individual stock standards above.

7.18 INTERNAL STANDARD SOLUTION -- Prepare a stock internal standard solution by accurately weighing approximately 0.050 g of pure DBOB. Dissolve the DBOB in methanol and dilute to volume in a 10-mL volumetric flask. Transfer the DBOB solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Prepare a primary dilution standard at approximately 1.00 µg/mL by the addition of 20 µL of the stock standard to 100 mL of methanol. Addition of 100 µL of the primary dilution standard solution to the final 5 mL of sample extract (Sect. 11) results in a final internal standard concentration of 0.020 µg/mL. Solution should be replaced when ongoing QC (Sect. 9) indicates a problem. Note that DBOB has been shown to be an effective internal standard for the method analytes, but other compounds may be used if the QC requirements in Sect. 9 are met.

7.19 SURROGATE ANALYTE SOLUTION -- Prepare a surrogate analyte stock standard solution by accurately weighing approximately 0.050 g of pure DCAA. Dissolve the DCAA in methanol and dilute to volume in a 10-mL volumetric flask. Transfer the surrogate analyte solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Prepare a primary dilution standard at approximately 2.0 µg/mL by addition of 40 µL at the stock standard to 100 mL of methanol. Addition of 250 µL of the surrogate analyte solution to a 250-mL sample prior to extraction results in a surrogate concentra-

tion in the sample of 2 µg/L and, assuming quantitative recovery of DCAA, a surrogate analyte concentration in the final 5 mL extract of 0.1 µg/mL. The surrogate standard solution should be replaced when ongoing QC (Sect. 9) indicates a problem. DCAA has been shown to be an effective surrogate standard for the method analytes, but other compounds may be used if the QC requirements in Sect. 9 are met.

7.20 INSTRUMENT PERFORMANCE CHECK SOLUTION -- Prepare a diluted dinoseb solution by adding 10 µL of the 1.0 µg/µL dinoseb stock solution to the MTBE and diluting to volume in a 10-mL volumetric flask. To prepare the check solution, add 40 µL of the diluted dinoseb solution, 16 µL of the 4-nitrophenol stock solution, 6 µL of the 3,5-dichlorobenzoic acid stock solution, 50 µL of the surrogate standard solution, 25 µL of the internal standard solution, and 250 µL of methanol to a 5-mL volumetric flask and dilute to volume with MTBE. Methylate sample as described in Sect. 11.4. Dilute the sample to 10 mL in MTBE. Transfer to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Solution should be replaced when ongoing QC (Sect. 9) indicates a problem.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Grab samples should be collected in 250 mL amber glass containers. Conventional sampling practices (7) should be followed; however, the bottle must not be prerinsed with sample before collection.

8.2 SAMPLE PRESERVATION AND STORAGE

8.2.1 If residual chlorine is present, add 80 mg of sodium thiosulfate (or 50 mg of sodium sulfite) per liter of sample to the sample bottle prior to collecting the sample. Demonstration data in Section 17 of this method was obtained using sodium thiosulfate.

8.2.2 After the sample is collected in the bottle containing the dechlorinating agent, seal the bottle and mix to dissolve the thiosulfate.

8.2.3 Add hydrochloric acid (diluted 1:1 in reagent water) to the sample at the sampling site in amounts to produce a sample pH ≤ 2. Short range (0-3) pH paper (Sect. 6.14) may be used to monitor the pH. Note: Do not attempt to mix sodium thiosulfate and HCl in the sample bottle prior to sample collection.

8.2.4 The samples must be iced or refrigerated at 4°C away from light from the time of collection until extraction. Preservation study results indicate that the sample analytes (measured as total acid), except 5-hydroxy-dicamba, are stable in water for 14 days when stored under these conditions (Tables 8 and 9). The concentration of 5-hydroxydicamba is seriously degraded over 14 days in a biologically active matrix. However, analyte stability will very likely be affected by the

ERRATA: Nov. 27, 1995
There is an error in Section 11.1.4. This sheet corrects that error. Remove pages 515.2-19 and 515.2-20 and replace them with this sheet.

7.19) to each 250-mL sample. The surrogate will be at a concentration of 2 µg/L. Dissolve 50 g sodium sulfate in the sample.

11.1.3 Add 4 mL of 6 N NaOH to each sample, seal, and shake. Check the pH of the sample with pH paper or a pH meter; 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 hr, shaking the separatory funnel and contents periodically. Note: Since many of the herbicides contained in this method are applied as a variety of esters and salts, it is vital to hydrolyze them to the parent acid prior to extraction. This step must be included in the analysis of all extracted field samples, LRBs, LFBs, LFMs, and QCS.

11.1.4 Use 15 mL mmethylene chloride to rinse the sample bottle and the granduated cylinder. Then transfer the methylene chloride to the separatory funnel 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 technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Discard the methylene chloride phase (Sect.14,15).

11.1.5 Add a second 15-mL volume of methylene chloride to the separatory funnel and repeat the extraction procedure a second time, discarding the methylene chloride layer. Perform a third extraction in the same manner.

11.1.6 Drain the contents of the separatory funnel into a 500-mL beaker. Adjust the pH to 1.0 ± 0.1 by the dropwise addition of concentrated sulfuric acid with constant stirring. Monitor the pH with a pH meter (Sect. 6.8) or short range (0-3) pH paper (Sect. 6.14).

11.2 SAMPLE EXTRACTION

11.2.1 Vacuum Manifold -- Assemble a manifold (Sect. 6.3) consisting of 6-8 vacuum flasks with filter funnels (Sect. 6.1,6.2). Individual vacuum control, on-off and vacuum release valves and vacuum gauges are desirable. Place the 47 mm extraction disks (Sect. 7.1) on the filter frits.

11.2.2 Add 20 mL of 10% by volume of methanol in MTBE to the top of each disk without vacuum and allow the solvent to remain for 2 min. Turn on full vacuum and draw the solvent through the disks, followed by room air for 5 min.

11.2.3 Adjust the vacuum to approximately 5 in. (mercury) and add the following in series to the filter funnel (a) 20 mL methanol (b) 20 mL reagent water (c) sample. Do not allow the disk to dry between steps and maintain the vacuum at 5 in.

11.2.4 After all the sample has passed through the disk, apply maximum vacuum and draw room air through the disks for 20 min.

11.2.5 Place the culture tubes (Sect. 6.4) in the vacuum tubes to collect the eluates. Elute the disks with two each 2-mL aliquots of 10% methanol in MTBE. Allow each aliquot to remain on the disk for one min before applying vacuum.

11.2.6 Rinse each 500-mL beaker (Sect.11.1.6) with 4 mL of pure MTBE and elute the disk with this solvent as in Sect. 11.2.5.

11.2.7 Remove the culture tubes and cap.

11.3 EXTRACT PREPARATION

11.3.1 Pre-rinse the drying tubes (Sect. 7.5.1) with 2 mL of MTBE.

11.3.2 Remove the entire extract with a 5-mL pipet and drain the lower aqueous layer back into the culture tube. Add the organic layer to the sodium sulfate drying tube (Sect. 7.5.1). Maintain liquid in the drying tube between this and subsequent steps. Collect the dried extract in a 15-mL graduated centrifuge tube or a 10-mL Kuderna-Danish tube.

11.3.3 Rinse the culture tube with an additional 1 mL of MTBE and repeat Sect. 11.3.2.

11.3.4 Repeat step Sect. 11.3.3 and finally add a 1-mL aliquot of MTBE to the drying tube before it empties. The final volume should be 6-9 mL. In this form the extract is esterified as described below.

11.4 EXTRACT ESTERIFICATION WITH DIAZOMETHANE -- See Section 11.5 for alternative procedure.

11.4.1 Assemble the diazomethane generator (Figure 1) in a hood.

11.4.2 Add 5 mL of ethyl ether to Tube 1. Add 4 mL of Diazald solution (Sect. 7.12) and 3 mL of 37% KOH solution (Sect. 7.16.1) to the reaction tube 2. Immediately place the exit tube into the collection tube containing the sample extract. Apply nitrogen flow (10 mL/min) to bubble diazo-methane through the extract. Each charge of the generator should be sufficient to esterify four samples. The appearance of a persistent yellow color is an indication that esterification is complete. The first sample should require 30 sec to 1 min

RRATA - Nov. 27, 1995
here is an equation missing in Sect. 10.4.3. This sheet corrects that error. Remove pages 24.2-21 and 524.-22 and replace them with this sheet.

10.3.4 Determine that the absolute areas of the quantitation ions of the internal standard and surrogates have not decreased by more than 30% from the areas measured in the most recent continuing calibration check, or by more than 50% from the areas measured during initial calibration. If these areas have decreased by more than these amounts, adjustments must be made to restore system sensitivity. These adjustments may require cleaning of the MS ion source, or other maintenance as indicated in Sect. 10.3.6, and recalibration. Control charts are useful aids in documenting system sensitivity changes.

10.3.5 Calculate the RF for each analyte of concern and surrogate compound from the data measured in the continuing calibration check. The RF for each analyte and surrogate must be within 30% of the mean value measured in the initial calibration. Alternatively, if a linear or second order regression is used, the concentration measured using the calibration curve must be within 30% of the true value of the concentration in the calibration solution. If these conditions do not exist, remedial action must be taken which may require recalibration. All data from field samples obtained after the last successful calibration check standard, should be considered suspect. After remedial action has been taken, duplicate samples should be analyzed if they are available.

10.3.6 Some possible remedial actions. Major maintenance such as cleaning an ion source, cleaning quadrupole rods, etc. require returning to the initial calibration step.

10.3.6.1 Check and adjust GC and/or MS operating conditions; check the MS resolution, and calibrate the mass scale.

10.3.6.2 Clean or replace the splitless injection liner; silanize a new injection liner. This applies only if the injection liner is an integral part of the system.

10.3.6.3 Flush the GC column with solvent according to manufacturer's instructions.

10.3.6.4 Break off a short portion (about 1 meter) of the column from the end near the injector; or replace GC column. This action will cause a slight change in retention times. Analyst may need to redefine retention windows.

10.3.6.5 Prepare fresh CAL solutions, and repeat the initial calibration step.

10.3.6.6 Clean the MS ion source and rods (if a quadrupole).

10.3.6.7 Replace any components that allow analytes to come into contact with hot metal surfaces.

10.3.6.8 Replace the MS electron multiplier, or any other faulty components.

10.3.6.9 Replace the trap, especially when only a few compounds fail the criteria in Sect. 10.3.5 while the majority are determined successfully. Also check for gas leaks in the purge and trap unit as well as the rest of the analytical system.

10.4 Optional calibration for vinyl chloride using a certified gaseous mixture of vinyl chloride in nitrogen can be accomplished by the following steps.

10.4.1 Fill the purging device with 25.0 mL (or 5-mL) of reagent water or aqueous calibration standard.

10.4.2 Start to purge the aqueous mixture. Inject a known volume (between 100 and 2000 µL) of the calibration gas (at room temperature) directly into the purging device with a gas tight syringe. Slowly inject the gaseous sample through a septum seal at the top of the purging device at 2000 µL/min. If the injection of the standard is made through the aqueous sample inlet port, flush the dead volume with several mL of room air or carrier gas. Inject the gaseous standard before 5 min of the 11-min purge time have elapsed.

10.4.3 Determine the aqueous equivalent concentration of vinyl chloride standard, in µg/L, injected with one of the following equations:

5 mL samples, $S = 0.51\ (C)(V)$
25 mL samples, $S = 0.102\ (C)(V)$

where S = Aqueous equivalent concentration of vinyl chloride standard in µg/L;
C = Concentration of gaseous standard in mg/L (v/v);
V = Volume of standard injected in mL.

11. PROCEDURE

11.1 SAMPLE INTRODUCTION AND PURGING

11.1.1 This method is designed for a 25-mL or 5-mL sample volume, but a smaller (5 mL) sample volume is recommended if the GC/MS system has adequate sensitivity to achieve the required method detection limits. Adjust the helium purge gas flow rate to 40 mL/min. Attach the trap inlet to the purging device and open the syringe valve on the purging device.

11.1.2 Remove the plungers from two 25-mL (or 5-mL depending on sample size) syringes and attach a closed syringe valve to each. Warm the sample to room temperature, open the sample

ERRATA: November 27, 1995
There is an error in the revision number. This sheet corrects that error. Remove pages 525.2-1 and 525.2-2 and replace them with this sheet.

METHOD 525.2 DETERMINATION OF ORGANIC COMPOUNDS IN DRINKING WATER BY LIQUID-SOLID EXTRACTION AND CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Revision 2.0

J.W. Eichelberger, T.D. Behymer, W.L. Budde - Method 525, Revision 1.0, 2.0, 2.1 (1988)

J.W. Eichelberger, T.D. Behymer, and W.L. Budde - Method 525.1 Revision 2.2 (July 1991)

J.W. Eichelberger, J.W. Munch, and J.A. Shoemaker Method 525.2 Revision 1.0 (February, 1994)

J.W. Munch - Method 525.2, Revision 2.0 (1995)

NATIONAL EXPOSURE RESEARCH LABORATORY
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METHOD 525.2

DETERMINATION OF ORGANIC COMPOUNDS IN DRINKING WATER BY LIQUID-SOLID EXTRACTION AND CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

1. SCOPE AND APPLICATION

1.1 This is a general purpose method that provides procedures for determination of organic compounds in finished drinking water, source water, or drinking water in any treatment stage. The method is applicable to a wide range of organic compounds that are efficiently partitioned from the water sample onto a C_{18} organic phase chemically bonded to a solid matrix in a disk or cartridge, and sufficiently volatile and thermally stable for gas chromatography. Single-laboratory accuracy and precision data have been determined with two instrument systems using both disks and cartridges for most of the following compounds:

Analyte	MW[1]	Chemical Abstracts Service Registry Number
Acenaphthylene	152	208-96-8
Alachlor	269	15972-60-8
Aldrin	362	309-00-2
Ametryn	227	834-12-8
Anthracene	178	120-12-7
Atraton	211	1610-17-9
Atrazine	215	1912-24-9
Benz[a]anthracene	228	56-55-3
Benzo[b]fluoranthene	252	205-82-3
Benzo[k]fluoranthene	252	207-08-9
Benzo[a]pyrene	252	50-32-8
Benzo[g,h,i]perylene	276	191-24-2
Bromacil	260	314-40-9
Butachlor	311	23184-66-9
Butylate	217	2008-41-5
Butylbenzylphthalate	312	85-68-7
Carboxin[2]	235	5234-68-4
Chlordane components		
Alpha-chlordane	406	5103-71-9
Gamma-chlordane	406	5103-74-2
Trans nonachlor	440	39765-80-5
Chlorneb	206	2675-77-6
Chlorobenzilate	324	510-15-6
Chlorpropham	213	101-21-3
Chlorothalonil	264	1897-45-6
Chlorpyrifos	349	2921-88-2
2-Chlorobiphenyl	188	2051-60-7

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There is an error in the analyte list. This sheet corrects that error. Remove pages 551.1-3 and 551.1.-4 and replace them with this sheet.

Hexachlorocyclopentadiene	77-47-4
Lindane (gamma-BHC)	58-89-9
Metolachlor	51218-45-2
Metribuzin	21087-64-9
Methoxychlor	72-43-5
Simazine	122-34-9
Trifluralin	1582-09-8

1.2 This analyte list includes twelve commonly observed chlorination disinfection byproducts (3,4), eight commonly used chlorinated organic solvents and sixteen halogenated pesticides and herbicides.

1.3 This method is intended as a stand-alone procedure for either the analysis of only the trihalomethanes (THMs) or for all the chlorination disinfection by-products (DBPs) with the chlorinated organic solvents or as a procedure for the total analyte list. The dechlorination/preservation technique presented in section 8 details two different dechlorinating agents. Results for the THMs and the eight solvents may be obtained from the analysis of samples employing either dechlorinating agent. (Sect. 8.1.2)

1.4 After an analyte has been identified and quantitated in an unknown sample with the primary GC column (Sect. 6.9.2.1) qualitative confirmation of results is strongly recommended by gas chromatography/mass spectrometry (GC/MS) (10,11), or by GC analysis using a dissimilar column (Sect. 6.9.2.2).

1.5 The experimentally determined method detection limits (MDLs) (12) for the above listed analytes are provided in Tables 2 and 8. Actual MDL values will vary according to the particular matrix analyzed and the specific instrumentation employed.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of GC 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 Sect. 9.4.

1.7 Methyl-t-butyl ether (MTBE) is recommended as the primary extraction solvent in this method since it effectively extracts all of the target analytes listed in Sect. 1.1. However, due to safety concerns associated with MTBE and the current use of pentane by some laboratories for certain method analytes, pentane is offered as an optional extraction solvent for all analytes except chloral hydrate. If project requirements specify the analysis of chloral hydrate, MTBE must be used as the extracting solvent. This method includes sections specific for pentane as an optional solvent.

2. SUMMARY OF METHOD

2.1 A 50 mL sample aliquot is extracted with 3 mL of MTBE or 5 mL of pentane. Two µL of the extract is then injected into a GC equipped

with a fused silica capillary column and linearized electron capture detector for separation and analysis. Procedural standard calibration is used to quantitate method analytes.

2.2 A typical sample can be extracted and analyzed by this method in 50 min for the chlorination by-products/chlorinated solvents and 2 hrs. for the total analyte list. Confirmation of the eluted compounds may be obtained using a dissimilar column (6.9.2.2) or by the use of GC-MS. Simultaneous confirmation can be performed using dual primary/confirmation columns installed in a single injection port (Sect. 6.9.3) or a separate confirmation analysis.

3. DEFINITIONS

3.1 INTERNAL STANDARD (IS) -- A pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component.

3.2 SURROGATE ANALYTE (SA) -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added directly to a sample aliquot in known amount(s) before extraction or other processing and is measured with the same procedures used to measure other sample components. The purpose of a surrogate analyte is to monitor method performance with each sample.

3.3 LABORATORY DUPLICATES (LD1 and LD2) -- Two sample aliquots, taken in the laboratory from a single sample bottle, and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures. This method cannot utilize laboratory duplicates since sample extraction must occur in the sample vial and sample transfer is not possible due to analyte volatility.

3.4 FIELD DUPLICATES (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures. Since laboratory duplicates cannot be analyzed, the collection and analysis of field duplicates for this method is critical.

3.5 LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water, or other blank matrix, that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

ERRATA - Nov. 27, 1995
There are several errors in Section 7.1.7.1 and 7.1.7.4. This sheet corrects those errors. Remove pages 551.1-11 and 551.1-12 and replace them with this sheet.

temperature to 400°C and hold for 30 min. Store in a capped glass bottle not in a plastic container.

7.1.7 Sample Preservation Reagents

7.1.7.1 Phosphate buffer - Used to lower the sample matrix pH to 4.8-5.5 in order to inhibit base catalyzed degradation of the haloacetonitriles (7), some of the chlorinated solvents, and to standardize the pH of all samples. Prepare a dry homogeneous mixture of 1% Sodium Phosphate, dibasic (Na_2HPO_4)/99% Potassium Phosphate, monobasic (KH_2PO_4) by weight (example: 2 g Na_2HPO_4 and 198 g KH_2PO_4 to yield a total weight of 200 g) Both of these buffer salts should be in granular form and of ACS grade or better. Powder would be ideal but would require extended cleanup time as outlined below in Sect. 7.1.7.5 to allow for buffer/solvent settling.

7.1.7.2 Ammonium Chloride, NH_4Cl, ACS Reagent Grade. Used to convert free chlorine to monochloramine. Although this is not the traditional dechlorination mechanism, ammonium chloride is categorized as a dechlorinating agent in this method.

7.1.7.3 Sodium Sulfite, Na_2SO_3, ACS Reagent Grade. Used as a dechlorinating agent for chloral hydrate sample analysis.

7.1.7.4 To simplify the addition of 6 mg of the dechlorinating agent to the 60 mL vial, the dechlorinating salt is combined with the phosphate buffer as a homogeneous mixture. Add 1.2 g of the appropriate dechlorinating agent to 200 g of the phosphate buffer. When 1 g of the buffer/dechlorinating agent mixture are added to the 60-mL sample vial, 6 mg of the dechlorinating agent are included reflecting an actual concentration of 100 mg/L. Two separate mixtures are prepared, one containing ammonium chloride and the other with sodium sulfite.

7.1.7.5 If background contaminants are detected in the salts listed in Sections 7.1.7.1 through 7.1.7.3, a solvent rinse cleanup procedure may be required. These contaminants may coelute with some of the high molecular weight herbicides and pesticides. These salts cannot be muffled since they decompose when heated to 400°C. This solvent rinsing procedure is applied to the homogeneous mixture prepared in Sect. 7.1.7.4.

FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The National Exposure Research Laboratory - Cincinnati (NERL-Cincinnati) conducts research to:

- Develop and evaluate analytical methods to identify and measure the concentration of chemical pollutants in drinking waters, surface waters, groundwaters, wastewaters, sediments, sludges, and solid wastes.

- Investigate methods for the identification and measurement of viruses, bacteria and other microbiological organisms in aqueous samples and to determine the responses of aquatic organisms to water quality.

- Develop and operate a quality assurance program to support the achievement of data quality objectives in measurements of pollutants in drinking water, surface water, groundwater, wastewater, sediment and solid waste.

- Develop methods and models to detect and quantify response in aquatic and terrestrial organisms exposed to environmental stressors and to correlate the exposure with effects on chemical and biological indicators.

This publication, "Determination of Organic Compounds in Drinking Water Supplement III," was prepared to gather together under a single cover a set of 15 new or improved laboratory analytical methods for organics compounds in drinking water. NERL-Cincinnati is pleased to provide this manual and believe that it will be of considerable value to many public and private laboratories that wish to determine organic compounds in drinking water for regulatory or other reasons.

Alfred P. Dufour, Acting Director
Aquatic Research Division
National Exposure Research
Laboratory - Cincinnati

ABSTRACT

Fifteen analytical methods for organic compounds in drinking water are documented in detail. Most of these methods were published as prior versions in other methods manuals in this series. The versions in Supplement III provide corrections, minor technical enhancements, and editorial improvements to the previously published analytical methods. Several previously distributed but not formally published methods are also included. Fourteen of the fifteen methods utilize high resolution gas chromatography (GC) for separation of analytes from each other and from other substances in the water sample. One method employs high performance reverse phase liquid chromatography for the separation. Two methods utilize a mass spectrometer for the unambiguous identification and measurement of the compounds separated by high resolution GC. These two methods are extremely versatile and have been single-laboratory validated for a total of 194 individual compounds and 8 commercial product mixtures. Most methods have also been multi-laboratory validated although not all possible analytes have been included in these studies. Essentially all of the major chlorine disinfection by-products that have been identified in drinking water are included in the methods in this manual.

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The many past and present researchers and authors who contributed to the current status of the methods in supplement III are recognized on the title pages of the 15 methods in Supplement III. Jean W. Munch deserves special recognition for Supplement III because she critically read every method and incorporated numerous corrections, technical enhancements, and editorial improvements into each of them. Thomas D. Behymer acquired the precision and accuracy data for the Aroclors in Method 525.2, proof read the next-to-last drafts of all the methods, and provided numerous additional corrections. Special thanks is due to Diane Schirmann who processed many of the final corrections, placed all 15 methods and the introductory material in the standard format, and prepared the camera-ready copies for printing. The authors would like to thank the many others who reviewed previous and current versions of these methods and provided comments, suggestions and corrections.

ANALYTE - METHOD CROSS REFERENCE

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Aldrin	505, 508, 508.1, 525.2
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Ametryn	507, 525.2
Anthracene	525.2
Atraton	507, 525.2
Atrazine	505, 507, 508.1, 525.2, 551.1
Baygon	531.1
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Benzo[b]fluoranthene	525.2
Benzo[k]fluoranthene	525.2
Benzo[a]pyrene	525.2
Benzo[g,h,i]perylene	525.2
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Bromacil	507, 525.2, 551.1
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Bromochloroacetonitrile	551.1
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Bromodichloroacetic acid	552.2
Bromodichloromethane	502.2, 524.2
Bromoform	502.2, 524.2, 551.1
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Chlorodibromoacetic acid	552.2
1-Chlorobutane	524.2
Chloroethane	502.2, 524.2
Chloroform	502.2, 524.2, 551.1
Chloromethane	502.2, 524.2
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Chloropicrin	551.1
Chlorothalonil	508, 508.1, 525.2
2-Chlorotoluene	502.2, 524.2
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Chlorpropham	507, 525.2
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Dibromochloromethane	502.2, 524.2, 551.1
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1,2-Dibromoethane	502.2, 504.1, 524.2, 551.1
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Dicamba	515.1, 515.2
Dichloroacetic acid	552.2
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1,2-Dichlorobenzene	502.2, 524.2
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1,4-Dichlorobenzene	502.2, 524.2
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1,2-Dichloroethane	502.2, 524.2
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2,3-Dichlorobiphenyl	525.2
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Diethyl ether	524.2
Diethyl phthalate	506, 525.2
Di(2-ethylhexyl)adipate	525.2
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Dimethyl phthalate	506, 525.2
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Hexachlorocyclohexane, alpha	525.2
Hexachlorocyclohexane, beta	525.2
Hexachlorocyclohexane, delta	525.2
Hexachlorocyclopentadiene	525.2
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5-Hydroxydicamba	515.1, 515.2
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Methyl iodide	524.2
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Trans-Permethrin	508, 508.1, 525.2
Phenanthrene	525.2
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Prometon	507, 525.2
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Pronamide	507, 525.2
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Propazine	507, 525.2
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Propylbenzene	502.2
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Styrene	502.2, 524.2
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2,4,5-TP	515.1, 515.2
Tebuthiuron	507, 525.2
Terbacil	507, 525.2
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2,2',4,4'-Tetrachlorobiphenyl	525.2
1,1,1,2-Tetrachloroethane	502.2, 524.2
1,1,2,2-Tetrachloroethane	502.2, 524.2
Tetrachloroethene	502.2, 524.2
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1,1,1-Trichloroethane	502.2, 524.2, 551.1
1,1,2-Trichloroethane	502.2, 524.2, 551.1
Trichloroethene	505.2, 524.2
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1,1,1-Trichloro-2-propanone	551.1
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1,2,4-Trimethylbenzene	502.2, 524.2
1,3,5-Trimethylbenzene	502.2, 524.2
Vernolate	507, 525.2
Vinyl chloride	502.2, 524.2
O-Xylene	505.2, 524.2
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Aroclor 1248	505, 508, 508.1, 525.2
Aroclor 1254	505, 508, 508.1, 525.2
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INTRODUCTION

William L. Budde and Jean W. Munch

The purpose of this third supplement to "Methods for the Determination of Organic Compounds in Drinking Water" is to provide corrections, minor technical enhancements, and editorial improvements to some previously published analytical methods and to document several significantly enhanced or previously unpublished methods. Some of these modifications were described in "Technical Notes on Drinking Water Methods", EPA/600/R-94/173, October, 1994 and these method changes have been incorporated into the body of the methods in this supplement. All methods in this supplement are written in a format specified by the United States Environmental Protection Agency's Environmental Monitoring Management Council.

As in other manuals in this series, each of the methods in Supplement III was intended to stand alone, that is, each method may be removed from the manual, photocopied, inserted into another binder, and used without loss of information. The stand-alone character of the methods comes at some cost of duplication of material, but the authors believe that the added bulk of the methods is a small price to pay for the flexibility of the format.

All the methods in supplement III have been given new dates and version numbers or slightly modified method numbers to distinguish them from previously published versions. A change in the revision number indicates a relatively small modification to the method and a change in the method number usually indicates a relatively larger change in the method. The cover page of each method gives the title, method number, revision, and date, and also lists the previous versions, previous authors, and dates if they are known. The purpose of this very brief method history is to assist users who may have older versions in their files in understanding the chronological relationship of methods as technical improvements were made over the years. It also gives due credit to previous authors who contributed to the development of the methods in this and previous manuals in this series. Unless otherwise indicated, all authors were direct Federal employees of the U. S. Environmental Protection Agency at the time of their contributions.

Some methods in supplement III utilize the liquid-solid extraction technology which was pioneered by the USEPA in the original Method 525 in 1988. The scientifically correct term liquid-solid extraction (LSE), in which both phases of the equilibrium partition process are named, is used throughout the manual in place of the misleading commercial term "solid phase extraction". Colloquial lab terms such as "clean-up" and "spike" are replaced by "sample preparation" or "interference separation" and "fortified" respectively.

While the title of supplement III, and previous manuals in this series, specifies drinking water, these methods will very likely be applicable to other aqueous matrices including surface water, ground water, beverages, and

waste water. However since some methods have been tested with only reagent water and/or drinking water, caution is needed when applying these methods to matrices other than reagent or drinking water. One exception is Method 524.2 which has been tested in a large multi-laboratory validation study with a variety of aqueous matrices.

During 1992 the USEPA and the American Society for Testing and Materials (ASTM) Committee D-19 on Water jointly conducted a multi-laboratory study of an ASTM version of Method 524.2, revision 3.0 using 68 of the volatile organic compound analytes. Over 40 volunteer laboratories participated in the study to characterize the performance of Method 524.2 in terms of accuracy, precision, and detection limits. Analyses were conducted using fortified reagent water, drinking water, ground water, several industrial waste waters, and a simulated hazardous waste site aqueous leachate. Fortified analyte concentrations ranged from 0.2 µg/L to 80 µg/L and generally excellent accuracy and precision was reported. Full details of that study will be published by the ASTM.

The methods in supplement III are listed below along with a comment for each that gives the previous version of the method, the citation and date of publication of the previous version, and the highlights of the changes in the version in supplement III.

Method in Supp. III	Comments
502.2 rev. 2.1	Rev. 2.0 was published in EPA/600/4-88/039 in Dec. 1988 and July 1991. Rev. 2.1 is modified to specify conditions under which alternative trapping materials may be used and instructions are clarified for sample preservation and dechlorination. Conditions which do not require a photoionization detector are specified.
504.1 rev. 1.1	Method 504.1 improves Method 504 rev. 2.0 which was published in EPA/600/4-88/039 in Dec. 1988 and July 1991. In 504.1 changes are made to the sampling procedures, the holding time, and the compound 1,2,3-trichloropropane is added to the analyte list. Cautions are included on the frequent coelution of ethylene dibromide and bromodichloromethane.
505 rev. 2.1	Rev. 2.0 was published in EPA/600/4-88/039 in Dec. 1988 and July 1991. Rev. 2.1 is modified to remove alternative detectors except mass spectrometry for qualitative confirmation and to provide additional instructions on the measurement of multi-component mixtures.
506 rev. 1.1	Rev. 1.0 was published in EPA/600/4-90/020 (Supp. I) in July, 1990. Rev. 1.1 is modified to correct errors in the method summary.

507	rev. 2.1	Rev. 2.0 was published in EPA/600/4-88/039 in Dec. 1988 and July 1991. Rev. 2.1 is modified to remove mercuric chloride as a preservative. Data tables are reorganized for clarity and addition of method detection limits. Alternative detectors are eliminated except mass spectrometry for qualitative confirmation.
508	rev. 3.1	Rev 3.0 was published in EPA/600/4-88/039 in Dec. 1988 and July 1991. Rev. 3.1 is modified to remove mercuric chloride as a preservative. Data tables are reorganized for clarity and addition of method detection limits. Alternative detectors are eliminated except mass spectrometry for qualitative confirmation.
508.1	rev. 2.0	Method 508.1 is a significant improvement to Method 508. It employs the liquid-solid extraction technology of Method 525.2 and has an analyte list consisting of many Method 507 and Method 508 substances including the former commercial Aroclor mixtures.
509	rev. 1.1	Method 509 is a single analyte method for the pesticide metabolite ethylenethiourea. This method is derived from national pesticide survey Method 6.
515.1	rev. 4.1	Rev. 4.0 was published in EPA/600/4-88/039 in Dec. 1988 and July 1991. Rev. 4.1 is modified to remove mercuric chloride as a preservative. Data tables are reorganized for clarity and addition of method detection limits. Trimethylsilyldiazomethane (TMSD) is added as an alternative methylating agent.
515.2	rev. 1.1	Rev. 1.0 was published in EPA/600/R-92/129 (Supp. II) in August, 1992. Rev. 1.1 is modified to include trimethylsilyldiazomethane (TMSD) as an alternative methylating agent.
524.2	rev. 4.1	Rev. 4.0 was published in EPA/600/R-92/129 (Supp. II) in August, 1992. Rev. 4.1 is modified to specify conditions under which alternative trapping materials may be used and instructions are clarified for sample preservation and dechlorination. The quality assurance section is clarified and data for two analytes are added.
525.2	rev. 2.0	Method 525.2, rev. 2.0 is an improvement to Method 525.1, rev. 2.2 which was published in EPA/600/4-88/039 in July, 1991. Method 525.2 includes criteria for judging the equivalency of alternative liquid-solid extraction cartridges and disks. The elution

		solvent is modified and data are included for additional analytes including all former commercial Aroclor mixtures.
531.1	rev. 3.1	Rev. 3.0 was published in EPA/600/4-88/039 in Dec. 1988 and July 1991. Rev. 3.1 is modified to remove the requirement to freeze the samples. Data tables are revised for clarity and method detection limits are included.
551.1	rev. 1.0	Method 551.1 is an improvement to Method 551 which was published in EPA/600/4-90/020 (Supp. I) in July 1990. Pentane is included as an alternative solvent for some analytes, the analyte list is expanded, and a new sample preservation technique is used.
552.2	rev. 1.0	Method 552.2 is similar to Method 552 which was published in EPA/600/4-90/020 (Supp. I) in July, 1990. Method 552.2 uses acidic methanol for methylation instead of diazomethane and expands the analyte list.

METHOD 502.2 VOLATILE ORGANIC COMPOUNDS IN WATER BY PURGE AND TRAP CAPILLARY COLUMN GAS CHROMATOGRAPHY WITH PHOTOIONIZATION AND ELECTROLYTIC CONDUCTIVITY DETECTORS IN SERIES

Revision 2.1

Edited by J.W. Munch (1995)

R.W. Slater, Jr. and J.S. Ho - Method 502.2, Revision 1.0 (1986)

J.S. Ho - Method 502.2, Revision 2.0 (1989)

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METHOD 502.2

VOLATILE ORGANIC COMPOUNDS IN WATER BY PURGE AND TRAP CAPILLARY COLUMN GAS CHROMATOGRAPHY WITH PHOTOIONIZATION AND ELECTROLYTIC CONDUCTIVITY DETECTORS IN SERIES

1. SCOPE AND APPLICATION

1.1 This is a general purpose method for the identification and simultaneous measurement of purgeable volatile organic compounds in finished drinking water, raw source water, or drinking water in any treatment stage (1-3). The method is applicable to a wide range of organic compounds, including the four trihalomethane disinfection by-products, that have sufficiently high volatility and low water solubility to be efficiently removed from water samples with purge and trap procedures. The following compounds can be determined by this method.

Analyte	Chemical Abstract Services Registry Number
Benzene	71-43-2
Bromobenzene	108-86-1
Bromochloromethane	74-97-5
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Bromomethane	74-83-9
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroethane	75-00-3
Chloroform	67-66-3
Chloromethane	74-87-3
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
Dibromochloromethane	124-48-1
1,2-Dibromo-3-chloropropane	96-12-8
1,2-Dibromoethane	106-93-4
Dibromomethane	74-95-3
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
Dichlorodifluoromethane	75-71-8
1,1-Dichloroethane	75-34-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-4
cis-1,2-Dichloroethene	156-59-4
trans-1,2-Dichloroethene	156-60-5
1,2-Dichloropropane	78-87-5

1,3-Dichloropropane	142-28-9
2,2-Dichloropropane	590-20-7
1,1-Dichloropropene	563-58-6
cis-1,3-Dichloropropene	10061-01-5
trans-1,3-Dichloropropene	10061-02-6
Ethylbenzene	100-41-4
Hexachlorobutadiene	87-68-3
Isopropylbenzene	98-82-8
4-Isopropyltoluene	99-87-6
Methylene chloride	75-09-2
Naphthalene	91-20-3
Propylbenzene	103-65-1
Styrene	100-42-5
1,1,1,2-Tetrachloroethane	630-20-6
1,1,2,2-Tetrachloroethane	79-34-5
Tetrachloroethene	127-18-4
Toluene	108-88-3
1,2,3-Trichlorobenzene	87-61-6
1,2,4-Trichlorobenzene	120-82-1
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethene	79-01-6
Trichlorofluoromethane	75-69-4
1,2,3-Trichloropropane	96-18-4
1,2,4-Trimethylbenzene	95-63-6
1,3,5-Trimethylbenzene	108-67-8
Vinyl chloride	75-01-4
o-Xylene	95-47-6
m-Xylene	108-38-3
p-Xylene	106-42-3

1.2 This method is applicable to the determination of total trihalomethanes and other volatile organic compounds (VOCs). Method detection limits (MDLs) (4) are compound and instrument dependent and vary from approximately 0.01-3.0 µg/L. The applicable concentration range of this method is also compound and instrument dependent and is approximately 0.02 to 200 µg/L. Analytes that are inefficiently purged from water will not be detected when present at low concentrations, but they can be measured with acceptable accuracy and precision when present in sufficient amounts.

1.3 Two of the three isomeric xylenes may not be resolved on the capillary column, and if not, must be reported as isomeric pairs.

2. SUMMARY OF METHOD

2.1 Highly volatile organic compounds with low water solubility are extracted (purged) from the sample matrix by bubbling an inert gas through a 5 mL aqueous sample. 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 thermally desorb trapped sample components onto a capillary gas

chromatography (GC) column. The column is temperature programmed to separate the method analytes which are then detected with a photoionization detector (PID) and an electrolytic conductivity detector (ELCD) placed in series. Analytes are quantitated by procedural standard calibration (Sect.3.14).

2.2 Identifications are made by comparison of the retention times of unknown peaks to the retention times of standards analyzed under the same conditions used for samples. Additional confirmatory information can be gained by comparing the relative response from the two detectors. For absolute confirmation, a gas chromatography/mass spectrometry (GC/MS) determination according to USEPA Method 524.2 is recommended.

2.3 This method requires the use of a PID to measure target analytes that cannot be measured with an electrolytic conductivity detector. If only halogenated analytes, such as the trihalomethanes are to be measured, a PID is not needed.

3. DEFINITIONS

3.1 INTERNAL STANDARD -- A pure analyte(s) added to a solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same solution. The internal standard must be an analyte that is not a sample component.

3.2 SURROGATE ANALYTE -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction and is measured with the same procedures used to measure other sample components. The purpose of a surrogate analyte is to monitor method performance with each sample.

3.3 LABORATORY DUPLICATES (LD1 and LD2) -- Two sample aliquots taken in the analytical laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.4 FIELD DUPLICATES (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.5 LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if

method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.6 FIELD REAGENT BLANK (FRB) -- Reagent water placed in a sample container in the laboratory and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.7 LABORATORY PERFORMANCE CHECK SOLUTION (LPC) -- A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.8 LABORATORY FORTIFIED BLANK (LFB) -- An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

3.9 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.10 STOCK STANDARD SOLUTION -- A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a single analyte prepared in the laboratory with an assayed reference compound. Stock standard solutions are used to prepare primary dilution standards.

3.11 PRIMARY DILUTION STANDARD SOLUTION -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.12 CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution and stock standard solutions of the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.13 QUALITY CONTROL SAMPLE (QCS) -- A sample matrix containing method analytes or a solution of method analytes in a water miscible solvent which is used to fortify reagent water or environmental samples. The QCS is obtained from a source external to the laboratory, and is used to check laboratory performance with externally prepared test materials.

3.14 PROCEDURAL STANDARD CALIBRATION -- A calibration method where aqueous calibration standards are prepared and processed (e.g. purged,extracted, and/or derivatized) in exactly the same manner as a sample. All steps in the process from addition of sampling preservatives through instrumental analyses are included in the calibration. Using procedural standard calibration compensates for any inefficiencies in the processing procedure.

4. INTERFERENCES

4.1 During analysis, 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) plastic tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of laboratory reagent blanks (Sect. 9.2) provide information about the presence of contaminants. When potential interfering peaks are noted in laboratory reagent blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter. Subtracting blank values from sample results is not permitted.

4.2 Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing relatively high concentrations of volatile organic compounds. A preventive technique is between-sample rinsing of the purging apparatus and sample syringes with two portions of reagent water. After analysis of a sample containing high concentrations of volatile organic compounds, one or more laboratory reagent blanks should be analyzed to check for cross contamination.

4.3 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 common liquid/liquid extraction procedures can contribute to sample contamination.

4.4 When traps containing combinations of silica gel and coconut charcoal are used, residual water from previous analyses collects in

the trap and can be randomly released into the analytical column. To minimize the possibility of this occurring, the trap is reconditioned after each use as described in Sect. 11.4.

5. SAFETY

5.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available (5-7) for the information of the analyst.

5.2 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichlorethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene, and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6. EQUIPMENT AND SUPPLIES (All specifications are suggested. Catalog numbers are included for illustration only.)

6.1 SAMPLE CONTAINERS - 40-mL to 120-mL screw cap vials each equipped with a PTFE-faced silicone septum. Prior to use, wash vials and septa with detergent and rinse with tap and distilled water. Allow the vials and septa to air dry at room temperature, place in a 105°C oven for one hour, then remove and allow to cool in an area known to be free of organics.

6.2 PURGE AND TRAP SYSTEM - The purge and trap system consists of three separate pieces of equipment: purging device, trap, and desorber. Systems are commercially available from several sources that meet all of the following specifications.

6.2.1 The all glass purging device (Figure 1) must be designed to accept 5-mL samples with a water column at least 5 cm deep. Gaseous volumes above the sample must be kept to a minimum (<15 mL) to eliminate dead volume effects. A glass frit should be installed at the base of the sample chamber so that the purge gas passes through the water column as finely divided bubbles with a diameter of <3 mm at the origin. Needle spargers may be used, however, the purge gas must be introduced at a point ≤5 mm from the base of the water column.

6.2.2 The trap (Figure 2) 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. If it is not necessary to analyze for dichlorodifluoromethane, 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 min 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. The use of alternative sorbents is acceptable provided the data acquired meets all quality control criteria described in Section 9, and provided the purge and desorption procedures specified in Section 11 of the method are not changed. Specifically, the purging time, the purge gas flow rate, and the desorption time may not be changed. Since many of the potential alternate sorbents may be thermally stable above 180°C, alternate traps may be desorbed and baked out at higher temperatures than those described in Section 11. If higher temperatures are used, the analyst should monitor the data for possible analyte and/or trap decomposition.

6.2.3 The use of the methyl silicone coated packing is recommended, but not mandatory. The packing serves a dual purpose of protecting the adsorbent from aerosols, and also of insuring that the adsorbent is fully enclosed within the heated zone of the trap thus eliminating potential cold spots. Alternatively, silanized glass wool may be used as a spacer at the trap inlet.

6.2.4 The desorber (Figure 2) must be capable of rapidly heating the trap to 180°C. The polymer section of the trap described in Sect.6.2.2 should not be heated higher than 200°C or the life expectancy of the trap will decrease. Trap failure is characterized by a pressure drop in excess of 3 pounds per square inch across the trap during purging or by poor bromoform sensitivities.

6.3 GAS CHROMATOGRAPHY SYSTEM

6.3.1 The GC must be capable of temperature programming and should be equipped with variable-constant differential flow

controllers so that the column flow rate will remain constant throughout desorption and temperature program operation. The column oven may need to be cooled to <10°C (Sect. 6.3.3), and therefore, a subambient oven controller may be required.

6.3.2 Capillary Gas Chromatography Columns. Any gas chromatography column that meets the performance specifications of this method may be used. Separations of the calibration mixture must be equivalent or better than those described in this method. If other GC columns or temperature programs are used, or whenever these procedures are changed, the method performance data in Sect. 9.3 must be repeated. Three useful columns have been identified: column 1 (Sect. 6.3.3) and column 2 (Sect. 6.3.4) both provide satisfied separations for sixty organic compounds. Column 3 (Sect. 6.3.5), which has been satisfactorily demonstrated for the GC/MS method 524.2, may also be used.

6.3.3 Column 1- 60m long x 0.75mm ID VOCOL (Supelco, Inc.) wide-bore capillary column with 1.5 µm film thickness, or equivalent. The flow rate of helium carrier gas is adjusted to about 6 mL/min. The column temperature is held for 8 min at 10°C, then programmed to 180°C at 4°C/min, and held until all expected compounds have eluted. A sample chromatogram obtained with this column is presented in Figure 3. Retention times that may be anticipated with this column are listed in Table 1. Data obtained with this column is presented in Sect. 13 and 17.

6.3.4 Column 2 - 105m long x 0.53mm ID, RTX-502.2 (O.I Corporation/RESTEK Corporation) mega-bore capillary column, with 3.0 µm film thickness, or equivalent. The flow rate of helium carrier gas is adjusted to about 8 mL/min. The column temperature is held for 10 min at 35°C, then programmed to 200°C at 4°C/min, and held until all expected compounds have eluted. A sample chromatogram obtained with this column is presented in Figure 4. Retention times that may be anticipated with this column are listed in Table 3. Data obtained with this column is presented in Sect. 13 and 17.

6.3.5 Column 3 - 30 m long x 0.53 mm ID DB-624 mega-bore (J&W Scientific, Inc.) column with 3 µm film thickness.

6.3.6 A series configuration of a high temperature photoionization detector (PID) equipped with 10 eV (nominal) lamp and electroconductivity detector (ELCD) is required. This allows the simultaneous analysis of VOCs that are aromatic or unsaturated by photoionization detector and organohalide by an electrolytic conductivity detector.

6.3.7 A Tracor 703 photoionization detector and a Tracor Hall model 700-A detector connected in series with a short piece of

uncoated capillary tube, 0.32 mm ID was used to develop the single laboratory method performance data described in Sect.13. The system and operating conditions used to collect these data are as follows:

Column:	Column 1 (Sect.6.3.3)
The purge-and-trap Unit:	Tekmar LSC-2
PID detector base temperature:	250°C
Reactor tube:	Nickel 1/16 in. OD
Reactor temperature:	810°C
Reactor base temperature:	250°C
Electrolyte:	100% n-propyl alcohol
Electrolyte flow rate:	0.8 mL/min
Reaction gas:	Hydrogen at 40 mL/min
Carrier gas plus make-up gas:	Helium at 30 mL/min

6.3.8 An O.I. Model 4430 photoionization detector mounting together with the model 4420 electrolytic conductivity detector (ELCD) as a dual detector set was used to develop the single laboratory method performance data for column 2 described in Sect. 13. The system and the operating conditions used to collect these data are as follows:

Column:	Column 2 (Sect.6.3.4)
The purge-and-trap unit:	O.I. 4460A
Reactor tube:	Nickel 1/16 in. OD & .02in.ID
Reactor temperature:	950°C
Reactor base temperature:	250°C
Electrolyte:	100 % n-propyl alcohol
Electrolyte flow rate:	0.050 mL/min
Reaction gas:	Hydrogen at 100 mL/min
Carrier gas plus make-up gas:	Helium at 30 mL/min

6.4 SYRINGE AND SYRINGE VALVES

6.4.1 Two 5-mL glass hypodermic syringes with Luer-Lok tip.

6.4.2 Three 2-way syringe valves with Luer ends.

6.4.3 One 25-µL micro syringe with a 2 in x 0.006 in ID, 22° bevel needle (Hamilton #702N or equivalent).

6.4.4 Micro syringes - 10, 100 µL.

6.4.5 Syringes - 0.5, 1.0, and 5-mL, gas tight with shut-off valve.

6.5 MISCELLANEOUS

6.5.1 Standard solution storage containers - 15-mL bottles with PTFE-lined screw caps.

7. REAGENT AND STANDARDS

7.1 TRAP PACKING MATERIALS

7.1.1 2,6-Diphenylene oxide polymer, 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

7.1.2 Methyl silicone packing (optional) - OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

7.1.3 Silica gel - 35/60 mesh, Davison, grade 15 or equivalent.

7.1.4 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26 lot #M-2649 (or equivalent) by crushing through 26 mesh screen.

7.2 REAGENTS

7.2.1 Ascorbic acid - ACS Reagent grade, granular.

7.2.2 Sodium thiosulfate - ACS Reagent grade, granular.

7.2.3 Hydrochloric acid (1+1) - Carefully add a measured volume of conc. HCl to equal volume of reagent water.

7.2.4 Reagent water - It should be demonstrated to be free of interferences. Prepare reagent water by passing tap water through a filter bed containing about 0.5 kg of activated carbon, by using a water purification system, or by boiling distilled water for 15 min followed by a 1-h purge with inert gas while the water temperature is held at 90°C. Store in clean, narrow-mouth bottles with PTFE-lined septa and screw caps.

7.2.5 Methanol - demonstrated to be free of analytes.

7.2.6 Vinyl chloride - 99.9% pure vinyl chloride is available from Ideal Gas Products, Inc., Edison, New Jersey and from Matheson, East Rutherford, New Jersey. Certified mixtures of vinyl chloride in nitrogen at 1.0 and 10.0 ppm (v/v) are available from several sources.

7.3 STOCK STANDARD SOLUTIONS - These solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedures:

7.3.1 Place about 9.8 mL of methanol into a 10-mL ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried. Weigh to the nearest 0.1 mg.

7.3.2 If the analyte is a liquid at room temperature, use a 100-μL syringe and immediately add two or more drops of reference standard to the flask. Be sure that the reference standard falls directly into the alcohol without contacting the neck of the flask. If the analyte is a gas at room temperature, fill a 5-mL valved gas-tight syringe with the standard to the 5.0-mL mark, lower the needle to 5 mm above the methanol meniscus, and slowly inject the standard into the neck area of the flask. The gas will rapidly dissolve in the methanol.

7.3.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter from the net gain in weight. When compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard.

7.3.4 Store stock standard solutions in 15-mL bottles equipped with PTFE-lined screw caps. Methanol solutions prepared from liquid analytes are stable for at least four weeks when stored at 4°C. Methanol solutions prepared from gaseous analytes are not stable for more than one week when stored at <0°C; at room temperature, they must be discarded after one day. Storage time may be extended only if the analyte proves their validity by analyzing quality control samples.

7.4 PRIMARY DILUTION STANDARD SOLUTION - Use stock standard solutions to prepare primary dilution standard solutions that contain the analytes in methanol. The primary dilution standards should be prepared at concentrations that can be easily diluted to prepare aqueous calibration standard solutions (Sect. 9.2) that will bracket the working concentration range. Store the primary dilution standard solutions with minimal headspace and check frequently for signs of deterioration or evaporation, especially just before preparing calibration standard solutions from them. Storage times described for stock standard solutions in Sect. 7.3.4 also apply to primary dilution standard solutions.

7.5 INTERNAL STANDARD SOLUTION - Prepare a fortified solution containing 1-chloro-2-fluorobenze or fluorobenzene and 2-bromo-1-chloropropane in methanol using the procedures described in Sect. 7.3 and 7.4. It is recommended that the primary dilution standard be prepared at a concentration of 5 μg/mL of each internal standard compound. The addition of 10 μL of such a standard to 5.0 mL of sample or calibration standard would be equivalent to 10 μg/L.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 SAMPLE COLLECTION AND DECHLORINATION

8.1.1 Collect all samples in duplicate. If samples, such as finished drinking water, are suspected to contain residual

chlorine, add a dechlorinating agent the bottle. The preferred dechlorinating agent is sodium thiosulfate, but ascorbic acid may also be used. Add 3 mg of sodium thiosulfate or 25 mg of ascorbic acid per 40 mL of sample to the sample bottle before filling NOTE: If the residual chlorine is likely to be present > 5 mg/L, a determination of the amount of the chlorine may be necessary. Diethyl-p-phenylenediamine (DPD) test kits are commercially available to determine residual chlorine in the field. Add an additional 3 mg of sodium thiosulfate or 25 mg of ascorbic acid per each 5 mg/L of residual chlorine.

8.1.2 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 10 min). Adjust the flow to about 500 mL/min and collect duplicate samples containing the desired dechlorinating agent from the flowing stream.

8.1.3 When sampling from an open body of water, partially fill a 1-quart wide-mouth bottle or 1-L beaker with sample from a representative area. Fill duplicate sample bottles containing the desired dechlorinating agent with sample from the larger container.

8.1.4 Fill sample bottles to overflowing, but take care not to flush out the rapidly dissolving dechlorinating agent. No air bubbles should pass through the sample as the bottle is filled, or be trapped in the sample when the bottle is sealed.

8.2 SAMPLE PRESERVATION

8.2.1 Adjust the pH of all samples to < 2 <u>at the time of collection</u>, but after dechlorination, by carefully adding two drops of 1:1 HCl for each 40 mL of sample. Seal the sample bottles, Teflon face down, and mix for 1 min. Exceptions to the acidification requirement are detailed in Sections 8.2.2 and 8.2.3. **NOTE:** Do not mix the ascorbic acid or sodium thiosulfate with the HCl in the sample bottle prior to sampling.

8.2.2 **When sampling for THM analysis only,** acidification may be omitted if sodium thiosulfate is used to dechlorinate the sample. This exception to acidification does not apply if ascorbic acid is used for dechlorination.

8.2.3 If a sample foams vigorously when HCl is added, discard that sample. Collect a set of duplicate samples but do not acidify them. These samples must be flagged as "not acidified" and must be stored at 4°C or below. These samples must be analyzed within 24 hr of collection time if they are to be analyzed for any compounds other than THMs.

8.2.4 The samples must be chilled to about 4°C when collected and maintained at that temperature until analysis. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to ensure that they will arrive at the laboratory with a substantial amount of ice remaining in the cooler.

8.3 SAMPLE STORAGE

8.3.1 Store samples at ≤ 4°C until analysis. The sample storage area must be free of organic solvent vapors and direct or intense light.

8.3.2 Analyze all samples within 14 days of collection. Samples not analyzed within this period must be discarded and replaced.

8.4 FIELD REAGENT BLANKS (FRB)

8.4.1 Duplicate FRBs must be handled along with each sample set, which is composed of the samples collected from the same general sample site at approximately the same time. At the laboratory, fill field blank sample bottles with reagent water and sample preservatives, seal, and ship to the sampling site along with empty sample bottles and back to the laboratory with filled sample bottles. Wherever a set of samples is shipped and stored, it is accompanied by appropriate blanks. FRBs must remain hermetically sealed until analysis.

8.4.2 Use the same procedures used for samples to add sodium thiosulfate or ascorbic acid and HCl to blanks (Sect. 8.1.1). The same batch of ascorbic acid and HCl should be used for the field reagent blanks in the field.

9. QUALITY CONTROL

9.1 Quality control (QC) requirements are the initial demonstration of laboratory capability followed by regular analyses of laboratory reagent blanks, field reagent blanks, and laboratory fortified blanks. A method detection limit (MDL) must also be determined for each analyte. The laboratory must maintain records to document the quality of the data generated. Additional quality control practices are recommended.

9.2 Initial demonstration of low system background. Before any samples are analyzed, it must be demonstrated that a laboratory reagent blank (LRB) is reasonably free of contamination that would prevent the determination of any analyte of concern. Sources of background contamination are glassware, purge gas, sorbents, and equipment. Background contamination must be reduced to an acceptable level

before proceeding with the next section. In general background from method analytes should be below the method detection limit.

9.3 Initial demonstration of capability.

9.3.1 Demonstration of laboratory accuracy and precision. Analyze four to seven replicates of a laboratory fortified blank containing each analyte of concern at a concentration in the range of 0.1-5 µg/L. This concentration should represent a concentration of ten times the MDL or a concentration near the middle of the calibration range demonstrated (Sect. 10). It is recommended that a QCS from a source different than the calibration standards be used for this set of LFBs, since it will serve as a check to verify the accuracy of the standards used to generate the calibration curve. This is particularly useful if the laboratory is using the method for the first time, and has no historical data base for standards. Prepare each replicate by adding an appropriate aliquot of a quality control sample to reagent water. Also add the appropriate amounts of internal standard and surrogates if they are being used. If it is expected that field samples will contain a dechlorinating agent and HCl, then add these to the LFBs in the same amounts prescribed in Sect. 8.1.1. If only THMs are to be determined and field samples do not contain HCl, then do not acidify LFBs. Analyze each replicate according to the procedures described in Sect. 11.

9.3.2 Calculate the measured concentration of each analyte in each replicate, the mean concentration of each analyte in all replicates, and mean accuracy (as mean percentage of true value) for each analyte, and the precision (as relative standard deviation, RSD) of the measurements for each analyte.

9.3.3 For each analyte and surrogate, the mean accuracy, expressed as a percentage of the true value, should be 80-120% and the RSD should be <20%. Some analytes, particularly the early eluting gases and late eluting higher molecular weight compounds, are measured with less accuracy and precision than other analytes. If these criteria are not met for an analyte, take remedial action and repeat the measurements for that analyte to demonstrate acceptable performance before samples are analyzed.

9.3.4 To determine the MDL, analyze a minimum of 7 LFBs prepared at a low concentration. MDLs in Tables 2 and 4 were calculated from samples fortified at 0.1 µg/L, which can be used as a guide, or use calibration data to estimate a concentration for each analyte that will yield a peak with a 3-5 signal to noise ratio. Analyze the 7 replicates as described in Sect.11, and on a schedule that results in the analyses being conducted over several days. Calculate the mean accuracy and

standard deviation for each analyte. Calculate the MDL using procedures described in Ref. 4. The equation for this calculation is also in Sect. 13.3.

9.3.5 Develop and maintain a system of control charts to plot the precision and accuracy of analyte and surrogate measurements as a function of time. Charting of surrogate recoveries is an especially valuable activity since these are present in every sample and the analytical results will form a significant record of data quality.

9.4 Laboratory reagent blanks (LRBs). With each batch of samples processed as a group within a work shift, analyze a laboratory reagent blank to determine the background system contamination. LRBs should contain the same additives (dechlorinating agent and HCl) as field samples.

9.5 Assessing Laboratory Performance. With each batch of samples processed as a group within a work shift, analyze a single laboratory fortified blank (LFB) containing each analyte of concern at a concentration as determined in 9.3.1. LFBs should contain a dechlorination agent and/or HCl as appropriate to match the field samples being analyzed. The minimum frequency of LFB analysis is once every twelve hours. Use the criteria described in 9.3.3 to evaluate the accuracy of the measurements, and to estimate whether the method detection limits can be obtained. If acceptable accuracy and method detection limits cannot be achieved, the problem must be located and corrected before further samples are analyzed. Data from all field samples analyzed since the last acceptable LFB should be considered suspect, and duplicate samples should be analyzed, if they are available, after the problem has been corrected. LFB results should be added to the on-going control charts to document data quality.

Since the calibration check sample in Sect. 10.3.2 and the LFB are made the same way and since procedural standards are used, the sample analyzed here may also be used as the calibration check in Sect. 10.3.2.

9.6 Assessing the Internal Standard. If internal standard calibration is used, the analyst must assess the response of the internal standard in every LRB, FRB, LFB, CAL, and field sample. The IS response (peak height or peak area units) must be within 20% of the mean peak response of the IS in the CAL standards used to develop the calibration. If this criteria cannot be met, take remedial action. If there are interferences in field samples that affect the measurement of the internal standard, external standard calibration should be used (Sect. 10.3.2).

9.7 Assessing the Surrogate Analyte. Calculate the amount of the surrogate analyte recovered in each LRB, LFB, FRB, CAL, and field sample (Sect.10). If the surrogate recovery in blanks or calibration standards does not meet the criteria in Sect. 9.3.3., take

remedial action. If the surrogate recovery in a field sample does not meet the criteria in Sect 9.3.3., and data from LFBs shows the laboratory to be in control, reanalyze the sample.

9.8 If a water sample is contaminated with an analyte, verify that it is not a sampling error by analyzing a field reagent blank. The results of these analyses will help define contamination resulting from field sampling, storage and transportation activities. If the field reagent blank shows unacceptable contamination, the analyst should identify and eliminate the contamination.

9.9 At least quarterly, replicates of laboratory fortified blanks should be evaluated to determine the precision of the laboratory measurements. Add these results to the on-going control charts to document data quality.

9.10 At least quarterly, analyze a quality control sample (QCS) from an external source. If measured analyte concentrations are not of acceptable accuracy, check the entire analytical procedure to locate and correct the problem source.

9.11 Sample matrix effects have not been observed when this method is used with distilled water, reagent water, drinking water, and ground water. Therefore, analysis of a laboratory fortified sample matrix (LFM) is not required.

9.12 Numerous other quality control measures are incorporated into other parts of this procedure, and serve to alert the analyst to potential problems.

10. CALIBRATION AND STANDARDIZATION

10.1 Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed. In addition, acceptable performance must be confirmed intermittently throughout analysis of samples by performing continuing calibration checks. These checks are required at the beginning of each work shift, but no less than every 12 hours. Additional periodic calibration checks are good laboratory practice. Since this method uses procedural standards, the analysis of the laboratory fortified blank, which is required in Sect. 9.5, may be used here as a calibration check sample.

10.2 PREPARATION OF CALIBRATION STANDARDS

10.2.1 The number of calibration solutions (CALs) needed depends on the calibration range desired. A minimum of three CAL solutions is required to calibrate a range of a factor of 20 in concentration. For a factor of 50 use at least four standards, and for a factor of 100 at least five standards. One calibration standard should contain each analyte of concern at a concentration 2 to 10 times greater than the method detection limit (Table 2 and 4) for that compound. The other

CAL standards should contain each analyte of concern at concentrations that define the range of the sample analyte concentrations. When internal standard calibration is being used, every CAL solution contains the internal standard at same concentration (10 µg/L).

10.2.2 To prepare a calibration standard, add an appropriate volume of a primary dilution standard solution to an aliquot of reagent water in a volumetric container or sample syringe. The reagent water used should also contain the appropriate dechlorinating agent and/or HCl so as to match the field samples to be analyzed. Use a microsyringe and rapidly inject the alcoholic standard into the water. Remove the needle as quickly as possible after injection. Accurate calibration standards can be prepared by injecting 20 µL of the primary dilution standards to 25 mL or more of reagent water using the syringe described in section 6.4.3. Aqueous standards are not stable in volumetric container and should be discarded after one hour unless transferred to sample bottle and sealed immediately as described in Sect. 8.1.2.

10.3 CALIBRATION

10.3.1 External standard calibration. Starting with the standard of lowest concentration, analyze each calibration standard according to Sect. 11 and tabulate peak height or area response versus the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (<10% relative standard deviation), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

10.3.2 Internal standard calibration. The organohalides recommended as internal standards are: 1-chloro-2-fluorobenze or 2-bromo-1-chloropropane and fluorobenzene. The internal standard is added to the sample just before purging. Check the validity of the internal standard response factors daily by analyzing a calibration standard. NOTE: Since the calculated concentrations can be strongly biased by inaccurate detector response measurements for the internal standard or by coelution of an unknown with the internal standard, it is required that the area measurement of the internal standard of each sample be within ± 3 standard deviations of those obtained from calibration standards, or ± 20% of the mean response obtained from calibration standards, whichever is greater. If they do not, then internal standards can not be used.

10.3.3 Following analysis, tabulate peak height or area responses against concentration for each compound and the internal

standard. Calculate the response factor (RF) for each compound using Equation 1.

Equation 1

$$RF = \frac{(A_s)\ (C_{is})}{(A_{is})\ (C_s)}$$

where

A_s = Response for the analyte to be measured
A_{is} = Response for the internal standard
C_{is} = Concentration of the internal standard (µg/L)
C_s = Concentration of the analyte to be measured (µg/L)

If RF value over the working range is constant (< 10% RSD), the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response versus analyte ratios, A_s/A_{is} vs. C_s/C_{is}.

10.3.4 The working calibration curve or calibration factor must be verified by the measurement of one or more calibration standards. This must be done at least once each work shift, but no less than once every twelve hours. Additional periodic calibration checks are good laboratory practice. It is highly recommended that an additional calibration check be performed at the end of any cycle of continuous instrument operation, so that each set of field samples is bracketed by calibration check standards. It is also recommended that more that one concentration of continuing calibration standard be analyzed, in order to evaluate the accuracy of the calibration at more than one point. If the response for any analyte varies from the predicted response by more than ± 20%, the test must be repeated using a fresh calibration standard. If the results still do not agree, generate a new calibration curve. Any field samples analyzed since the last acceptable calibration check should be considered suspect, and should be reanalyzed if they are available.

10.4 CALIBRATION FOR VINYL CHLORIDE USING A CERTIFIED GASEOUS MIXTURE (OPTIONAL)

10.4.1 Fill the purging device with 5.0 mL of reagent water or aqueous calibration standard, and add internal standards.

10.4.2 Start to purge the aqueous mixture (Sect. 7.2.6). Inject a known volume (between 100 and 2000 µL) of the calibration gas (at room temperature) directly into the purging device with a gas tight syringe. Slowly inject the gaseous sample through the aqueous sample inlet needle. After completion, inject 2 mL of clean room air to sweep the gases from the inlet needle

into the purging device. Inject the gaseous standard before five min of the 11-min purge time have elapsed.

10.4.3 Determine the aqueous equivalent concentration of vinyl chloride standard injected in μg/L, according to the equation:

$$S = 0.51\ (C)\ (V) \qquad \text{Equation 1}$$

where: S = Aqueous equivalent concentration of vinyl chloride standard in μg/L;
C = Concentration of gaseous standard in ppm (v/v);
V = Volume of standard injected in milliliter

11. PROCEDURE

11.1 INITIAL CONDITIONS

11.1.1 Recommended chromatographic conditions are summarized in Sect. 6.3. Other columns or GC conditions may be used if the requirements of Sect. 9.3 are met.

11.1.2 Calibrate the system daily as described in Sect. 10.

11.1.3 Adjust the purge gas (nitrogen or helium) flow rate to 40 mL-/min. Attach the trap inlet to the purging device and open the syringe valve on the purging device.

11.2 SAMPLE INTRODUCTION AND PURGING

11.2.1 To generate accurate data, samples and calibration standards must be analyzed under identical conditions. Remove the plungers from two 5-mL syringes and attach a closed syringe valve to each. Allow the sample to come to room temperature, open the sample (or standard) bottle, and carefully pour the sample into one of the syringe barrels to just short of overflowing. Replace the syringe plunger, invert the syringe, and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. Add 10 μL of the internal calibration standard to the sample through the syringe valve. Close the valve. Fill the second syringe in an identical manner from the same sample bottle. Reserve this second syringe for a reanalysis if necessary.

11.2.2 Attach the sample syringe valve to the syringe valve on the purging device. Be sure that the trap is cooler than 25°C, then open the sample syringe valve and inject the sample into the purging chamber. Close both valves and initiate purging. Purge the sample for 11.0 ± 0.1 min at ambient temperature. Note: Ambient room temperature must be relatively constant. If it varies by more than 10°C during an analysis day, or be-

tween calibration and sample analysis, precision and accuracy of some analytes will be affected.

11.3 SAMPLE DESORPTION - After the 11-min purge, couple the trap to the chromatograph by switching the purge and trap system to the desorb mode, initiate the temperature program sequence of the gas chromatograph and start data acquisition. Introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while backflushing the trap with an appropriate inert gas flow for 4.0 ± 0.1 min. While the extracted sample is being introduced into the gas chromatograph, empty the purging device using the sample syringe and wash the chamber with two 5-mL flushes of reagent water.

11.4 TRAP RECONDITIONING - After desorbing the sample for four min, recondition the trap by returning the purge and trap system to the purge mode. Maintain the trap temperature at 180°C. After approximately seven min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Identify each analyte in the sample chromatogram by comparing the retention time of the suspect peak to retention times generated by the calibration standards, the LFB and other fortified quality control samples. If the retention time of the suspect peak agrees within ± 3 standard deviations of the retention times of those generated by known standards (Table 1 and 3) then the identification may be considered as positive. If the suspect peak falls outside this range or coelutes with other compounds (Table 1 and 3), then the sample should be reanalyzed. When applicable, determine the relative response of the alternate detector to the analyte. The relative response should agree to within 20% of the relative response determined from standards.

12.2 Xylenes and other structural isomers can be explicitly identified only if they have sufficiently different GC retention times. Acceptable 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.

12.3 When both detectors respond to an analyte, quantitation is usually performed on the detector which exhibits the greater response. However, in cases where greater specificity or precision would result, the analyst may choose the alternate detector. Do not extrapolate beyond the calibration range established in Sect. 10. If peak response exceeds the highest calibration standard, a duplicate sample must be diluted and reanalyzed. Use only the multipoint calibration data obtained in Sect. 10 for all calculations. Do not use the daily calibration verification standard to quantitate method analyte in samples.

12.4 Determine the concentration of the unknowns when external standards are used, by using the calibration curve or by comparing the peak height or area of the unknowns to the peak height or area of the standards as follows:

Concentration of unknown (µg/L) = (Peak height sample/Peak height standard) x Concentration of standard (µg/L).

12.5 Calculate analyte and surrogate concentrations when internal standards are used with the equation in Sect. 10.3.3.

12.6 Calculations should utilize all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures(one digit of uncertainty). Experience indicates that three significant figures may be used for concentrations above 99 µg/L, two significant figures for concentrations between 1 to 99 µg/L, and 1 significant figure for lower concentrations.

12.7 Calculate the total trihalomethane concentrations by summing the four individual trihalomethane concentrations in µg/L.

13. METHOD PERFORMANCE

13.1 This method was tested in a single laboratory using reagent water fortified at 10 µg/L (1). Single laboratory precision and accuracy data for each detector are presented for the method analytes in Tables 2 and 4.

13.2 Method detection limits for these analytes have been calculated from data collected by fortifying reagent water at 0.1 µg/L.(1). These data are presented in Tables 2 and 4.

13.3 Method detection limits were calculated using the formula:

$$MDL = S\ t_{(n-1,1-alpha = 0.99)}$$

where:

$t_{(n-1,1-alpha = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom,

n = number of replicates

S = the standard deviation of the replicate analyses.

14. POLLUTION PREVENTION

14.1 No solvents are utilized in this method except the extremely small volumes of methanol needed to make calibration standards. The only other chemicals used in this method are the neat materials in

preparing standards and sample preservatives. All are used in extremely small amounts and pose no threat to the environment.

15. WASTE MANAGEMENT

15.1 There are no waste management issues involved with this method. Due to the nature of this method, the discarded samples are chemically less contaminated than when they were collected.

16. REFERENCES

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17. TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. RETENTION TIMES FOR VOLATILE ORGANIC COMPOUNDS ON PHOTOIONIZATION DETECTOR (PID) AND ELECTROLYTIC CONDUCTIVITY DETECTOR (ELCD) FOR COLUMN 1

	Analyte[b]	Retention Time (min)[a] PID	ELCD
1	Dichlorodifluoromethane	-(c)	8.47
2	Chloromethane	-	9.47
3	Vinyl Chloride	9.88	9.93
4	Bromomethan	-	11.95
5	Chloroethane	-	12.37
6	Trichlorofluoromethane	-	13.49
7	1,1-Dichloroethene	6.14	16.18
8	Methylene Chloride	-	18.39
9	trans-1,2-Dichloroethene	19.30	19.33
10	1,1-Dichloroethane	-	20.99
11	2,2-Dichloropropane	-	22.88
12	cis-1,2-Dichloroethene	23.11	23.14
13	Chloroform	-	23.64
14	Bromochloromethane	-	24.16
15	1,1,1-Trichloroethane	-	24.77
16	1,1-Dichloropropene	25.21	25.24
17	Carbon Tetrachloride	-	25.47
18	Benzene	26.10	-
19	1,2-Dichloroethane	-	26.27
20	Trichloroethene	27.99	28.02
21	1,2-Dichloropropane	-	28.66
22	Bromodichloromethane	-	29.43
23	Dibromomethane	-	29.59
	Cis-1,3-Dichloropropene	31.38	31.41
24	Toluene	31.95	-
	Trans-1,3-Dichloropropene	33.01	33.04
25	1,1,2-Trichloroethane	-	33.21
26	Tetrachloroethene	33.88	33.90
27	1,3-Dichloropropane	-	34.00
28	Dibromochloromethane	-	34.73
29	1,2-Dibromoethane	-	35.34
30	Chlorobenzene	36.56	36.59
31	Ethylbenzene	36.72	-
32	1,1,1,2-Tetrachloroethane	-	36.80
33	m-Xylene	36.98	-
34	p-Xylene	36.98	-
35	o-Xylene	38.39	-
36	Styrene	38.57	-
37	Isopropylbenzene	39.58	-
38	Bromoform	-	39.75
39	1,1,2,2-Tetrachloroethane	-	40.35
40	1,2,3-Trichloropropane	-	40.81
41	n-Propylbenzene	40.87	-

TABLE 1 (CONTINUED)

	Analyte[b]	Retention Time (min)[a] PID	ELCD
42	Bromobenzene	40.99	41.03
43	1,3,5-Trimethylbenzene	41.41	-
44	2-Chlorotoluene	41.41	41.45
45	4-Chlorotoluene	41.60	41.63
46	tert-Butylbenzene	42.71	
47	1,2,4-Trimethylbenzene	42.92	-
48	sec-Butylbenzene	43.31	-
49	p-Isopropyltoluene	43.81	-
50	1,3-Dichlorobenzene	44.08	44.11
51	1,4-Dichlorobenzene	44.43	44.47
52	n-Butylbenzene	45.20	-
53	1,2-Dichlorobenzene	45.71	45.74
54	1,2-Dibromo-3-Chloropropane	-	48.57
55	1,2,4-Trichlorobenzene	51.43	51.46
56	Hexachlorobutadiene	51.92	51.96
57	Naphthalene	52.38	-
58	1,2,3-Trichlorobenzene	53.34	53.37
Internal Standards			
	Fluorobenzene	26.84	-
	2-Bromo-1-chloropropane[d]	-	33.08

a. Column and analytical conditions are described in Sect. 6.3.
b. Number refers to peaks in Figure 502.2-1.
c. - Dash indicates detector does not respond.
d. Interferes with trans-1,3-dichloropropene and 1,1,2-trichloroethane on the column. Use with care.

TABLE 2. SINGLE LABORATORY ACCURACY, PRECISION, AND METHOD DETECTION LIMITS FOR VOLATILE ORGANIC COMPOUNDS IN REAGENT WATER FOR COLUMN 1[a]

	Photoionization Detector			Electrolytic Conductivity Detector		
Analyte	Average Recovery (µg/L)	Rel. Std. Deviation (%)	MDL (µg/L)	Average Recovery (µg/L)	Rel. Std. Deviation (%)	MDL (µg/L)
Benzene	99	1.2	0.01	-(b)	-	-
Bromobenzene	99	1.7	0.01	97	2.7	0.03
Bromochloromethane-	-	-	-	96	3.0	0.01
Bromodichloromethane	-	-	-	97	2.9	0.02
Bromoform	-	-	-	106	5.2	1.6
Bromomethane	-	-	-	97	3.8	1.1
n-Butylbenzene	100	4.4	0.02	-	-	-
sec-Butylbenzene	97	2.7	0.02	-	-	-
tert-Butylbenzene	98	2.3	0.06	-	-	-
Carbon tetrachloride	-	-	-	92	3.6	0.01
Chlorobenzene	100	1.0	0.01	103	3.6	0.01
Chloroethane	-	-	-	96	3.9	0.1
Chloroform	-	-	-	98	2.5	0.02
Chloromethane	-	-	-	96	9.2	0.03
2-Chlorotoluene	N.D.(c)	N.D.	N.D.	97	2.7	0.01
4-Chlorotoluene	101	1.0	0.02	97	3.2	0.01
1,2-Dibromo-3-chloropropane	-	-	-	86	11.3	3.0
Dibromochloromethane	-	-	-	102	3.3	0.3
1,2-Dibromoethane	-	-	-	97	2.8	0.8
Dibromomethane	-	-	-	109	6.7	2.2
1,2-Dichlorobenzene	102	2.1	0.05	100	1.5	0.02
1,3-Dichlorobenzene	104	1.6	0.02	106	4.0	0.02
1,4-Dichlorobenzene	103	2.1	0.01	98	2.3	0.01
Dichlorodifluoromethane	-	-	-	89	6.6	0.05
1,1-Dichloroethane	-	-	-	100	5.7	0.07
1,2-Dichloroethane	-	-	-	100	3.8	0.03
1,1-Dichloroethene	100	2.4	N.D.	103	2.8	0.07
cis-1,2 Dichloroethene	N.D.	N.D.	0.02	105	3.3	0.01
trans-1,2-Dichloroethene	93	4.0	0.05	99	3.7	0.06
1,2-Dichloropropane	-	-	-	103	3.7	0.01
1,3-Dichloropropane	-	-	-	100	3.4	0.03

TABLE 2. (CONTINUED)

Analyte	Photoionization Detector Average Recovery (µg/L)	Photoionization Detector Rel. Std. Deviation (%)	Photoionization Detector MDL (µg/L)	Electrolytic Conductivity Detector Average Recovery (µg/L)	Electrolytic Conductivity Detector Rel. Std. Deviation (%)	Electrolytic Conductivity Detector MDL (µg/L)
2,2-Dichloropropane	-	-	-	105	3.4	0.05
1,1-Dichloropropene	103	3.5	0.02	103	3.3	0.02
Ethylbenzene	101	1.4	0.01	-	-	-
Hexachlorobutadiene	99	9.5	0.06	98	8.3	0.02
Isopropylbenzene	98	0.9	0.05	-	-	-
p-Isopropyltoluene	98	2.4	0.01	-	-	-
Methylene chloride	-	-	-	97	2.9	0.02
Naphthalene	102	6.2	0.06	-	-	-
n-Propylbenzene	103	2.0	0.01	-	-	-
Styrene	104	1.3	0.01	-	-	-
1,1,1,2-Tetrachloroethane	-	-	-	99	2.3	0.01
1,1,2,2-Tetrachloroethane	-	-	-	99	6.8	0.01
Tetrachloroethene	101	1.8	0.05	97	2.5	0.04
Toluene	99	0.8	0.01	-	-	-
1,2,3-Trichlorobenzene	106	1.8	N.D.	98	3.1	0.03
1,2,4-Trichlorobenzene	104	2.2	0.02	102	2.1	0.03
1,1,1-Trichloroethane	-	-	-	104	3.3	0.03
1,1,2-Trichloroethane	-	-	-	109	5.6	N.D.
Trichloroethene	100	0.78	0.02	96	3.6	0.01
Trichlorofluoromethane	-	-	-	96	3.5	0.03
1,2,3-Trichloropropane	-	-	-	99	2.3	0.4
1,2,4-Trimethylbenzene	99	1.2	0.05	-	-	-
1,3,5-Trimethylbenzene	101	1.4	0.01	-	-	-
Vinyl chloride	109	5.0	0.02	95	5.9	0.04
o-Xylene	99	0.8	0.02	-	-	-
m-Xylene	100	1.4	0.01	-	-	-
p-Xylene	99	0.9	0.01	-	-	-

a. Recoveries and relative standard deviations were determined from seven samples fortified at 10 µg/L of each analyte. Recoveries were determined by internal standard method. Internal standards were: Fluorobenzene for PID, 2-Bromo-1-chloropropane for ELCD.
b. Detector does not respond.
c. N.D. = not determined.

TABLE 3. RETENTION TIMES FOR VOLATILE ORGANIC COMPOUNDS ON PHOTOIONIZATION DETECTOR (PID) AND ELECTROLYTIC CONDUCTIVITY DETECTOR(ELCD) FOR COLUMN 2

	Analyte[b]	PID RT(min)[a]	PID RSD	ECLD RT(min)[a]	ECLD RSD
1	Dichlorodifluoromethane	-(c)		7.36	0.06
2	Chloromethane	-		8.09	0.06
3	Vinyl Chloride	8.57	0.06	8.58	0.08
4	BromomethanE	-		10.39	0.06
5	Chloroethane	-		10.74	0.05
6	Trichlorofluoromethane	-		11.85	0.07
7	1,1-Dichloroethene	14.46	0.08	14.47	0.07
8	Methylene Chloride	-		16.46	0.04
9	trans-1,2-Dichloroethene	17.61	0.02	17.62	0.03
10	1,1-Dichloroethane	-		19.25	0.03
11	2,2-Dichloropropane	-		21.36	0.03
12	cis-1,2-Dichloroethene	21.52	0.02	21.52	0.02
13	Chloroform	-		22.08	0.02
14	Bromochloromethane	-		22.69	0.02
15	1,1,1-Trichloroethane	-		23.53	0.02
16	1,1-Dichloropropene	24.07	0.01	24.08	0.02
17	Carbon Tetrachloride	-		24.47	0.02
18	1,2-Dichloroethane	-		24.95	0.01
19	Benzene	25.06	0.01	-	
20	Trichloroethene	27.99	0.01	27.15	0.01
21	1,2-Dichloropropane	-		27.73	0.01
22	Bromodichloromethane	-		28.57	0.02
23	Dibromomethane	-		28.79	0.01
24	Cis-1,3-Dichloropropene	30.40	0.01	30.41	0.02
25	Toluene	31.58	0.01	-	
26	Trans-1,3-Dichloropropene	32.11	0.01	32.13	0.01
27	1,1,2-Trichloroethane	-		32.69	0.01
28	1,3-Dichloropropane	-		33.57	0.01
29	Tetrachloroethene	33.85	0.01	33.86	0.01
30	Dibromochloromethane	-		34.58	0.01
31	1,2-Dibromoethane	-		35.29	0.01
32	Chlorobenzene	36.76	0.01	36.87	0.01
33	1,1,1,2-Tetrachloroethane	-		36.87	0.01
34	Ethylbenzene	36.92	0.01	-	
35	m-Xylene	37.19	0.01	-	
36	p-Xylene	37.19	0.01	-	
37	o-Xylene	38.77	0.01	-	
38	Styrene	38.90	0.01	-	
39	Isopropylbenzene	40.04	0.01	-	
40	Bromoform	-		40.19	0.01
41	1,1,2,2-Tetrachloroethane	-		40.64	0.01
42	1,2,3-Trichloropropane	-	0.01	41.18	0.01
43	n-Propylbenzene	41.51	0.01	-	
44	Bromobenzene	41.73	0.01	41.75	0.01

TABLE 3 (CONTINUED)

	Analyte[b]	PID RT(min)[a]	PID RSD	ECLD RT(min)[a]	ECLD RSD
45	1,3,5-Trimethylbenzene	42.08	0.01	-	
46	2-Chlorotoluene	42.20	0.01	42.21	0.01
47	4-Chlorotoluene	42.36	0.01	42.36	0.01
48	tert-Butylbenzene	43.40	0.01	-	
49	1,2,4-Trimethylbenzene	43.55	0.01	-	
50	sec-Butylbenzene	44.19	0.01	-	
51	p-Isopropyltoluene	44.69	0.01	-	
52	1,3-Dichlorobenzene	45.08	0.01	45.09	0.01
53	1,4-Dichlorobenzene	45.48	0.01	45.48	0.01
54	n-Butylbenzene	46.22	0.01	-	
55	1,2-Dichlorobenzene	46.88	0.01	46.89	0.01
56	1,2-Dibromo-3-Chloropropane		-	49.84	0.01
57	1,2,4-Trichlorobenzene	53.26	0.01	53.26	0.01
58	Hexachlorobutadiene	53.86	0.01	53.87	0.01
59	Naphthalene	54.45	0.01	-	
60	1,2,3-Trichlorobenzene	55.54	0.01	55.54	0.01
	Internal Standards				
	1-Chloro-2-Fluorobenzene	37.55	0.01	37.56	0.01

a. Column and analytical conditions are described in Sect. 6.3.4.
b. Number refers to peaks in Figure 502.2-2.
c. - Dash indicates detector does not respond.

TABLE 4. SINGLE LABORATORY ACCURACY, PRECISION, AND METHOD DETECTION LIMITS FOR VOLATILE ORGANIC COMPOUNDS IN REAGENT WATER FOR COLUMN 2[a]

	PID			ELCD		
Analyte	Average Recovery (µg/L)	Rel. Std. Deviation (%)	MDL (µg/L)	Average Recovery (µg/L)	Rel. Std. Deviation (%)	MDL (µg/L)
Benzene	97	1.6	0.01	-(b)	-	-
Bromobenzene	98	1.1	0.04	96	3.2	0.14
Bromochloromethane-	-	-	-	95	2.5	0.01
Bromodichloromethane	-	-	-	96	2.6	0.10
Bromoform	-	-	-	98	4.0	0.09
Bromomethane	-	-	-	97	2.4	0.19
n-Butylbenzene	95	2.4	0.03	-	-	-
sec-Butylbenzene	96	2.1	0.03	-	-	-
tert-Butylbenzene	98	2.1	0.06	-	-	-
Carbon tetrachloride	-	-	-	97	2.4	0.02
Chlorobenzene	98	1.5	0.02	98	2.2	N.D.(c)
Chloroethane	-	-	-	97	3.2	0.13
Chloroform	-	-	-	92	4.2	0.01
Chloromethane	-	-	-	98	2.3	0.10
2-Chlorotoluene	94	3.1	0.03	99	2.3	0.04
4-Chlorotoluene	97	1.6	0.02	97	2.3	0.07
1,2-Dibromo-3-chloropropane	-	-	-	97	2.2	0.20
Dibromochloromethane	-	-	-	99	2.0	0.05
1,2-Dibromoethane	-	-	-	99	2.8	0.17
Dibromomethane	-	-	-	98	3.5	0.10
1,2-Dichlorobenzene	97	1.4	0.03	98	2.0	0.04
1,3-Dichlorobenzene	97	1.6	0.02	97	2.2	0.07
1,4-Dichlorobenzene	97	1.5	0.03	97	2.2	0.04
Dichlorodifluoromethane	-	-	-	96	3.2	0.29
1,1-Dichloroethane	-	-	-	97	2.3	0.03
1,2-Dichloroethane	-	-	-	98	1.8	0.03
1,1-Dichloroethene	96	2.2	0.10	97	2.3	0.04
cis-1,2 Dichloroethene	97	1.7	0.03	96	3.3	0.05
trans-1,2-Dichloroethene	97	1.8	0.03	98	1.5	0.05
1,2-Dichloropropane	-	-	-	98	1.8	0.03
1,3-Dichloropropane	-	-	-	100	1.3	0.02
2,2-Dichloropropane	-	-	-	95	14.2	N.D.

TABLE 4. (CONTINUED)

Analyte	PID Average Recovery (µg/L)	PID Rel. Std. Deviation (%)	PID MDL (µg/L)	ELCD Average Recovery (µg/L)	ELCD Rel. Std. Deviation (%)	ELCD MDL (µg/L)
1,1-Dichloropropene	96	2.1	0.05	97	2.6	0.02
Cis-1,3-Dichloropropene	98	1.6	0.06	98	2.0	0.08
Trans-1,3-Dichloropropene	99	1.7	0.06	97	1.4	0.10
Ethylbenzene	98	1.2	0.04	-	-	-
Hexachlorobutadiene	95	2.6	0.09	97	2.3	0.05
Isopropylbenzene	97	1.4	0.02	-	-	-
p-Isopropyltoluene	96	2.0	0.02	-	-	-
Methylene chloride	-	-	-	100	3.1	0.01
Naphthalene	96	2.1	0.02	-	-	-
n-Propylbenzene	97	1.8	0.03	-	-	-
Styrene	96	1.9	0.10	-	-	-
1,1,1,2-Tetrachloroethane	-	-	-	98	2.2	N.D.
1,1,2,2-Tetrachloroethane	-	-	-	100	2.8	0.02
Tetrachloroethene	97	1.6	0.04	97	1.9	0.02
Toluene	98	1.3	0.02	-	-	-
1,2,3-Trichlorobenzene	95	2.3	0.05	98	2.8	0.06
1,2,4-Trichlorobenzene	94	3.0	0.06	96	2.5	0.08
1,1,1-Trichloroethane	-	-	-	96	2.6	0.01
1,1,2-Trichloroethane	-	-	-	99	1.6	0.04
Trichloroethene	97	1.7	0.03	98	1.2	0.06
Trichlorofluoromethane	-	-	-	97	6.0	0.34
1,2,3-Trichloropropane	-	-	-	100	2.0	0.02
1,2,4-Trimethylbenzene	96	2.0	0.02	-	-	-
1,3,5-Trimethylbenzene	98	1.6	0.03	-	-	-
Vinyl chloride	95	1.1	0.01	96	2.6	0.18
o-Xylene	98	1.1	0.02	-	-	-
m-Xylene	98	1.1	0.02	-	-	-
p-Xylene	98	0.9	0.02	-	-	-

a. Recoveries and relative standard deviations were determined from seven samples fortified at 10 µg/L of each analyte. Recoveries were determined by external standard method.
b. Detector does not respond.
c. N.D. = not determined.

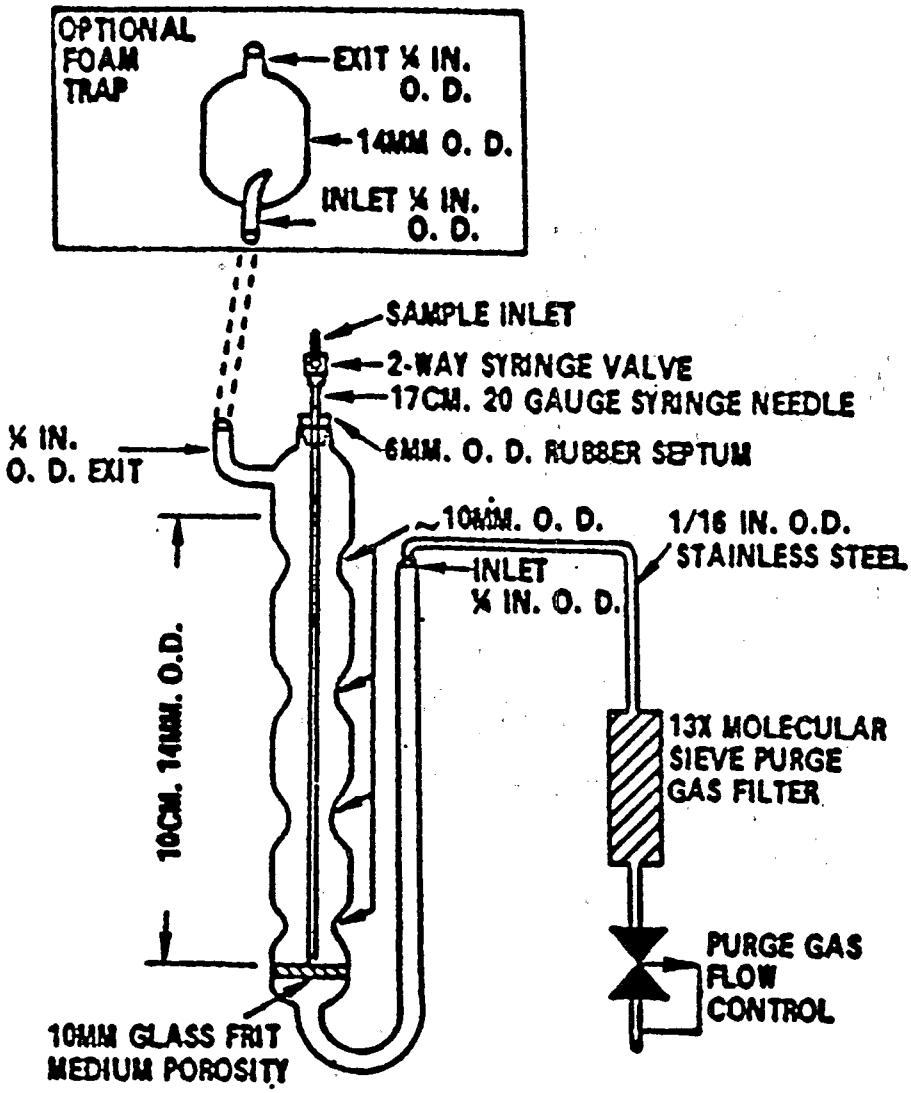

FIGURE 1. PURGING DEVICE

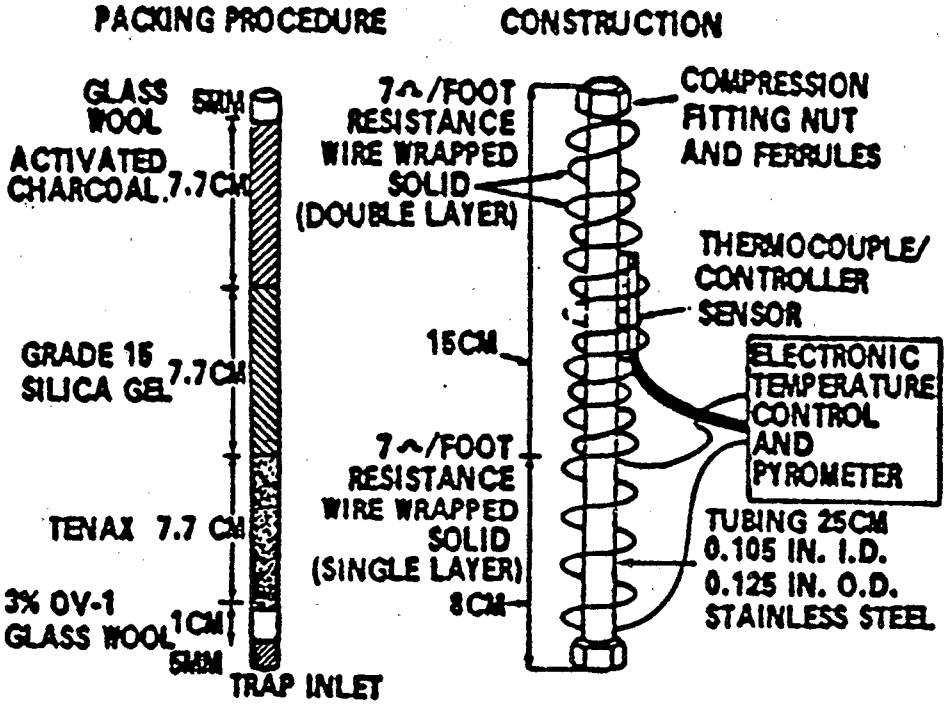

FIGURE 2. TRAP PACKINGS AND CONSTRUCTION TO INCLUDE DESORB CAPABILITY

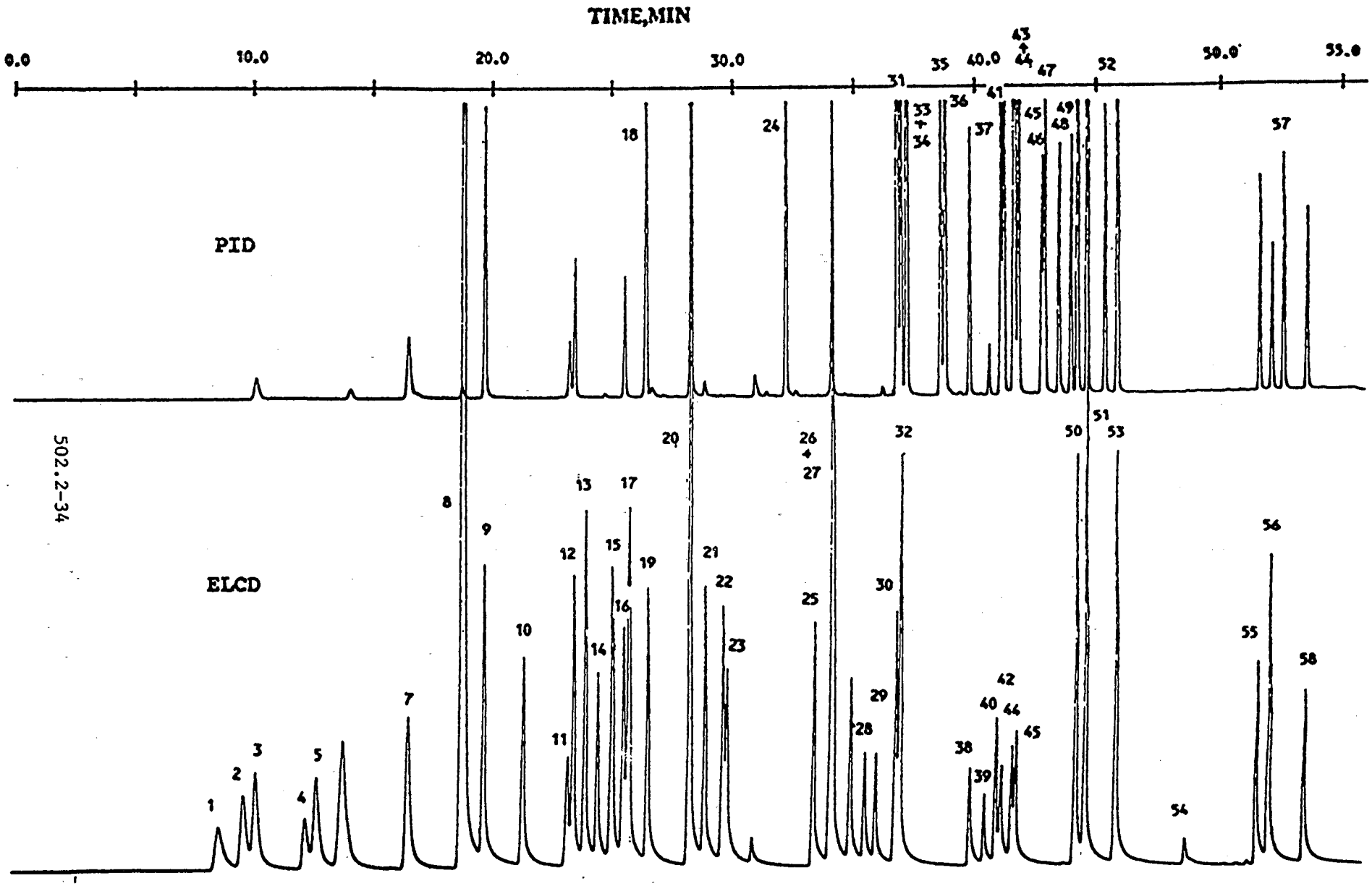

FIGURE 3. DUAL CHROMATOGRAM OF ORGANIC COMPOUNDS FOR COLUMN 1

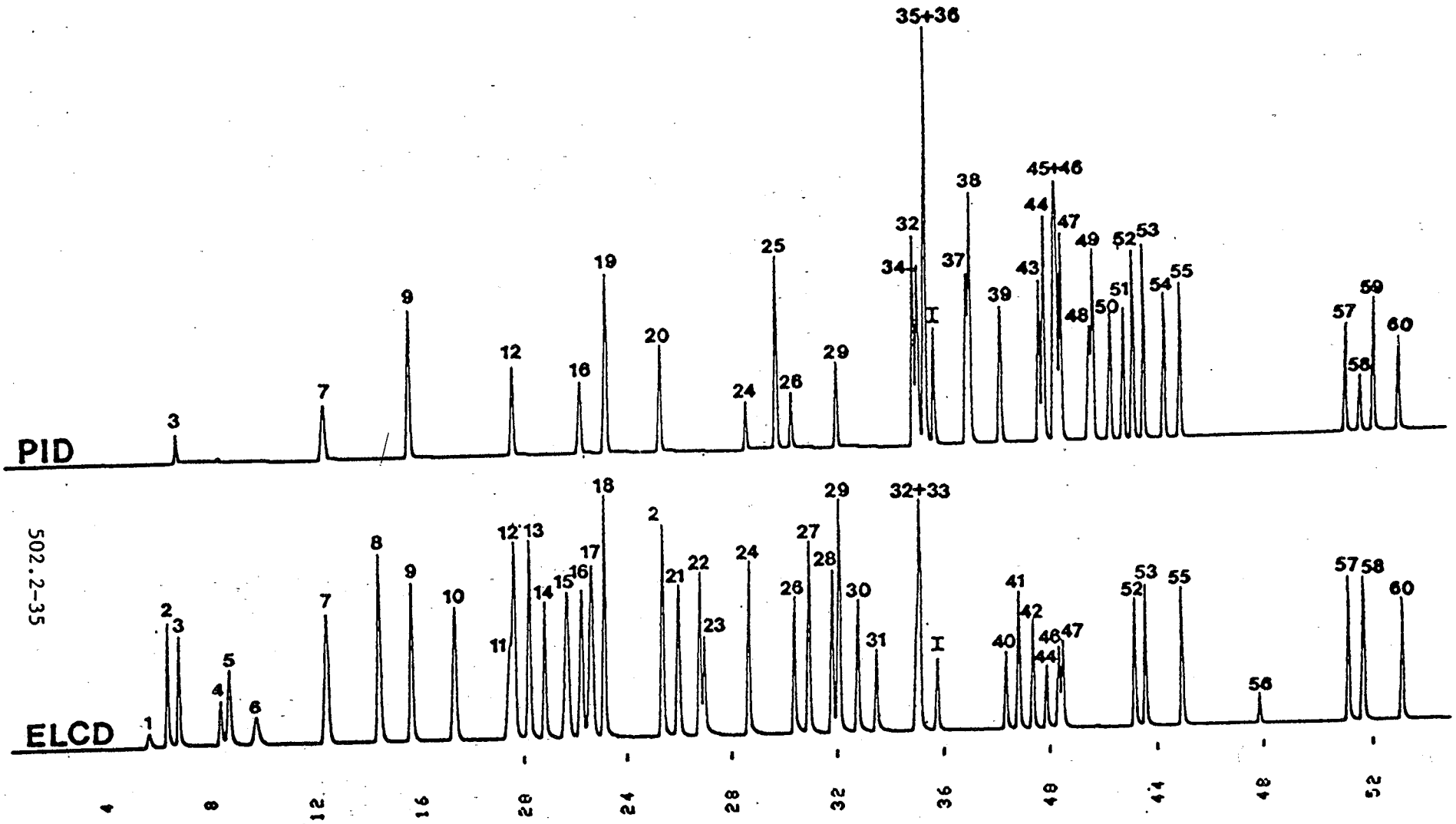

FIGURE 4. DUAL CHROMATOGRAM OF ORGANIC COMPOUNDS FOR COLUMN 2

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METHOD 504.1 1,2-DIBROMOETHANE (EDB), 1,2-DIBROMO-3-CHLORO-PROPANE (DBCP), AND 1,2,3-TRICHLOROPROPANE (123TCP) IN WATER BY MICROEXTRACTION AND GAS CHROMATOGRAPHY

Revision 1.1

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METHOD 504.1

1,2-DIBROMOETHANE (EDB), 1,2-DIBROMO-3-CHLOROPROPANE (DBCP), AND 1,2,3-TRICHLOROPROPANE (123TCP) IN WATER BY MICROEXTRACTION AND GAS CHROMATOGRAPHY

1. SCOPE AND APPLICATION

1.1 This method (1-3) is applicable to the determination of the following compounds in finished drinking water and groundwater:

Analyte	Chemical Abstract Services Registry Number
1,2-Dibromoethane	106-93-4
1,2-Dibromo-3-Chloropropane	96-12-8
1,2,3-Trichloropropane	96-18-4

1.2 For compounds other than the above mentioned analytes, or for other sample sources, the analyst must demonstrate the usefulness of the method by collecting precision and accuracy data on actual samples and provide qualitative confirmation of results by gas chromatography/mass spectrometry (GC/MS) (4).

1.3 The experimentally determined method detection limits (MDL) (5) for EDB and DBCP were calculated to be 0.01 µg/L and the MDL for 123TCP was calculated to be 0.02 µg/L. The method has been useful for these analytes over a concentration range from approximately 0.03 to 200 µg/L. Actual detection limits are highly dependent upon the characteristics of the gas chromatographic system used.

2. SUMMARY OF METHOD

2.1 Thirty-five mL of sample are extracted with 2 mL of hexane. Two µL of the extract are then injected into a gas chromatograph equipped with a linearized electron capture detector for separation and detection. Analytes are quantitated using procedural standard calibration (Sect. 3.12).

2.2 The extraction and analysis time is 30 to 50 min per sample depending upon the analytical conditions chosen.

2.3 Confirmatory evidence should be obtained for all positive results. This data may be obtained by using retention data from a dissimilar column, or when concentrations are sufficiently high by GC/MS. Purge and trap techniques using Methods 502.2 or 524.2 may also be used. Confirmation of all positive results of EDB are especially important, because of the potential for misidentification of dibromochloromethane (DBCM) as EDB.

3. DEFINITIONS

3.1 LABORATORY DUPLICATES (LD1 and LD2) -- Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.2 FIELD DUPLICATES (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.3 LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.4 FIELD REAGENT BLANK (FRB) -- An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.5 INSTRUMENT PERFORMANCE CHECK SOLUTION (IPC) -- A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.6 LABORATORY FORTIFIED BLANK (LFB) -- An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.7 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.8 STOCK STANDARD SOLUTION (SSS) -- A concentrated solution containing one or method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

3.9 PRIMARY DILUTION STANDARD SOLUTION (PDS) -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.10 CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution and stock standard solutions of the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.11 QUALITY CONTROL SAMPLE (QCS) -- A solution of method analytes of known concentrations that is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.12 PROCEDURAL STANDARD CALIBRATION -- A calibration method where aqueous calibration standards are prepared and processed (e.g. purged,extracted, and/or derivatized) in exactly the same manner as a sample. All steps in the process from addition of sampling preservatives through instrumental analyses are included in the calibration. Using procedural standard calibration compensates for any inefficiencies in the processing procedure.

4. INTERFERENCES

4.1 Impurities contained in the extracting solvent usually account for the majority of the analytical problems. Solvent blanks should be analyzed on each new bottle of solvent before use. Indirect daily checks on the extracting solvent are obtained by monitoring the reagent water blanks (Sect. 7.2.4). Whenever an interference is noted in the reagent water blank, the analyst should reanalyze the extracting solvent. Low level interferences generally can be removed by distillation or column chromatography (3). When a solvent is purified, preservatives put into the solvent by the manufacturer are removed thus potentially making the shelf-life short. It is generally more economical to obtain a new source of solvent. Interference-free solvent is defined as a solvent containing less than the MDL of an individual analyte interference. Protect interference-free solvents by storing in an area free of organochlorine solvents.

4.2 This liquid/liquid extraction technique efficiently extracts a wide boiling range of non-polar organic compounds and, in addition, extracts polar organic components of the sample with varying efficiencies.

4.3 Dibromochloromethane is a common disinfection byproduct in chlorinated drinking waters that frequently occurs at relatively high concentrations. DBCM can elute very close to EDB, and a high concentration of DBCM may mask a low concentration of EDB, or be misidentified as EDB. Therefore, special care should be taken in the identification and confirmation of EDB.

4.4 It is important that samples and working standards be contained in the same solvent. The solvent for working standards must be the same as the final solvent used in sample preparation. If this is not the case, chromatographic comparability of standards to sample may be affected.

5. SAFETY

5.1 The toxicity and carcinogenicity of chemicals used in this method have not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available (5-7) for the information of the analyst.

5.2 EDB, DBCP, and 123TCP have all been tentatively classified as known or suspected human or mammalian carcinogens. Pure standard materials and stock standard solutions of these compounds should be handled in a hood or glovebox. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6. EQUIPMENT AND SUPPLIES (All specifications are suggested. Catalog numbers are included for illustration only.)

6.1 SAMPLE CONTAINERS -- 40-mL screw cap vials each equipped with a Teflon-lined cap. Individual vials shown to contain at least 40.0 mL can be calibrated at the 35.0 mL mark so that volumetric, rather than gravimetric, measurements of sample volumes can be performed. Prior to use, wash vials and septa with detergent and rinse with tap and distilled water. Allow the vials and septa to air dry at room temperature, place in a 105°C oven for one hr, then remove and allow to cool in an area free of organic solvent vapors.

6.2 VIALS, auto sampler, screw cap with Teflon faced septa, 1.8 mL.

6.3 MICRO SYRINGES -- 10, 25, and 100 µL.

6.4 PIPETTES -- 2.0 and 5.0 mL transfer.

6.5 STANDARD SOLUTION STORAGE CONTAINERS -- 15-mL bottles with Teflon lined screw caps.

6.6 GAS CHROMATOGRAPHY SYSTEM

6.6.1 The gas chromatograph must be capable of temperature programming and should be equipped with a linearized electron capture detector and a capillary column split/splitless injector.

6.6.2 Two gas chromatography columns are recommended. Column A provides separation of the method analytes without interferences from trihalomethanes (Sect. 4.3). Column A should be used as the primary analytical column unless routinely occurring analytes are not adequately resolved. Column B is recommended for use as a confirmatory column when GC/MS confirmation is not viable. Retention times for the method analytes on these columns are presented in Table 1.

6.6.3 Column A (primary column) -- DB-1, 30 m x 0.25 mm ID, 1.0 µm film thickness fused silica capillary column or equivalent. The linear velocity of the helium carrier gas should be about 25 cm/sec at 100°C. The column temperature is programmed to hold at 40°C for 4 min, to increase to 240°C at 10°C/min, and hold at 240°C for 5 min or until all expected compounds have eluted.

6.6.4 Column B (alternative column) -- DB-624, 30 m x 0.32 mm ID, 1.8 µm film thickness fused silica capillary column or equivalent. The linear velocity of the helium carrier gas should be about 25 cm/sec at 100°C. The column temperature is programmed as described in Sect.6.6.3.

7. REAGENTS AND STANDARDS

7.1 REAGENTS

7.1.1 Hexane extraction solvent -- UV Grade, distilled in glass

7.1.2 Methyl alcohol -- ACS Reagent Grade, demonstrated to be free of method analytes above the MDLs.

7.1.3 Sodium chloride, NaCl -- ACS Reagent Grade - For pretreatment before use, pulverize a batch of NaCl and place in a muffle furnace at room temperature. Increase the temperature to 400°C for 30 min. Place in a bottle and cap.

7.1.4 Sodium thiosulfate, $Na_2S_2O_3$, ACS Reagent Grade -- For preparation of solution (40 mg/mL), dissolve 1 g of $Na_2S_2O_3$ in reagent water and bring to 25-mL volume in a volumetric flask.

7.2 REAGENT WATER -- Reagent water is defined as water free of interferences above the analyte MDLs.

7.2.1 Reagent water can be generated by passing tap water through a filter bed containing activated carbon. Change the activated

carbon when there is evidence that volatile organic compounds are breaking through the carbon.

7.2.2 A Millipore Super-Q Water System or its equivalent may be used to generate deionized reagent water.

7.2.3 Reagent water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water at 100 mL/min for 1 hr. While still hot, transfer the water to a narrow mouth screw cap bottle with a Teflon seal.

7.2.4 Test reagent water each day it is used by analyzing it according to Sect. 11.

7.3 STOCK STANDARD SOLUTIONS -- These solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedures:

7.3.1 Place about 9.8 mL of methanol into a 10-mL ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min and weigh to the nearest 0.1 mg.

7.3.2 Use a 100-μL syringe and immediately add two or more drops of standard material to the flask. Be sure that the standard material falls directly into the methanol without contacting the neck of the flask.

7.3.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter from the net gain in weight.

7.3.4 Store stock standard solutions in 15-mL bottles equipped with Teflon lined screw caps. Methanol solutions prepared from liquid analytes are stable for at least four weeks when stored at 4°C.

7.4 PRIMARY DILUTION STANDARD SOLUTIONS -- Use stock standard solutions to prepare primary dilution standard solutions that contain all three analytes in methanol. The primary dilution standards should be prepared at concentrations that can be easily diluted to prepare aqueous calibration standards (Sect. 10.1.1) that will bracket the working concentration range. Store the primary dilution standard solutions with minimal headspace and check frequently for signs of deterioration or evaporation, especially just before preparing calibration standards. The storage time described for stock standard solutions in Sect. 7.3.4 also applies to primary dilution standard solutions.

7.5 LABORATORY FORTIFIED BLANK (LFB) SAMPLE CONCENTRATE (0.25 µg/mL) -- Prepare an LFB sample concentrate of 0.25 µg/mL of each analyte from the stock standard solutions prepared in Sect. 7.3.

7.6 MDL CHECK SAMPLE CONCENTRATE (0.02 µg/mL) -- Dilute 2 mL of LFB sample concentrate (Sect. 7.5) to 25 mL with methanol.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 SAMPLE COLLECTION

8.1.1 Replicate field reagent blanks (FRB) must be handled along with each sample set, which is composed of the samples collected from the same general sampling site at approximately the same time. At the laboratory, fill a minimum of two sample bottles with reagent water, seal, and ship to the sampling site along with sample bottles. Wherever a set of samples is shipped and stored, it must be accompanied by the FRB.

8.1.2 Collect all samples in 40-mL bottles into which 3 mg of sodium thiosulfate crystals have been added to the empty bottles just prior to shipping to the sampling site. Alternatively, 75 µL of freshly prepared sodium thiosulfate solution (40 mg/mL) may be added to empty 40-mL bottles just prior to sample collection. This dechlorinating agent must be added to each sample to avoid the possibility of reactions that may occur between residual chlorine and indeterminant contaminants present in some solvents, yielding compounds that may subsequently interfere with the analysis. The presence of sodium thiosulfate will arrest further formation of DBCM (See Sect. 4.3).

8.1.3 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 10 min). Adjust the flow to about 500 mL/min and collect samples from the flowing stream.

8.1.4 When sampling from a well, fill a wide-mouth bottle or beaker with sample, and carefully fill 40-mL sample bottles.

8.2 SAMPLE PRESERVATION

8.2.1 The samples must be chilled to 4°C or less at the time of collection and maintained at that temperature until analysis. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to ensure that they will be ≤4°C on arrival at the laboratory.

8.3 SAMPLE STORAGE

8.3.1 Store samples and field reagent blanks together at 4°C until analysis. The sample storage area must be free of organic solvent vapors.

8.3.2 Because 1,2,3-trichloropropane has been added to the analyte list in this method and has been found to have a 14 day maximum holding time in studies conducted for Method 524.2 (4), all samples must be extracted within 14 days of collection. Samples not analyzed within this period must be discarded and replaced. Because of the potential for solvent evaporation, it is preferred that extracts be analyzed immediately following preparation. When necessary, extracts may be stored in tightly capped vials (Sect. 6.2) at 4°C or less for up to 24 hr.

9. QUALITY CONTROL

9.1 Each laboratory that uses this method 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 field reagent blanks (FRB), laboratory reagent blanks (LRB), laboratory fortified blanks (LFB), laboratory fortified sample matrix (LFM), and quality control samples (QCS) to evaluate and document data quality. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1.1 The analyst must make an initial determination of the method detection limits and demonstrate the ability to generate acceptable precision with this method. This is established as described in Sect. 9.2.

9.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Sect. 9.2.

9.1.3 Each day, the analyst must analyze a laboratory reagent blank (LRB) and a field reagent blank, if applicable (Sect. 8.1.1), to demonstrate that interferences from the analytical system are under control before any samples are analyzed. In general, background interferences co-eluting with method analytes should be below the method detection limits.

9.1.4 The laboratory must, on an ongoing basis, demonstrate through the analyses of laboratory fortified blanks (LFB) that the operation of the measurement system is in control. This

procedure is described in Sect. 9.3. The frequency of the LFB analyses is equivalent to 10% of all samples analyzed.

9.1.5 The laboratory should demonstrate the ability to analyze low level samples weekly. The procedure for low level LFB samples is described in Sect. 9.4.

9.2 Initial Demonstration of Capability

9.2.1 Prepare four to seven LFBs at a concentration equal to 10 times the MDL or at a concentration in the middle of the calibration range established in Sect. 10.

9.2.2 Analyze the LFBs according to the method beginning in Sect. 11.

9.2.3 Calculate the mean concentration found (X) in µg/L, and the standard deviation of the concentrations in µg/L, for each analyte.

9.2.4 For each analyte, X should be between 70% and 130% of the true value. The RSD should be 20% or less. If the results for all three analytes meet these criteria, the system performance is acceptable. If any analyte fails to meet the criteria, correct the source of the problem and repeat the test.

CAUTION: No attempts to establish low detection limits should be made before instrument optimization and adequate conditioning of both the column and the GC system. Conditioning includes the processing of LFB and LFM samples containing moderate analyte concentrations.

9.2.5 Determination of MDL. Prepare 4-7 LFBs at a low concentration. Use the concentrations in Tables 2 and 3 as a guideline, or use calibration data obtained (Sect. 10) to estimate a concentration for each analyte that will produce a chromatographic peak with a 3-5 signal to noise ratio. It is recommended that LFBs for determination of the MDL be prepared and analyzed over a period of several days, so that day to day variations will be reflected in the precision data.

9.2.6 Analyze the LFBs as directed in Sect. 11. Calculate the mean amount recovered and the standard deviation of these measurements. Use the standard deviation and the equation in Sect. 13 to calculate the MDL.

9.3 Assessing Laboratory Performance. The laboratory must demonstrate that the measurement system is in control by analyzing an LFBs of the analytes at 0.25 µg/L concentration level. This must be

demonstrated on a frequency equivalent to 10% of the sample load, or 1 per batch of samples extracted, whichever is greater.

9.3.1 Prepare an LFB sample (0.25 µg/L) by adding 35 µL of LFB concentrate (Sect. 7.5) to 35 mL of reagent water in a 40-mL bottle.

9.3.2 Immediately analyze the LFB sample according to Sect. 11 and calculate the recovery for each analyte. The recovery should be between 70% and 130% of the expected value.

9.3.3 If the recovery for either analyte falls outside the designated range, the analyte fails the acceptance criteria. A second LFB containing each analyte that failed must be analyzed. 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.

9.3.4 Since this LFB is prepared in the same manner as a calibration verification standard, this LFB data can also be used to satisfy the calibration requirement in Sect. 10.1.4.

9.4 Assessing Laboratory Sensitivity. The laboratory should demonstrate the ability to analyze low level samples for EDB and DBCP weekly.

9.4.1 Prepare an MDL check sample (a LFB fortified at 0.02 µg/L) and immediately analyze according to the method in Sect. 11.

9.4.2 The instrument response must indicate that the laboratory's MDL is distinguishable from instrument background signal. If it is not, correct the problem (increase sensitivity) and repeat Sect. 9.4.1.

9.4.3 For each analyte, the recovery must be between 60% and 140% of the expected value. These criteria are looser than those in Sect. 9.2.4 and 9.3.2 because of the low concentration.

9.4.4 When either analyte fails the test, the analyst should repeat the test for that analyte. Repeated failure, however, will confirm a general problem with the measurement system or faulty samples and/or standards. If this occurs, locate and correct the source of the problem and repeat the test.

9.5 Assessing Matrix Effects. At least once in every 20 samples, fortify an aliquot of a randomly selected routine sample with known amounts of the analytes. The added concentration should not be less than the background concentration of the sample selected for fortification. To simplify these checks, it would be convenient to use LFM concentrations ≈10X MDL. Over time, recovery should be evaluated on fortified samples from all routine sources. Calculate the percent recovery (R_i) for each analyte, corrected for background concentrations measured in the unfortified sample. If the recovery

of any such analyte falls outside the range of ± 35% of the fortified amount, and the laboratory performance for that analyte is shown to be in control (Sect. 9.3), the recovery problem encountered with the dosed sample is judged to be matrix related, not system related. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

9.6 It is highly recommended that a laboratory establish its ability to distinguish DBCM from EDB. This is particularly important if samples from chlorinated sources or unfamiliar sources are to be analyzed (Sect. 4.3). Standards of DBCM should be analyzed periodically to establish its retention time relative to that of EDB. When evaluating this retention time difference, the analyst should keep in mind that DBCM is likely to be present in concentrations much larger than EDB, and that the ability to detect EDB may deteriorate with increasing DBCM concentration.

9.7 At least quarterly, a quality control sample (QCS) should be analyzed. If measured analyte concentrations are not of acceptable accuracy, check the entire analytical procedure to locate and correct the problem source.

9.8 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. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

10. CALIBRATION AND STANDARDIZATION

10.1 CALIBRATION AND STANDARDIZATION

10.1.1 At least three calibration standards are needed; five are recommended. Guidance on the number of standards is as follows: A minimum of three calibration standards are required to calibrate a range of a factor of 20 in concentration. For a factor of 50 use at least four standards, and for a factor of 100 at least five standards. The lowest standard should represent analyte concentrations near, but above, their respective MDLs. The remaining standards should bracket the analyte concentrations expected in the sample extracts, or should define the working range of the detector.

10.1.2 To prepare a calibration standard (CAL), add an appropriate volume of a primary dilution standard solution to an aliquot

of reagent water in a volumetric flask. If < 20 µL of a standard is added to the reagent water, poor precision may result. Use a 25-µL micro syringe 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 several times. Discard the contents contained in the neck of the flask. Aqueous standards should be prepared fresh and extracted immediately after preparation unless sealed and stored without headspace as described in Sect. 8. Alternatively, measure a 35-mL volume of reagent water in a 50-mL graduated cylinder and transfer it to a 40-mL sample container (Sect. 6.1). Use a micro syringe to inject the standard into the reagent water. Cap and mix gently.

10.1.3 Analyze each calibration standard according to Sect. 11 and record the peak height or area response from each standard. Create a calibration curve by plotting peak area response versus the concentration in the standard. Alternatively, if the ratio of concentration to response (calibration factor) is a constant over the working range (< 20% relative standard deviation), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

10.1.4 Verify the calibration daily by the analysis of 1 or more calibration standards for each 12 hr shift of operation. It is recommended that a calibration standard be analyzed at the beginning of each period of operation, and also at the end of each period of continuous instrument operation. Vary the concentration of the calibration standards used for verification, so that several points in the calibration range are verified. NOTE: The data presented in Tables 1-3 were obtained on a chromatographic system that was calibrated daily. Because of the sensitivity required in this method it may be necessary for some laboratories to calibrate daily, in order to meet the QC criteria in Section 9.

10.2 INSTRUMENT PERFORMANCE -- Check the performance of the entire analytical system daily using data gathered from analyses of laboratory reagent blanks and standards.

10.2.1 Significant peak tailing of the target compounds in the chromatogram must be corrected. Tailing problems are generally traceable to active sites on the GC column, improper column installation, or problems with the operation of the detector.

11. PROCEDURE

11.1 SAMPLE PREPARATION

11.1.1 Remove samples and standards from storage and allow them to reach room temperature.

11.1.2 For samples and field reagent blanks, contained in 40-mL bottles, remove the container cap. Discard a 5-mL volume using a 5-mL transfer pipette or 10-mL graduated cylinder. Replace the container cap and weigh the container with contents to the nearest 0.1 g and record this weight for subsequent sample volume determination (Sect. 11.3). **NOTE:** It is important not to use a graduated cylinder or other means to transfer the sample to another container prior to extraction. Loss of volatile compounds will occur each time the sample is poured or otherwise transferred.

11.2 MICROEXTRACTION AND ANALYSIS

11.2.1 Remove the container cap and add 6 g NaCl (Sect. 7.1.3) to the sample.

11.2.2 Recap the sample container and dissolve the NaCl by swirling for about 20 sec.

11.2.3 Remove the cap and add exactly 2.0 mL of hexane using a class A, TD, transfer or automatic dispensing pipette. Recap and shake vigorously for 1 min. Allow the water and hexane phases to separate. (If stored at this stage, keep the container upside down.)

11.2.4 Remove the cap and carefully transfer 0.5 mL of the hexane layer into an autoinjector using a disposable glass pipette.

11.2.5 Transfer the remaining hexane phase, being careful not to include any of the water phase, into a second autoinjector vial. Reserve this second vial at 4°C for a reanalysis if necessary.

11.2.6 Transfer the first sample vial to an autoinjector set up to inject 2 µL portions into the gas chromatograph for analysis. Alternatively, 2 µL portions of samples, blanks and standards may be manually injected, although an autoinjector is recommended.

11.3 DETERMINATION OF SAMPLE VOLUME

11.3.1 For samples and field blanks, remove the cap from the sample container.

11.3.2 Discard the remaining sample/hexane mixture. Shake off the remaining few drops using short, brisk wrist movements.

11.3.3 Reweigh the empty container with original cap and calculate the net weight of sample by difference to the nearest 0.1 g.

This net weight (grams) is equivalent to the volume of water (in mL) extracted (Sect. 12.3).

12. DATA ANALYSIS AND CALCULATIONS

12.1 Identify the method analytes in the sample chromatogram by comparing the retention time of the suspect peaks to retention times of the calibration standards and the laboratory control standards analyzed using identical conditions. The analyst should use caution in the identification of EDB in samples from chlorinated and unknown sources that may contain DBCM (Sect. 4.3). Confirmation procedures in Section 2.3 should be used to verify identification of EDB.

12.2 Use the calibration curve or calibration factor (Sect. 10.1.3) to directly calculate the uncorrected concentration (C_i) of each analyte in the sample (e.g., calibration factor x response). Extracts that contain method analytes beyond the calibration range established in Sect. 10., must be diluted and reanalyzed. Do not extrapolate beyond the range of instrument calibration. Use the multi-point calibration established in Sect.10 for all calculations. Do not use the daily calibration verification standard to quantitate method analytes in samples.

12.3 Calculate the sample volume (V_s) as equal to the net sample weight: V_s = gross weight (Sect. 11.1.2) - bottle tare (Sect. 11.3.3).

12.4 Calculate the corrected sample concentration as:

$$\text{Concentration, } \mu g/L = C_i \times \frac{35}{V_s}$$

12.5 Results should be reported with an appropriate number of significant figures. Experience indicates that three significant figures may be used for concentrations above 99 µg/L, two significant figures for concentrations between 1-99 µg/L, and 1 significant figure for lower concentrations.

13. METHOD PERFORMANCE

13.1 Single laboratory accuracy and precision data are presented for the three method analytes in reagent water at concentrations of 0.1 µg/L and 0.2 µg/L. Table 2 lists the data generated using Column A and Table 3 lists data gathered using Column B. The method detection limits are presented in Table 1. The method detection limits (MDL) in the table were calculated using the formula:

$$MDL = S\ t_{(n-1,1-alpha\ =\ 0.99)}$$

where:

$t_{(n-1,1-alpha\ =\ 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom

n = number of replicates

S = standard deviation of replicate analyses.

14. POLLUTION PREVENTION

14.1 This method utilizes a microextraction procedure that requires the use of very small volumes of hexane, thus making this method safe for use by the laboratory analyst and harmless to the environment. For information concerning pollution prevention that may be applicable to laboratory operations, consult "Less is Better: Laboratory Chemical Management for Waste Reduction" available from the American Chemical Society's Department of Government Relations, and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

15. WASTE MANAGEMENT

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing the waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and regulations. For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel," also available from the American Chemical Society at the address in Sect. 14.1.

16. REFERENCES

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17. TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS FOR METHOD ANALYTES USING CONDITIONS IN SECTION 6.6.3

	Retention Time, Min		MDL, µg/L
Analyte	Column A	Column B	
EDB	9.37	12.47	0.01
123TCP	12.00	15.37	0.02
DBCP	17.3	15.0	0.01

MDLs were calculated from 8 replicate samples fortified at a concentration of 0.04 µg/L of each analyte.

TABLE 2. ACCURACY AND PRECISION USING COLUMN A

Analytes fortified at 0.10 µg/L

	Recovered Concentration, µg/L		
Replicate #	EDB	123TCP	DBCP
1	0.1098	0.1157	0.1093
2	0.1121	0.1090	0.1108
3	0.1109	0.1144	0.1114
4	0.1125	0.1041	0.1118
5	0.1133	0.1101	0.1088
6	0.1228	0.1085	0.1122
7	0.1370	0.1139	0.1090
mean	0.1169	0.1108	0.1105
STD DEV (n-1)	0.0098	0.0041	0.0014
Spk Lev, µg/L	0.1000	0.1000	0.1000
% RECOVERY	116.9	110.8	110.5
% RSD	8.41	3.69	1.28

Analytes Fortified at 0.20 µg/L

	Recovery Concentration, µg/L		
Replicate #	EDB	123TCP	DBCP
1	0.2473	0.2175	0.2171
2	0.2640	0.2232	0.2209
3	0.2767	0.2214	0.2160
4	0.3114	0.2186	0.2196
5	0.3146	0.2186	0.2160
6	0.2838	0.2307	0.2162
7	0.3126	0.2258	0.2257
mean	0.2872	0.2223	0.2188
STD DEV (n-1)	0.0266	0.0047	0.0036
Spk Lev, µg/L	0.2000	0.2000	0.2000
% RECOVERY	143.6	111.1	109.4
% RSD	9.25	2.13	1.65

TABLE 3. ACCURACY AND PRECISION USING COLUMN B

Analytes fortified at 0.10 µg/L

	Recovered Concentration, µg/L		
Replicate #	EDB	123TCP	DBCP
1	0.1010	0.0718	0.0989
2	0.1086	0.0915	0.1085
3	0.1068	0.1091	0.1140
4	0.1055	0.0894	0.1197
5	0.1124	0.0920	0.1129
6	0.1182	0.0835	0.1062
7	0.1374	0.1060	0.1117
mean	0.1128	0.0919	0.1103
STD DEV (n-1)	0.0121	0.0128	0.0066
Spk Lev, µg/L	0.1000	0.1000	0.1000
% RECOVERY	112.8	91.9	110.3
% RSD	10.74	13.88	5.98

Analytes Fortified at 0.20 µg/L

	Recovery Concentration, µg/L		
Replicate #	EDB	123TCP	DBCP
1	0.2361	0.1789	0.2164
2	0.2486	0.1859	0.2309
3	0.2784	0.2051	0.2199
4	0.3099	0.1934	0.2211
5	0.3138	0.1979	0.2173
6	0.2641	0.2171	0.2205
7	0.2924	0.1994	0.2303
mean	0.2776	0.1968	0.2223
STD DEV (n-1)	0.0298	0.0125	0.0059
Spk Lev, µg/L	0.2000	0.2000	0.2000
% RECOVERY	138.8	98.4	111.2
% RSD	10.7	6.36	2.65

TABLE 4. INTERLABORATORY STUDY OF METHOD 504 REGRESSION EQUATIONS FOR RECOVERY AND PRECISION*

Water Type	1,2-Dibromoethane	1,2-Dibromo-3-chloropropane
Applicable Conc. Range	(0.05 - 6.68) µg/L	(0.05 - 6.40) µg/L
Reagent Water		
Single-Analyst Precision	SR = 0.041X + 0.004	SR = 0.065X + 0.000
Overall Precision	S = 0.075X + 0.008	S = 0.143X - 0.000
Recovery	X = 1.072C - 0.006	X = 0.987C - 0.000
Ground Water		
Single-Analyst Precision	SR = 0.046X + 0.002	SR = 0.076X - 0.000
Overall Precision	S = 0.102X + 0.006	S = 0.160X + 0.006
Recovery	X = 1.077C - 0.001	X = 0.972C + 0.007

X = Mean recovery

C = True value for the concentration

* No interlaboratory method validation data is available for 1,2,3-Trichloropropane using Method 504, Revision 3.0.

METHOD 505. ANALYSIS OF ORGANOHALIDE PESTICIDES AND COMMERCIAL POLYCHLORINATED BIPHENYL (PCB) PRODUCTS IN WATER BY MICROEXTRACTION AND GAS CHROMATOGRAPHY

Revision 2.1

Edited by J.W. Munch (1995)

T. W. Winfield - Method 505, Revision 1.0 (1986)

T. W. Winfield - Method 505, Revision 2.0 (1989)

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METHOD 505

ANALYSIS OF ORGANOHALIDE PESTICIDES AND COMMERCIAL POLYCHLORINATED BIPHENYL (PCB) PRODUCTS IN WATER BY MICROEXTRACTION AND GAS CHROMATOGRAPHY

1. SCOPE AND APPLICATION

1.1 This method (1,2,3) is applicable to the determination of the following analytes in finished drinking water, drinking water during intermediate stages of treatment, and the raw source water:

Analyte	Chemical Abstract Service Registry Number
Alachlor	5972-60-8
Aldrin	309-00-2
Atrazine	1912-24-9
Chlordane	57-74-9
alpha-Chlorodane	5103-71-9
gamma-Chlorodane	5103-74-2
Dieldrin	60-57-1
Endrin	72-20-8
Heptachlor	76-44-8
Heptachlor Epoxide	1024-57-3
Hexachlorobenzene	118-74-1
Hexachlorocyclopentadiene	77-74-4
Lindane	58-89-9
Methoxychlor	72-43-5
cis-Nonachlor	
trans-Nonachlor	39765-80-5
Simazine	122-34-9
Toxaphene	8001-35-2
Aroclor 1016	12674-11-2
Aroclor 1221	11104-28-2
Aroclor 1232	11141-16-5
Aroclor 1242	53469-21-9
Aroclor 1248	12672-29-6
Aroclor 1254	11097-69-1
Aroclor 1260	11096-82-5

1.2 The analyst must demonstrate the applicability of the method by collecting precision and accuracy data on fortified samples (i.e., groundwater, tap water) (4) and provide qualitative confirmation of results by Gas Chromatography/Mass Spectrometry (GC/MS) (5), or by GC analysis using dissimilar columns.

1.3 Method detection limits (MDL) (6) for the above organohalides and Aroclors have been experimentally determined (Sect. 13.2). Actual detection limits are highly dependent upon the characteristics of the gas chromatographic system used (e.g. column type, age, and proper conditioning; detector condition; and injector mode and condition).

1.4 This method is restricted to use by or under the supervision of analysts experienced in the use of GC 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 Sect. 11.

2. SUMMARY OF METHOD

2.1 Thirty-five mL of sample are extracted with 2 mL of hexane. One to two µL of the extract are then injected into a gas chromatograph equipped with a linearized electron capture detector for separation and analysis. Analytes are quantitated using procedural standard calibration (Sect 3.12).

2.2 The extraction and analysis time is 40 to 70 min per sample depending upon the analytes and the analytical conditions chosen. (See Sect. 6.9).

3. DEFINITIONS

3.1 LABORATORY DUPLICATES (LD1 and LD2) -- Two sample aliquots taken in the analytical laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.2 FIELD DUPLICATES (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.3 LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.4 FIELD REAGENT BLANK (FRB) -- Reagent water placed in a sample container in the laboratory and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.5 LABORATORY PERFORMANCE CHECK SOLUTION (LPC) -- A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.6 LABORATORY FORTIFIED BLANK (LFB) -- An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

3.7 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.8 STOCK STANDARD SOLUTION -- A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a single analyte prepared in the laboratory with an assayed reference compound. Stock standard solutions are used to prepare primary dilution standards.

3.9 PRIMARY DILUTION STANDARD SOLUTION -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.10 CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution and stock standard solutions of the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.11 QUALITY CONTROL SAMPLE (QCS) -- A sample matrix containing method analytes or a solution of method analytes in a water miscible solvent which is used to fortify reagent water or environmental samples. The QCS is obtained from a source external to the laboratory, and is used to check laboratory performance with externally prepared test materials.

3.12 PROCEDURAL STANDARD CALIBRATION -- A calibration method where aqueous calibration standards are prepared and processed (e.g. purged, extracted, and/or derivatized) in <u>exactly</u> the same manner as a sample. All steps in the process from addition of sampling preservatives through instrumental analyses are included in the calibration. Using procedural standard calibration compensates for any inefficiencies in the processing procedure.

4. INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing apparatus that lead to

discrete artifacts or elevated baselines in gas chromatograms. All reagents and apparatus must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Sect. 9.2.

4.1.1 Glassware must be scrupulously cleaned (2). Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot water and detergent and thorough rinsing with tap and reagent water. Drain dry, and heat in an oven or muffle furnace at 400°C for 1 hr. Do not heat volumetric ware. Thermally stable materials, such as PCBs, might not be eliminated by this treatment. Thorough rinsing with acetone may be substituted for the heating. After drying and cooling, seal and store glassware in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

4.1.2 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. WARNING: When a solvent is purified, stabilizers put into the solvent by the manufacturer are removed thus potentially making the solvent hazardous. Also, when a solvent is purified, preservatives put into the solvent by the manufacturer are removed thus potentially reducing the shelf-life.

4.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. Between-sample rinsing of the sample syringe and associated equipment with hexane can minimize sample cross contamination. After analysis of a sample containing high concentrations of analytes, one or more injections of hexane should be made to ensure that accurate values are obtained for the next sample.

4.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. Also, note that all the analytes listed in the scope and application section are not resolved from each other on any one column, i.e., one analyte of interest may be an interferant for another analyte of interest. The extent of matrix interferences will vary considerably from source to source, depending upon the water sampled. Cleanup of sample extracts may be necessary. Analyte identifications should be confirmed (Sect. 11.4).

4.4 It is important that samples and working standards be contained in the same solvent. The solvent for working standards must be the same as the final solvent used in sample preparation. If this is not the case, chromatographic comparability of standards to sample may be affected.

4.5 Caution must be taken in the determination of endrin since it has been reported that the splitless injector may cause endrin degradation (7). The analyst should be alerted to this possible interference resulting in an erratic response for endrin.

4.6 Variable amounts of pesticides and commercial PCB products from aqueous solutions adhere to glass surfaces. It is recommended that sample transfers and glass surface contacts be minimized, and that adequate rinsing of glass surfaces be performed.

4.7 Aldrin, hexachlorocyclopentadiene and methoxychlor are rapidly oxidized by chlorine. Dechlorination with sodium thiosulfate at time of collection will stop further oxidation of these compounds.

4.8 WARNING: An interfering, erratic peak has been observed within the retention window of heptachlor during many analyses of reagent, tap, and groundwater. It appears to be related to dibutyl phthalate; however, the specific source has not yet been definitively determined. The observed magnitude and character of this peak randomly varies in numerical value from successive injections made from the same vial.

5. SAFETY

5.1 The toxicity and carcinogenicity of chemicals used in this method have not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available (8-10) for the information of the analyst.

5.2 The following organohalides have been tentatively classified as known or suspected human or mammalian carcinogens: aldrin, commercial PCB products, chlordane, dieldrin, heptachlor, hexachlorobenzene, and toxaphene. Pure standard materials and stock standard solutions of these compounds should be handled in a hood or glovebox.

5.3 WARNING: When a solvent is purified, stabilizers put into the solvent by the manufacturer are removed thus potentially making the solvent hazardous.

6. EQUIPMENT AND SUPPLIES (All specifications are suggested. Catalog numbers are included for illustration only.)

6.1 SAMPLE CONTAINERS - 40-mL screw cap vials (Pierce #13075 or equivalent) each equipped with a size 24 cap with a flat, disc-like TFE facing backed with a polyethylene film/foam extrusion (Fisher #02-883-3F or equivalent). Prior to use, wash vials and septa with detergent and rinse with tap and distilled water. Allow the vials and septa to air dry at room temperature, place the vials in a 400°C oven

for one hour, then remove and allow to cool in an area known to be free of organics.

6.2 VIALS - auto sampler, screw cap with septa, 1.8 mL, Varian #96-000099-00 or equivalent or any other autosampler vials not requiring more than 1.8 mL sample volumes.

6.3 AUTO SAMPLER - Hewlett-Packard 7671A, or equivalent.

6.4 MICRO SYRINGES - 10 and 100 µL.

6.5 MICRO SYRINGE - 25 µL with a 2-inch by 0.006-inch needle - Hamilton 702N or equivalent.

6.6 PIPETTES - 2.0 and 5.0 mL transfer.

6.7 VOLUMETRIC FLASKS - 10 and 100 mL, glass stoppered.

6.8 STANDARD SOLUTION STORAGE CONTAINERS - 15-mL bottles with PTFE-lined screw caps.

6.9 GAS CHROMATOGRAPH -- Analytical system complete with temperature programmable GC and split/splitless injector suitable for use with capillary columns and all required accessories including syringes, analytical columns, gases, a linearized electron capture detector and stripchart recorder. A data system is recommended for measuring peak areas. Table 1 lists retention times observed for method analytes using the columns and analytical conditions described below.

6.9.1 Three gas chromatographic columns are recommended. Column 1 (Sect. 6.9.2) should be used as the primary analytical column unless routinely occurring analytes are not adequately resolved. Validation data presented in this method were obtained using this column. Columns 2 and 3 are recommended for use as confirmatory columns when GC/MS confirmation is not available. Alternative columns may be used in accordance with the provisions described in Sect. 9.4.

6.9.2 Column 1 (Primary Column) - 0.32 mm ID x 30 M long fused silica capillary with chemically bonded methyl polysiloxane phase (DB-1, 1.0 µm film, or equivalent). Helium carrier gas flow is about 25 cm/sec linear velocity, measured at 180° with 9 psi column head pressure. The oven temperature is programmed from 180°C to 260°C at 4°C/min and held at 260°C until all expected compounds have eluted. Injector temperature: 200°C. Splitless Mode: 0.5 min. Detector temperature: 290°C. Sample chromatograms for selected pesticides are presented in Figures 1 and 2. Chromatograms of the Aroclors, toxaphene, and technical chlordane are presented in Figures 3 through 11.

6.9.3 Column 2 (alternative column 1) - 0.32mm ID x 30 M long fused silica capillary with a 1:1 mixed phase of dimethyl silicone

and polyethylene glycol (Durawax-DX3, 0.25μm film, or equivalent). Helium carrier gas flow is about 25 cm/sec linear velocity and oven temperature is programmed from 100°C to 210°C at 8°C/min, and held at 210°C until all expected compounds have eluted. Then the post temperature is programmed to 240°C at 8°C/min for 5 min.

6.9.4 Column 3 (alternative column 2) - 0.32mm ID x 25 M long fused silica capillary with chemically bonded 50:50 Methyl-Phenyl silicone (OV-17, 1.5μm film thickness, or equivalent). Helium carrier gas flow is about 40 cm/sec linear velocity and oven temperature is programmed from 100°C to 260°C at 4°C/min and held at 260°C until all expected compounds have eluted.

7. <u>REAGENTS AND STANDARDS</u> - - WARNING: When a solvent is purified, stabilizers put into the solvent by the manufacturer are removed thus potentially making the solvent hazardous. Also, when a solvent is purified, preservatives put into the solvent by the manufacturer are removed thus potentially making the shelf-life short.

7.1 REAGENTS

7.1.1 Hexane extraction solvent - UV Grade, Burdick and Jackson #216 or equivalent.

7.1.2 Methyl alcohol - ACS Reagent Grade, demonstrated to be free of analytes.

7.1.3 Sodium chloride, NaCl - ACS Reagent Grade - For pretreatment before use, pulverize a batch of NaCl and place in a muffle furnace at room temperature. Increase the temperature to 400°C and hold for 30 min. Store in a glass (not plastic) bottle to avoid phthalate contamination..

7.1.4 Sodium thiosulfate, $Na_2S_2O_3$, ACS Reagent Grade--For preparation of solution (0.04 g/mL), mix 1 g of $Na_2S_2O_3$ with reagent water and bring to 25-mL volume in a volumetric flask. Verify the stability of this solution and replace as necessary.

7.2 REAGENT WATER - Reagent water is defined as water free of interference when employed in the procedure described herein.

7.2.1 A Millipore Super-Q Water System or its equivalent may be used to generate deionized reagent water.

7.2.2 Test reagent water each day it is used by analyzing it according to Sect. 9.2.

7.3 STOCK STANDARD SOLUTIONS - These solutions may be obtained as certified solutions or prepared from pure standard materials using the following procedures:

7.3.1 Prepare stock standard solutions (5000 µg/mL) by accurately weighing about 0.0500 g of pure material. Dissolve the material in methanol 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 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.

7.3.2 Transfer the stock standard solutions into Teflon-sealed 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.

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

7.4 PRIMARY DILUTION STANDARD SOLUTIONS -- Use stock standard solutions to prepare primary dilution standard solutions that contain the analytes in methanol. The primary dilution standards should be prepared at concentrations that can be easily diluted to prepare aqueous calibration standards (Sect. 10.2.1) that will bracket the working concentration range. Store the primary dilution standard solutions with minimal headspace and check frequently for signs of deterioration or evaporation, especially just before preparing calibration standards. The storage time described for stock standard solutions in Sect. 7.3.3 also applies to primary dilution standard solutions. Note: Primary dilution standards for toxaphene, chlordane and each of the Aroclors must be prepared individually.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 SAMPLE COLLECTION

8.1.1 Collect all samples in 40-mL bottles into which 3 mg of sodium thiosulfate crystals have been added to the empty bottles just prior to shipping to the sampling site. Alternately, 75 µL of freshly prepared sodium thiosulfate solution (0.04 g/mL) may be added to empty 40-mL bottles just prior to sample collection.

8.1.2 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 10 min). Adjust the flow to about 500 mL/min and collect samples from the flowing stream.

8.1.3 When sampling from a well, fill a wide-mouth bottle or beaker with sample, and carefully fill 40-mL sample bottles.

8.2 SAMPLE PRESERVATION

8.2.1 The samples must be chilled to 4°C at the time of collection and maintained at that temperature until the analyst is prepared for the extraction process. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to insure that they will be maintained at 4°C until arrival at the laboratory.

8.3 SAMPLE STORAGE

8.3.1 Store samples and extracts at 4°C until extraction and analysis.

8.3.2 Extract all samples as soon as possible after collection. Results of holding time studies suggest that all analytes with the possible exception of heptachlor were adequately stable for 14 days when stored under these conditions. In general, heptachlor showed inconsistent results. If heptachlor is to be determined, samples should be extracted within 7 days of collection. The maximum holding time for all other analytes is 14 days. Analyte stability may be affected by the matrix; therefore, the analyst should verify that the preservation technique is applicable to the samples under study.

8.3.3 Because of the potential for extract volume loss due to evaporation, it is recommended that extracts be analyzed immediately after preparation. If this is not possible, extracts may be stored at 4°C or less in tightly capped vials (Sect. 6.2) for up to 24 hours.

9. QUALITY CONTROL

9.1 Minimum quality control (QC) requirements are initial demonstration of laboratory capability, analysis of laboratory reagent blanks (LRB), laboratory fortified blanks (LFB), laboratory fortified sample matrix (LFM), and quality control samples (QCS). A MDL for each analyte must also be determined.

9.2 Laboratory Reagent Blanks. Before processing any samples, the analyst must demonstrate that all glassware and reagent interferences are under control. Each time a set of samples is extracted or reagents are changed, an LRB must be analyzed. If within the retention time window of any analyte the LRB produces a peak that would prevent the determination of that analyte, determine the source of contamination and eliminate the interference before processing samples.

9.3 Initial Demonstration of Capability

9.3.1 Select a representative fortified concentration (about 10 times MDL or at a concentration in the middle of the calibration range established in Section 10) for each analyte. Prepare a standard concentrate containing each analyte at 1000 times the selected concentration. With a syringe, add 35 μL of the

concentrate to each of four to seven 35 mL aliquots of reagent water, and analyze each aliquot according to procedures beginning in Sect. 11.

9.3.2 For each analyte the mean recovery value for these samples must fall in the range of ± 30% of the fortified amount. The RSD for these measurements must be 20% or less. For those compounds that meet the acceptance criteria, performance is considered acceptable. For those compounds that fail these criteria, this procedure must be repeated using fresh replicate samples until satisfactory performance has been demonstrated.

9.3.3 For each analyte, determine the MDL. Prepare a minimum of 7 LFBs at a low concentration. Use calibration data obtained in Section 10 to estimate a concentration for each analyte that will produce a peak with a 3-5 times signal to noise response. Extract and analyze each replicate according to Sections 11 and 12. It is recommended that these LFBs be prepared and analyzed over a period of several days, so that day to day precision is reflected in the precision measurements. Calculate mean recovery and standard deviation for each analyte. Use the equation given in Sect.13 to calculate the MDL.

9.3.4 The initial demonstration of capability is used primarily to preclude a laboratory from analyzing unknown samples via a new, unfamiliar method prior to obtaining some experience with it. It is expected that as laboratory personnel gain experience with this method the quality of data will improve beyond those required here.

9.4 The analyst is permitted to modify GC columns, GC conditions, concentration techniques (i.e. evaporation techniques), internal standards or surrogate compounds. Each time such method modifications are made, the analyst must repeat the procedures in Sect. 9.3.

9.5 Assessing Laboratory Performance - Laboratory Fortified Blank (LFB)

9.5.1 The laboratory must analyze at least one laboratory fortified blank (LFB) per sample set (all samples extracted within a 24-h period). If the sample set contains more than 20 samples, analyze one LFB for every 20 samples. Ideally the fortifying concentration of each analyte in the LFB sample should be the same as that selected in Sect. 9.3.1. Calculate accuracy as percent recovery (X_i). If the recovery of any analyte falls outside the control limits (see Sect. 9.5.2), that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses. Because this LFB is prepared and analyzed in the same way as a calibration verification standard, it can be used to satisfy the calibration requirement in Sect.10.2.3.

Note: It is suggested that one multi-component analyte (toxaphene, chlordane or an Aroclor) LFB also be analyzed with each sample set. By selecting a different multi-component analyte for this LFB each work shift, LFB data can be obtained for all of these analytes over the course of several days

9.5.2 Until sufficient data become available from within their own laboratory, usually a minimum of results from 20 to 30 analyses, the laboratory may assess laboratory performance against the control limits in Sect. 9.3.2 that are derived from the data in Table 2. When sufficient internal performance data becomes available, develop control limits from the mean percent recovery (X) and standard deviation (S) of the percent recovery. These data are used to establish upper and lower control limits as follows:

$$\text{UPPER CONTROL LIMIT} = X + 3S$$
$$\text{LOWER CONTROL LIMIT} = X - 3S$$

After each five to ten new recovery measurements, new control limits should be calculated using only the most recent 20-30 data points. These calculated control limits should <u>not</u> exceed the fixed limits in Sect. 9.3.2.

9.5.3 It is recommended that the laboratory periodically determine and document its detection limit capabilities for analytes of interest. CAUTION: No attempts to establish low detection limits should be made before instrument optimization and adequate conditioning of both the column and the GC system. Conditioning includes the processing of LFB and LFM samples containing moderate concentration levels of these analytes.

9.5.4 At least quarterly the laboratory should analyze quality control samples (QCS). If acceptance criteria are not met, corrective action should be taken and documented.

9.6 Assessing Analyte Recovery - Laboratory Fortified Sample Matrix (LFM)

9.6.1 The laboratory must add a known concentration to a minimum of 10% of the routine samples or one LFM per set, whichever is greater. The fortified concentration should not be less than the background concentration of the sample selected for fortification. Ideally the LFM concentration should be the same as that used for the LFB (Sect. 9.3.1). Periodically, samples from all routine sample sources should be fortified.

9.6.2 Calculate the percent recovery (R_i) for each analyte, corrected for background concentrations measured in the unfortified sample.

9.6.3 If the recovery of any such analyte falls outside the range of ± 35% of the fortified amount, and the laboratory performance

for that analyte is shown to be in control (Sect. 9.5), the recovery problem encountered with the dosed sample is judged to be matrix related, not system related. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

9.7 The laboratory may adopt additional quality control 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. For example, field or laboratory duplicates may be analyzed to assess the precision of the environmental measurements or field reagent blanks may be used to assess contamination of samples under site conditions, transportation and storage.

10. CALIBRATION AND STANDARDIZATION

10.1 Establish GC operating parameters equivalent to those indicated in Sect. 6.9. WARNING: Endrin is easily degraded in the injection port if the injection port or front of the column is dirty. This is the result of buildup of high boiling residue from sample injection. Check for degradation problems daily by injecting a mid-level standard containing only endrin. Look for the degradation products of endrin (endrin ketone and endrin aldehyde). If degradation of endrin exceeds 20%, take corrective action before proceeding with calibration. Calculate percent breakdown as follows:

$$\frac{\text{Total endrin degradation peak area (endrin aldehyde + endrin ketone)}}{\text{Total endrin peak area (endrin + endrin aldehyde + endrin ketone)}} \times 100\%$$

10.2 At least three calibration standards are needed; five are recommended. Guidance on the number of standards is as follows: A minimum of three calibration standards are required to calibrate a range of a factor of 20 in concentration. For a factor of 50 use at least four standards, and for a factor of 100 at least five standards. The lowest standard should represent analyte concentrations near, but above, their respective MDLs. The remaining standards should bracket the analyte concentrations expected in the sample extracts, or should define the working range of the detector.

10.2.1 To prepare a calibration standard (CAL), add an appropriate volume of a secondary dilution standard to a 35 mL aliquot of reagent water in a 40-mL bottle. Do not add less than 20 µL of an alcoholic standard to the reagent water. Use a 25-µL micro syringe and rapidly inject the methanolic standard into the middle point of the water volume. Remove the needle as quickly as possible after injection. Mix by inverting and shaking the capped bottle several times. Aqueous standards must be prepared fresh daily.

10.2.2 Starting with the standard of lowest concentration, prepare, extract, and analyze each calibration standard beginning with Sect. 11.2 and tabulate peak height or area response versus the concentration in the standard. The results are to be used to prepare a calibration curve for each compound by plotting the peak height or area response versus the concentration. Alternatively, if the ratio of concentration to response (calibration factor) is a constant over the working range (20% RSD or less), linearity to the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve. NOTE: Toxaphene, chlordane, and Aroclor standards must be injected separately. See Section 12.2 for information on quantitation of multi-component analytes.

10.2.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of a minimum of two calibration check standards, one at the beginning and one at the end of the analysis day. These check standards should be at two different concentration levels to verify the calibration curve. For extended periods of analysis (greater than 8 hrs.), it is strongly recommended that check standards be interspersed with samples at regular intervals during the course of the analyses. If the response for any analyte varies from the predicted response by more than the criteria in Sect. 9.3.2, the test must be repeated using a fresh calibration standard. If the results still do not agree, generate a new calibration curve. For those analytes that failed the calibration verification, results from field samples analyzed since the last passing calibration should be considered suspect. Reanalyze sample extracts for these analytes after acceptable calibration is restored.

Note: It is suggested that a calibration verification standard of one multi-component analyte, either chlordane, toxaphene or an Aroclor also be analyzed each work shift. By selecting a different multi-component analyte for this calibration verification each work shift, continuing calibration data can be obtained for all of these analytes over the course of several days.

10.3 INSTRUMENT PERFORMANCE - Check the performance of the entire analytical system daily using data gathered from analyses of laboratory reagent blanks (LRB), (CAL), and laboratory duplicate samples (LD1 and LD2).

10.3.1 Significant peak tailing in excess of that shown for the target compounds in the method chromatograms (Figures 1-11) must be corrected. Tailing problems are generally traceable to active sites on the GC column, improper column installation, or operation of the detector.

10.3.2 Check the precision between replicate analyses. Poor precision is generally traceable to pneumatic leaks, especially at the injection port. If the GC system is apparently performing acceptably but with decreased sensitivity, it may be necessary to generate a new curve or set of calibration factors to verify the decreased responses before searching for the source of the problem.

10.3.3 Observed relative area responses of endrin (Sect. 10.1) must meet the following general criteria:

10.3.3.1 The breakdown of endrin into its aldo and keto forms must be adequately consistent during a period in which a series of analyses is made. Equivalent relative amounts of breakdown should be demonstrated in the LRB, LFB, CAL and QCS. Consistent breakdown resulting in these analyses would suggest that the breakdown occurred in the instrument system and that the methodology is in control.

10.3.3.2 Analyses of laboratory fortified matrix (LFM) samples must also be adequately consistent after corrections for potential background concentrations are made.

11. PROCEDURE

11.1 SAMPLE PREPARATION

11.1.1 Remove samples from storage and allow them to equilibrate to room temperature.

11.1.2 Remove the container caps. Withdraw and discard a 5 mL volume using a 10-mL graduated cylinder. Replace the container caps and weigh the containers with contents to the nearest 0.1 g and record these weights for subsequent sample volume determinations (Sect. 11.3).

11.2 EXTRACTION AND ANALYSIS

11.2.1 Remove the container cap of each sample, and add 6 g NaCl (Sect. 7.1.3) to the sample bottle. Using a class A, TD transfer or automatic dispensing pipet, add 2.0 mL of hexane. Recap and shake vigorously by hand for 1 min. Invert the bottle and allow the water and hexane phases to separate.

11.2.2 Remove the cap and carefully transfer approximately 0.5 mL of hexane layer into an autosampler vial using a disposable glass pipet.

11.2.3 Transfer the remaining hexane phase, being careful not to include any of the water phase, into a second autosampler

vial. Reserve this second vial at 4°C for reanalysis if necessary.

11.2.4 Transfer the first sample vial to an autosampler set up to inject 1-2 μL portions into the gas chromatograph for analysis (See Sect. 6.9 for GC conditions). Alternately, 1-2 μL portions of samples, blanks, and standards may be manually injected, although an autosampler is strongly recommended.

11.3 DETERMINATION OF SAMPLE VOLUME IN BOTTLES NOT CALIBRATED

11.3.1 Discard the remaining sample/hexane mixture from the sample bottle. Shake off the remaining few drops using short, brisk wrist movements.

11.3.2 Reweigh the empty container with original cap and calculate the net weight of sample by difference to the nearest 0.1 g (Sect. 11.1.2 minus Sect. 11.3.2). This net weight (in grams) is equivalent to the volume (in mL) of water extracted (Sect. 12.4). Alternatively, by using 40-mL bottles precalibrated at 35-mL levels, the gravimetric steps can be omitted, thus increasing the speed and ease of this extraction process.

11.4 IDENTIFICATION OF ANALYTES

11.4.1 Identify a sample component by comparison of its retention time to the retention time of a reference chromatogram. If the retention time of an unknown compound corresponds, within limits, to the retention time of a standard compound, then identification is considered positive.

11.4.2 The width of the retention time window used to make identifications should be based upon 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.

11.4.3 Identification requires expert judgement when sample components are not resolved chromatographically. When peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), or any time doubt exists over the identification of a peak on a chromatogram, appropriate alternative techniques to help confirm peak identification need be employed. For example, more positive identification may be made by the use of an alternative detector which operates on a chemical/physical principle different from that originally used, e.g., mass spectrometry, or the use of a second

chromatography column. Suggested alternative columns are described in Sect. 6.9.

Note: Identify multi-component analytes by comparison of the sample chromatogram to the corresponding calibration standard chromatograms of chlordane, toxaphene and the Aroclors. Identification of multi-component analytes is made by pattern recognition, in which the experience of the analyst is an important factor.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Identify the organohalides in the sample chromatogram by comparing the retention time of the suspect peak to retention times generated by the calibration standards and the laboratory fortified blanks. Identify the multicomponent compounds using all peaks that are characteristic of the specific compound from chromatograms generated with individual standards.

12.2 To quantitate multi-component analytes, one of the following methods should be used.
Option 1- Calculate an average response factor or linear regression equation for each multi-component analyte using the combined area of all the component peaks in each of the calibration standard chromatograms.
Option 2- Calculate an average response factor or linear regression equation for each multi-component analyte using the combined areas of 3-6 of the most intense and reproducible peaks in each of the calibration standard chromatograms.

When quantifying multi-component analytes in samples, the analyst should use caution to include only those peaks from the sample that are attributable to the multi-component analyte. Option 1 should not be used if there are significant interference peaks within the chlordane, Aroclor or toxaphene pattern.

12.3 Use the multi-point calibration curve or calibration factor (Sect. 10.2.3) to directly calculate the uncorrected concentration (Ci) of each analyte in the sample (e.g., calibration factor x response). Do not use the daily calibration standard to quantitate method analytes in samples. If any analyte response exceeds the calibration range, dilute the extract and reanalyze.

12.4 Calculate the sample volume (Vs) as equal to the net sample weight:

Vs = gross weight (Sect. 11.1.2) - bottle tare (Sect. 11.3.2).

12.5 Calculate the corrected sample concentration as:

$$\text{Concentration, } \mu g/L = \frac{35(C_i)}{(V_s)}$$

12.6 Results should be reported with an appropriate number of significant figures. Experience indicates that three significant figures may be used for concentrations above 99 µg/L, two significant figures for concentrations between 1-99 µg/L, and 1 significant figure for lower concentrations.

13. METHOD PERFORMANCE

13.1 Single laboratory (NERL-Cincinnati) accuracy and precision at several concentrations in reagent, ground, and tap water matrices are presented in Table 2. These results were obtained from data generated with a DB-1 column, and with quantitation Option 2 as described in Section 12.2.

13.2 With these data, the method detection limits (MDL) in Table 2 were calculated using the formula:

$$MDL = S\ t_{(n-1,1-alpha\ =\ 0.99)}$$

where:

$t_{(n-1,1-alpha\ =\ 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom
n = number of replicates
S = standard deviation of replicate analyses.

13.3 This method has been tested by 10 laboratories using reagent water and groundwater fortified at three concentration levels. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte and virtually independent of the sample matrix. Linear equations to describe the relationships are presented in Table 3.

14. POLLUTION PREVENTION

14.1 This method utilizes a microextraction procedure that requires the use of very small volumes of hexane, thus making this method safe for use by the laboratory analyst and harmless to the environment. For information concerning pollution prevention that may be applicable to laboratory operations, consult "Less is Better: Laboratory Chemical Management for Waste Reduction" available from the American Chemical Society's Department of Government Relations, and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

15. WASTE MANAGEMENT

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing the waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench

operations. Also, compliance is required with any sewage discharge permits and regulations. For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel," also available from the American Chemical Society at the address in Sect. 14.1.

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17. TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. RETENTION TIMES FOR METHOD ANALYTES

Analyte	Retention Time(a), Min Primary	Confirm. 1	Confirm. 2
Hexachlorocyclopentadiene	5.5	6.8	5.2
Simazine	10.9	25.7	19.9
Atrazine	11.2	22.6	19.6
Hexachlorobenzene	11.9	13.4	15.6
Lindane	12.3	18.4	18.7
Alachlor	15.1	19.7	21.1
Heptachlor	15.9	17.5	20.0
Aldrin	17.6	18.4	21.4
Heptachlor Epoxide	19.0	24.6	24.6
gamma-Chlordane	19.9	25.9	26.0
alpha-Chlordane	20.9	26.6	26.6
trans-Nonachlor	21.3	24.8	26.3
Dieldrin	22.1	45.1	27.8
Endrin	23.2	33.3	29.2
cis-Nonachlor	24.3	39.0	30.4
Methoxychlor	30.0	58.5	36.4

	Primary(b)
Aroclor 1016	13.6, 14.8, 15.2, 16.2, 17.7
Aroclor 1221	7.7, 9.0, 15.9, 19.1, 24.7
Aroclor 1232	11.2, 14.7, 13.6, 15.2, 17.7
Aroclor 1242	11.2, 13.6, 14.7, 15.2, 17.7, 19.8
Aroclor 1248	14.8, 16.2, 17.1, 17.7, 19.8, 22.0
Aroclor 1254	19.1, 21.9, 23.4, 24.9, 26.7
Aroclor 1260	23.4, 24.9, 26.7, 28.2, 29.9, 32.6
Chlordane	15.1, 15.9, 20.1, 20.9, 21.3
Toxaphene	21.7, 22.5, 26.7, 27.2

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[a]. Columns and analytical conditions are described in Sect. 6.9.2, 6.9.3, and 6.9.4.

[b]. Column and conditions described in Sect. 6.9.2. More than one peak listed does not indicate the total number of peaks characteristic of the multi-component analyte. Listed peaks indicate only the ones chosen for summation in the quantification.

TABLE 2. SINGLE LABORATORY ACCURACY, PRECISION AND METHOD DETECTION LIMITS (MDLS) FOR ANALYTES FROM REAGENT WATER, GROUNDWATER, AND TAP WATER[a]

Analyte	MDL µg/L	Concentration* µg/L	Accuracy and Standard Deviation Data: Reagent Water R[c]	Reagent Water S_R[d]	Groundwater R	Groundwater S_R	Tap Water R	Tap Water S_R
Alachlor	0.225	0.50	102	13.4	-	-	-	-
Aldrin	0.007	0.05	106	20.0	86	16.3	-	-
Atrazine	2.4	5.0	85	16.2	95	7.3	108	10.9
		20.0	95	5.2	86	9.1	91	3.1
alpha-Chlordane	0.006	0.06	95	3.5	83	4.4	85	7.1
		0.35	86	17.0	94	10.2	91	2.4
gamma-Chlordane	0.012	0.06	95	0.4	86	5.3	83	14.7
		0.35	86	18.5	95	14.5	91	6.0
Chlordane	0.14	0.17	-	8.0	-	-	105	12.4
		3.4	-	3.6	-	-	95	9.6
Dieldrin	0.012	0.10	87	17.1	67	10.1	92	15.7
		3.6	114	9.1	94	8.6	81	14.0
Endrin	0.063	0.10	119	29.8	94	20.2	106	14.0
		3.6	99	6.5	100	11.3	85	12.4
Heptachlor	0.003	0.032	77	10.2	37	6.8	200	22.6
		1.2	80	7.4	71	9.8	106	16.8
Heptachlor Epoxide	0.004	0.04	100	15.6	90	14.2	112	7.5
		1.4	115	6.6	103	6.9	81	5.9
Hexachlorobenzene	0.002	0.003	104	13.5	91	10.9	100	15.6
		0.09	103	6.6	101	4.4	88	13.4
Hexachlorocyclopentadiene	0.13	0.15	73	5.1	87	5.1	191	18.5
		0.35	73	11.7	69	4.8	109	14.3
Lindane	0.003	0.03	91	6.5	88	7.7	103	8.1
		1.2	111	5.0	109	3.4	93	18.4
Methoxychlor	0.96	2.10	100	21.0	-	-	-	-
		7.03	98	10.9	-	-	-	-
cis-Nonachlor	0.027	0.06	110	15.2	101	7.2	93	14.3
		0.45	82	21.3	93	18.3	87	5.4
trans-Nonachlor	0.011	0.06	95	9.6	83	7.1	73	4.1
		0.35	86	21.8	94	17.2	86	5.1
Simazine	6.8	25	99	8.3	97	9.2	102	13.4
		60	65	3.6	59	18.0	67	
6.2								
Toxaphene	1.0	10	-	-	-	-	110	9.5
		80	-	-	-	-	114	13.5
Aroclor 1016	0.08	1.0	-	-	-	-	97	7.5
Aroclor 1221	15.0	180	-	-	-	-	92	9.6
Aroclor 1232	0.48	3.9	-	-	-	-	86	7.3
Aroclor 1242	0.31	4.7	-	-	-	-	96	7.4
Aroclor 1248	0.102	3.6	-	-	-	-	-	-
		3.4	-	-	-	-	84	9.9
Aroclor 1254	0.102	1.8	-	-	-	-	-	-
		1.7	-	-	-	-	85	11.8
Aroclor 1260	0.189	2.0	-	-	-	-	-	-
		1.8	-	-	-	-	88	19.8

Table 2 (Continued)

[a]Data corrected for amount detected in blank and represents the mean of 5-8 samples.

[b]MDL = method detection limit in sample in μg/L; calculated by multiplying standard deviation (S) times the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.

[c]R = average percent recovery.

[d]S_R = Standard deviation about percent recovery.

* Refers to concentration levels used to generate R and S_R data for the three types of water Matrices, not for MDL determinations.

- No analyses conducted.

TABLE 3. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION-METHOD 505

REAGENT WATER

Parameter	Applicable Conc. Range (μg/L)	Accuracy as Recovery X (μg/L)	Single Analyst Precision S_r (μg/L)	Overall Precision S (μg/L)
Atrazine	(3.06-45.90)	1.122C+0.97	$0.000\bar{x}+1.21$	$0.045\bar{x}+2.23$
Simazine	(12.55-50.20)	0.892C+1.446	$-0.049\bar{x}+3.52$	$0.209\bar{x}+1.23$
Hexachlorobenzene	(0.01-0.37)	1.028C-0.00	$0.108\bar{x}+0.00$	$0.227\bar{x}+0.00$
Lindane	(0.04-1.39)	1.009C-0.00	$0.057\bar{x}+0.01$	$0.142\bar{x}+0.00$
Alachlor	(0.50-37.50)	1.004C-0.08	$0.077\bar{x}+0.10$	$0.105\bar{x}+0.16$
Heptachlor	(0.04-1.41)	1.002C+0.02	$0.107\bar{x}+0.01$	$0.211\bar{x}+0.02$
Aldrin	(0.04-1.42)	1.066C+0.00	$0.031\bar{x}+0.02$	$0.264\bar{x}-0.00$
Heptachlor epoxide	(0.04-1.42)	0.952C+0.00	$0.032\bar{x}+0.02$	$0.129\bar{x}+0.02$
Dieldrin	(0.10-7.53)	1.027C+0.00	$0.091\bar{x}+0.01$	$0.198\bar{x}+0.02$
Endrin	(0.10-7.50)	0.958C+0.01	$0.116\bar{x}+0.01$	$0.136\bar{x}+0.02$
Methoxychlor	(0.20-15.00)	0.950C+0.15	$0.115\bar{x}+0.12$	$0.125\bar{x}+0.20$
Chlordane	(0.51-50.90)	1.037C+0.06	$0.084\bar{x}+0.06$	$0.125\bar{x}+0.19$
Toxaphene	(5.63-70.40)	1.087C+0.24	$0.131\bar{x}-0.31$	$0.269\bar{x}+0.69$
PCB-1016	(0.50-49.80)	0.856C+0.31	$0.106\bar{x}+0.31$	$0.147\bar{x}+0.45$
PCB-1254	(0.50-50.40)	0.872C-0.01	$0.122\bar{x}+0.11$	$0.281\bar{x}+0.05$

* The concentration range applicable to the multi-laboratory study from which the data was generated.

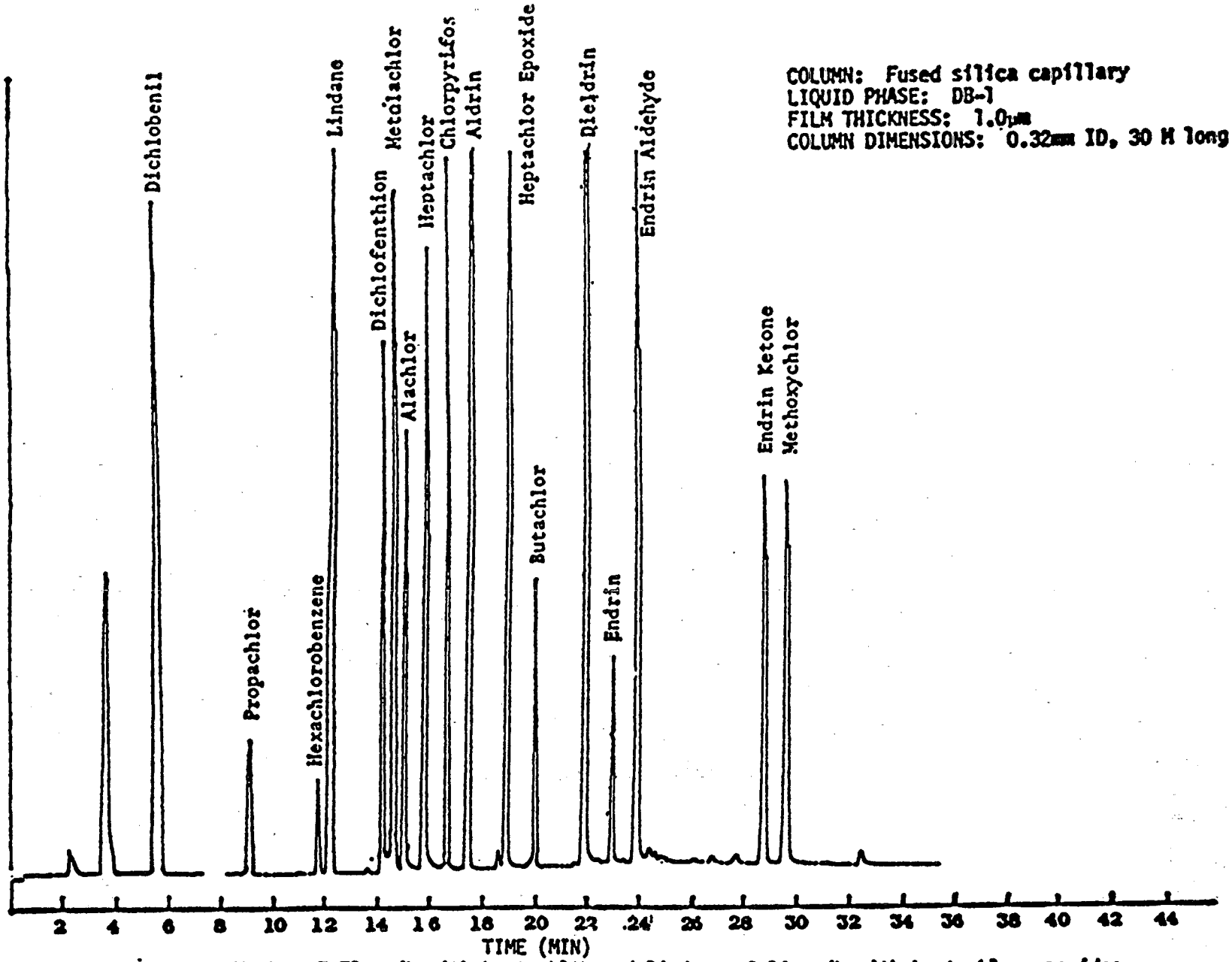

Figure 1. Hexane spiked at 7.71 ug/L with heptachlor and lindane; 9.14 ug/L with heptachlor epoxide; 11.4 ug/L with aldrin and hexachlorobenzene; 23 ug/L with butachlor, chlorpyrifos, chlorpyrifos-methyl, diclobenil, dieldrin, endrin, metolochlor, and propachlor; and 44.9 ug/L with methoxychlor.

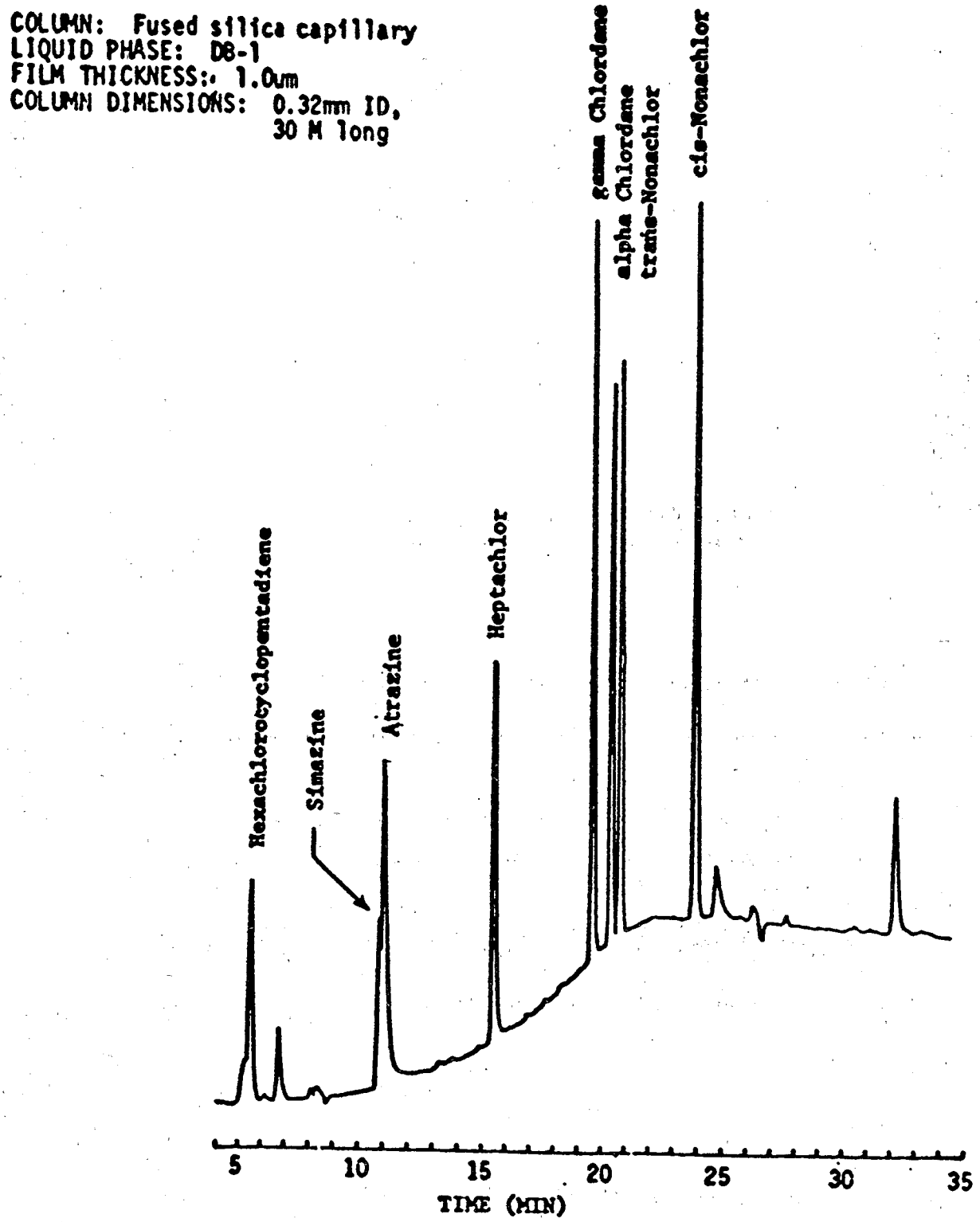

Figure 2. Extract of reagent water spiked at 20 ug/L with atrazine, 60 ug/L with simazine, 0.45 ug/L with cis-nonachlor, and 0.35 ug/L with hexachlorocyclopentadiene, heptachlor, alpha chlordane, gamma chlordane, and trans-nonachlor.

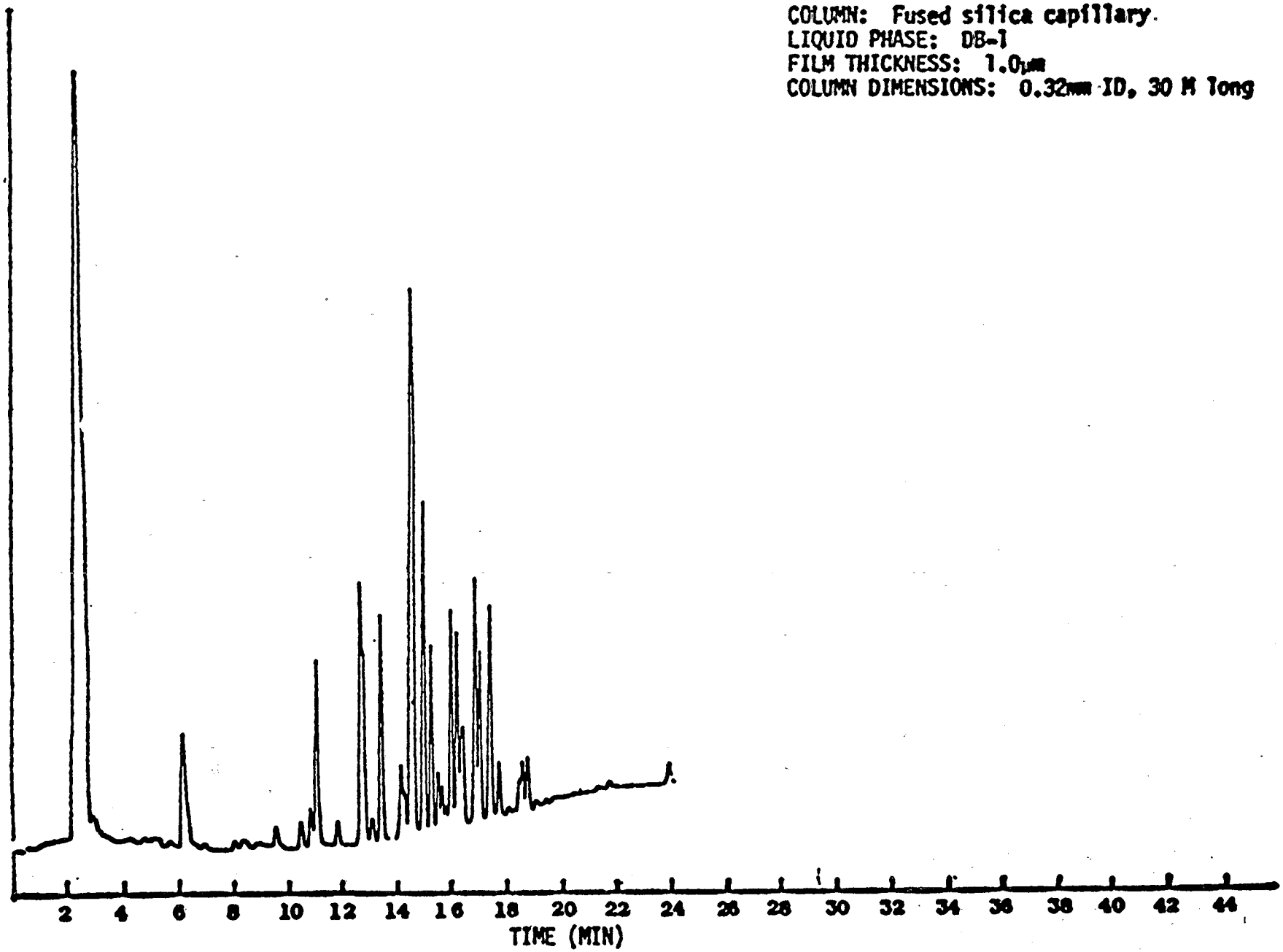

Figure 3. Hexane spiked at 11.4 ug/L with Aroclor 1016.

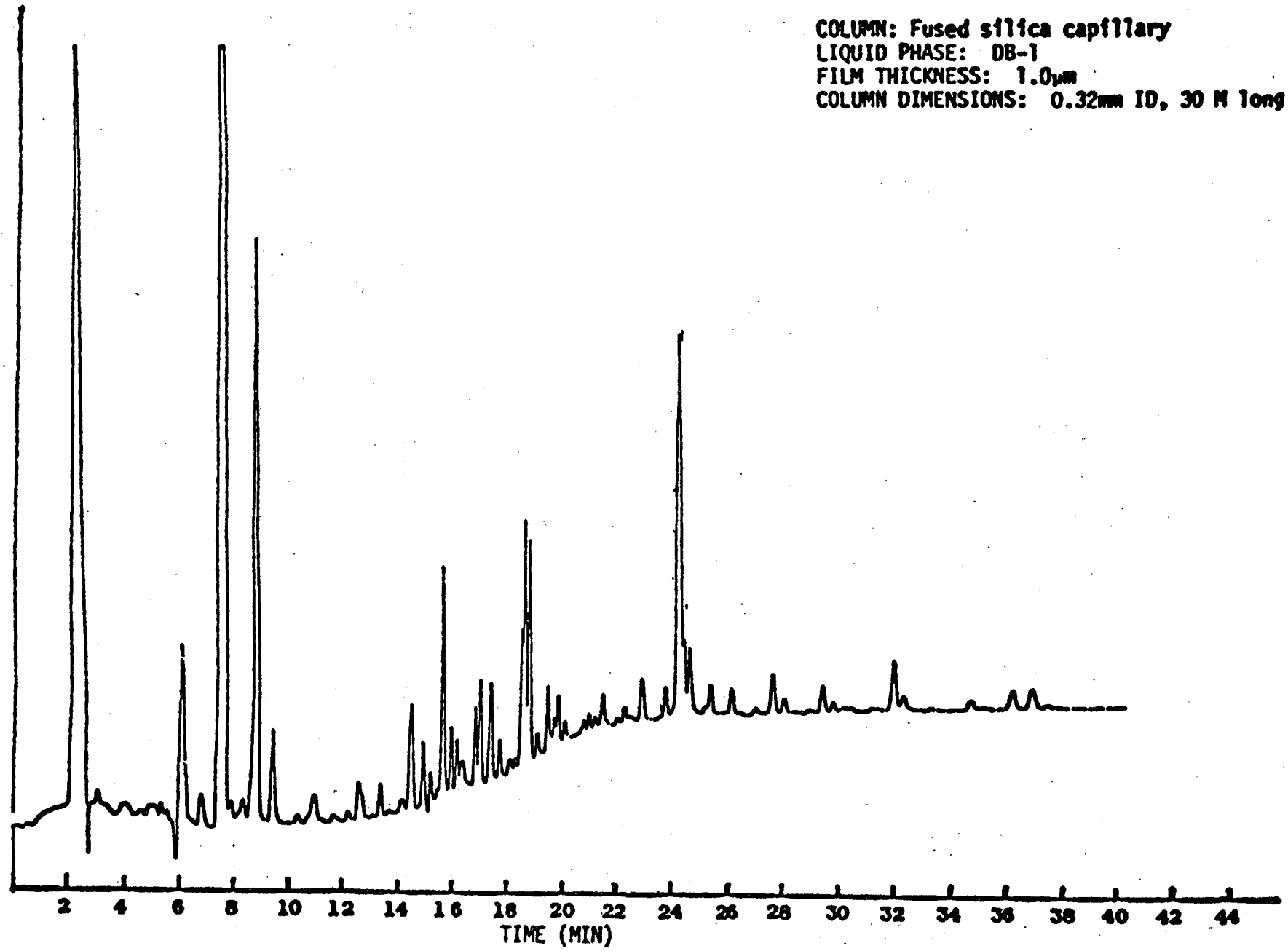

Figure 4. Hexane spiked at 171.4 ug/L with Aroclor 1221.

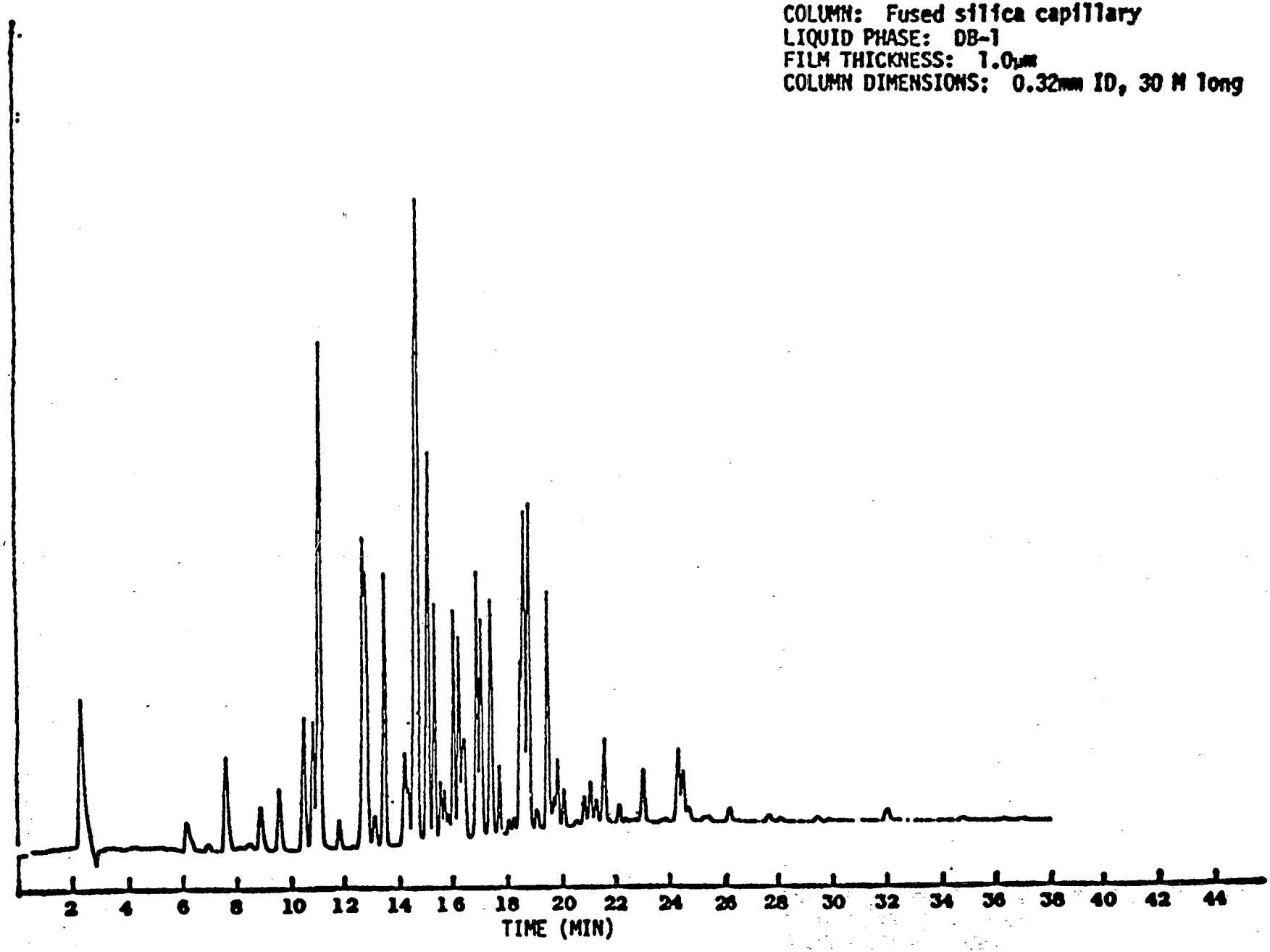

Figure 5. Hexane spiked at 57.1 ug/L with Aroclor 1232.

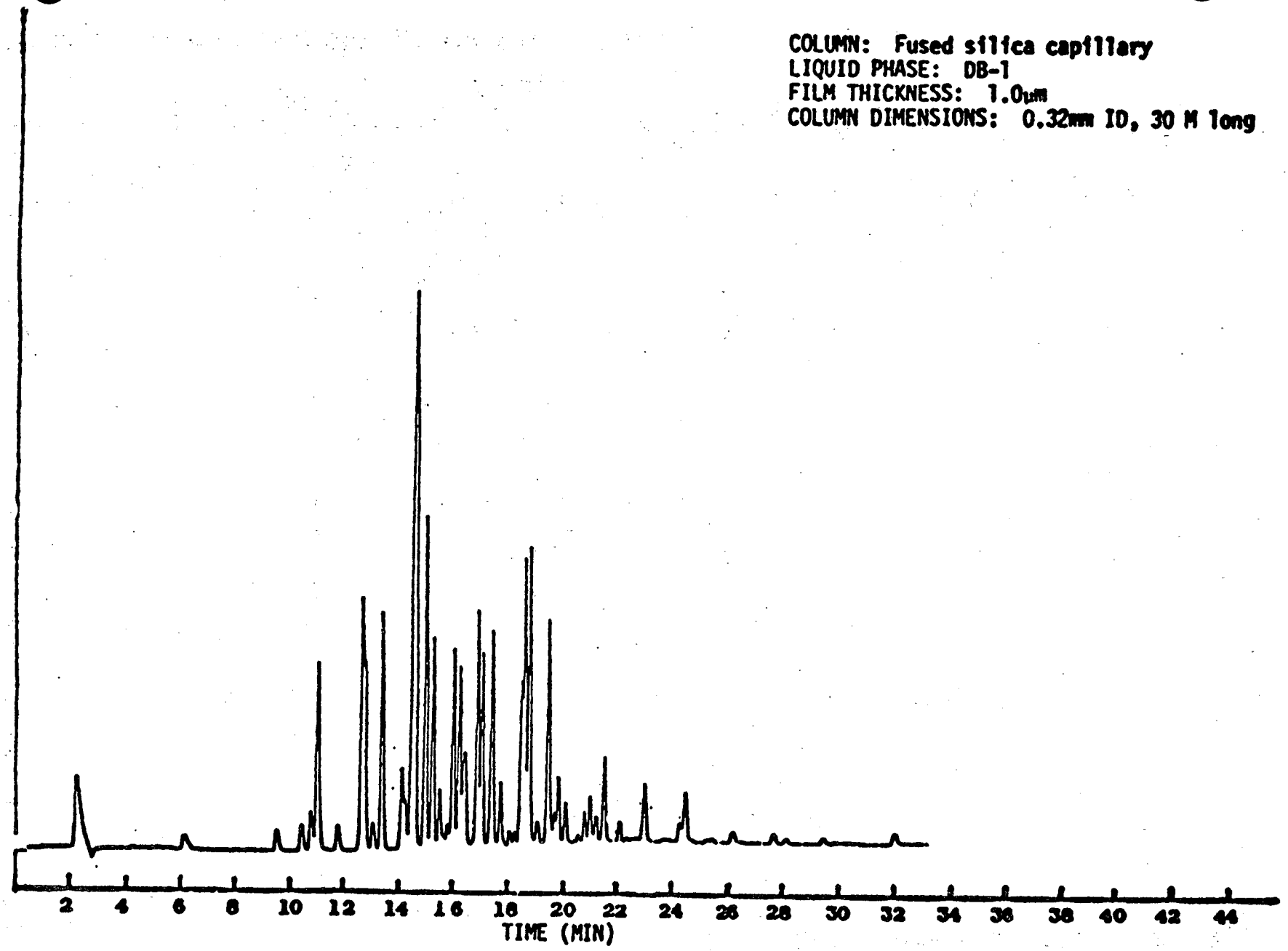

Figure 6. Hexane spiked at 57.1 ug/L with Aroclor 1242.

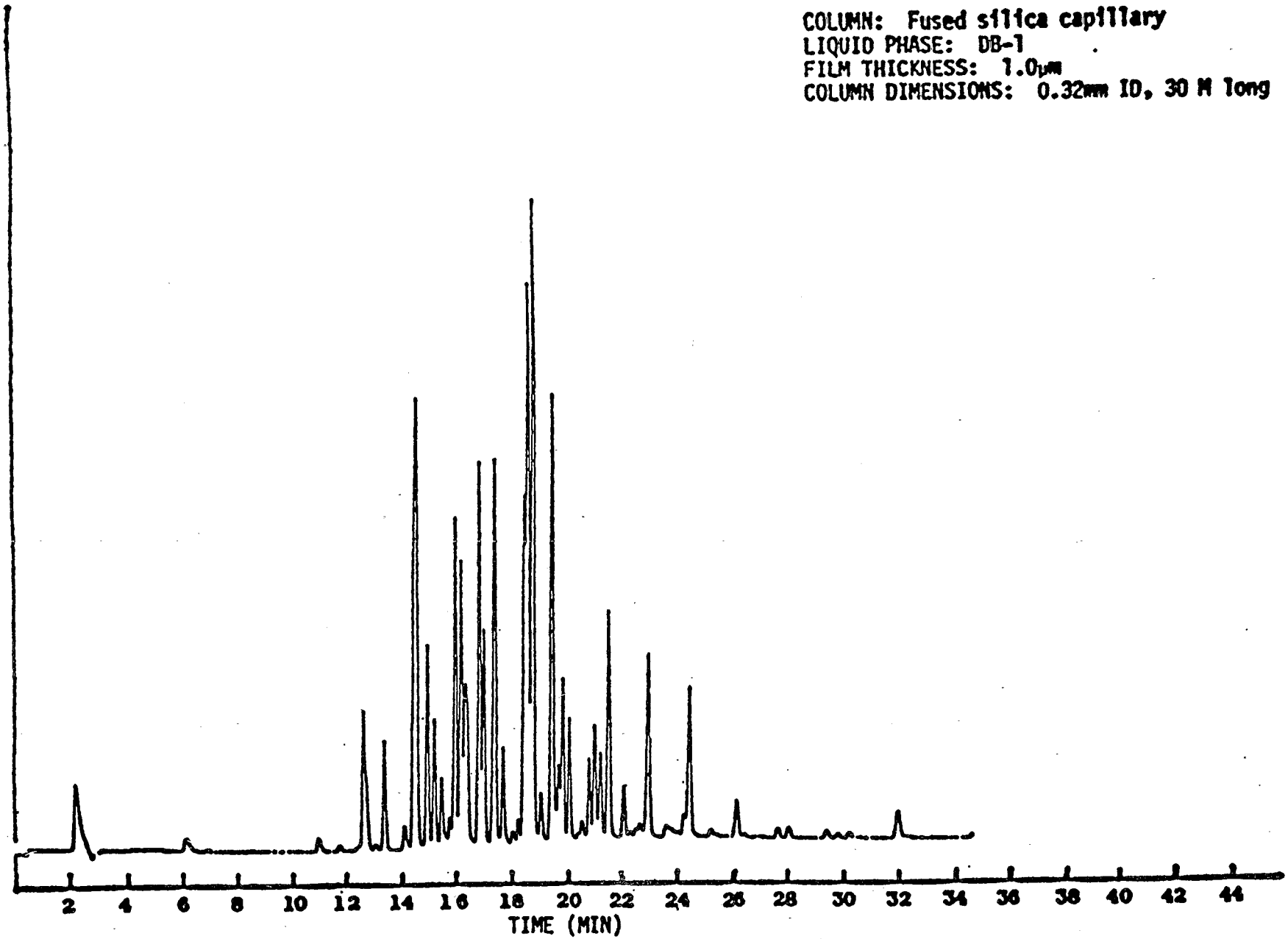

Figure7. Hexane spiked at 57.1 ug/L with Aroclor 1248.

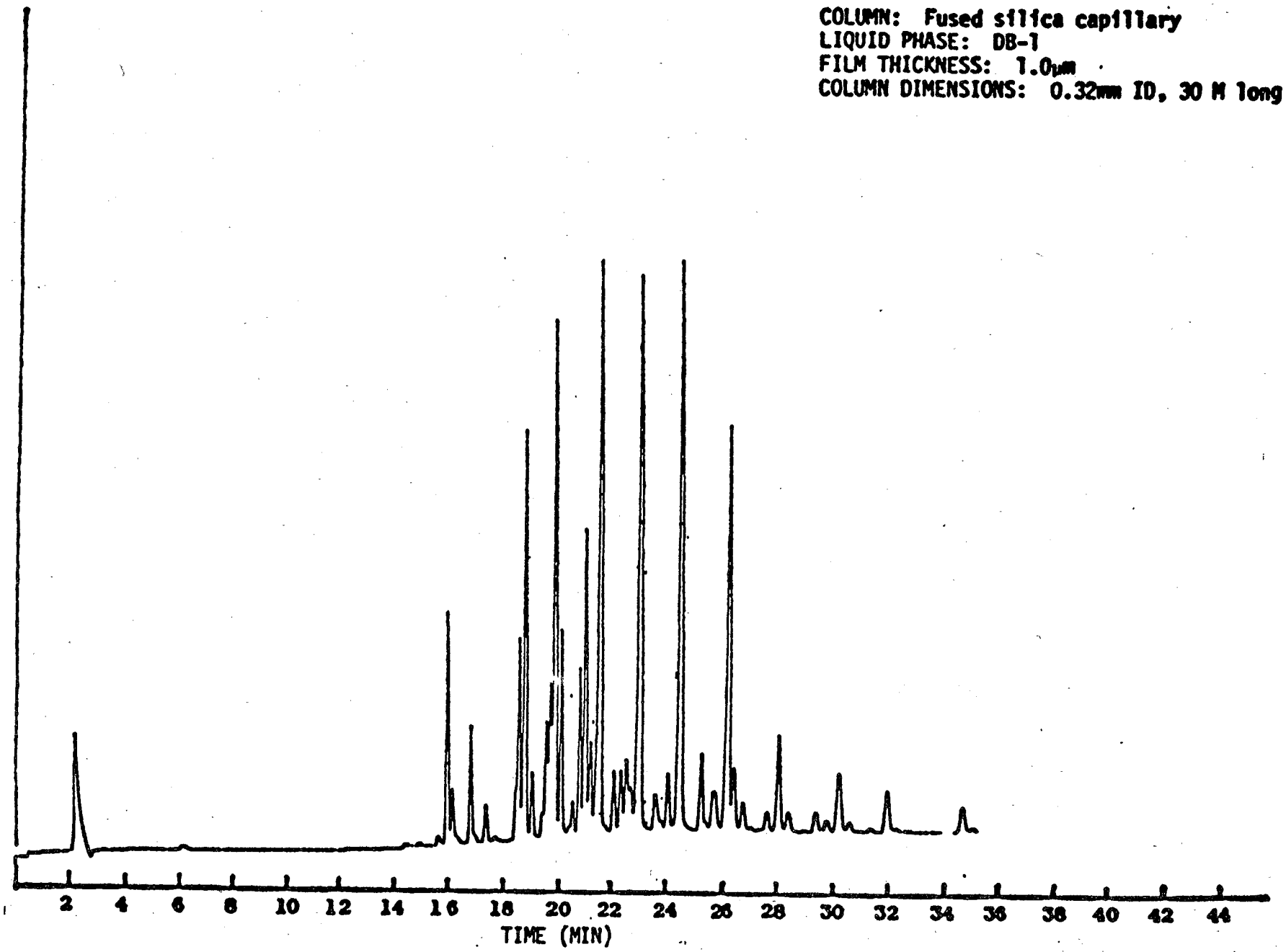

Figure 8. Hexane spiked at 42.9 ug/L with Aroclor 1254.

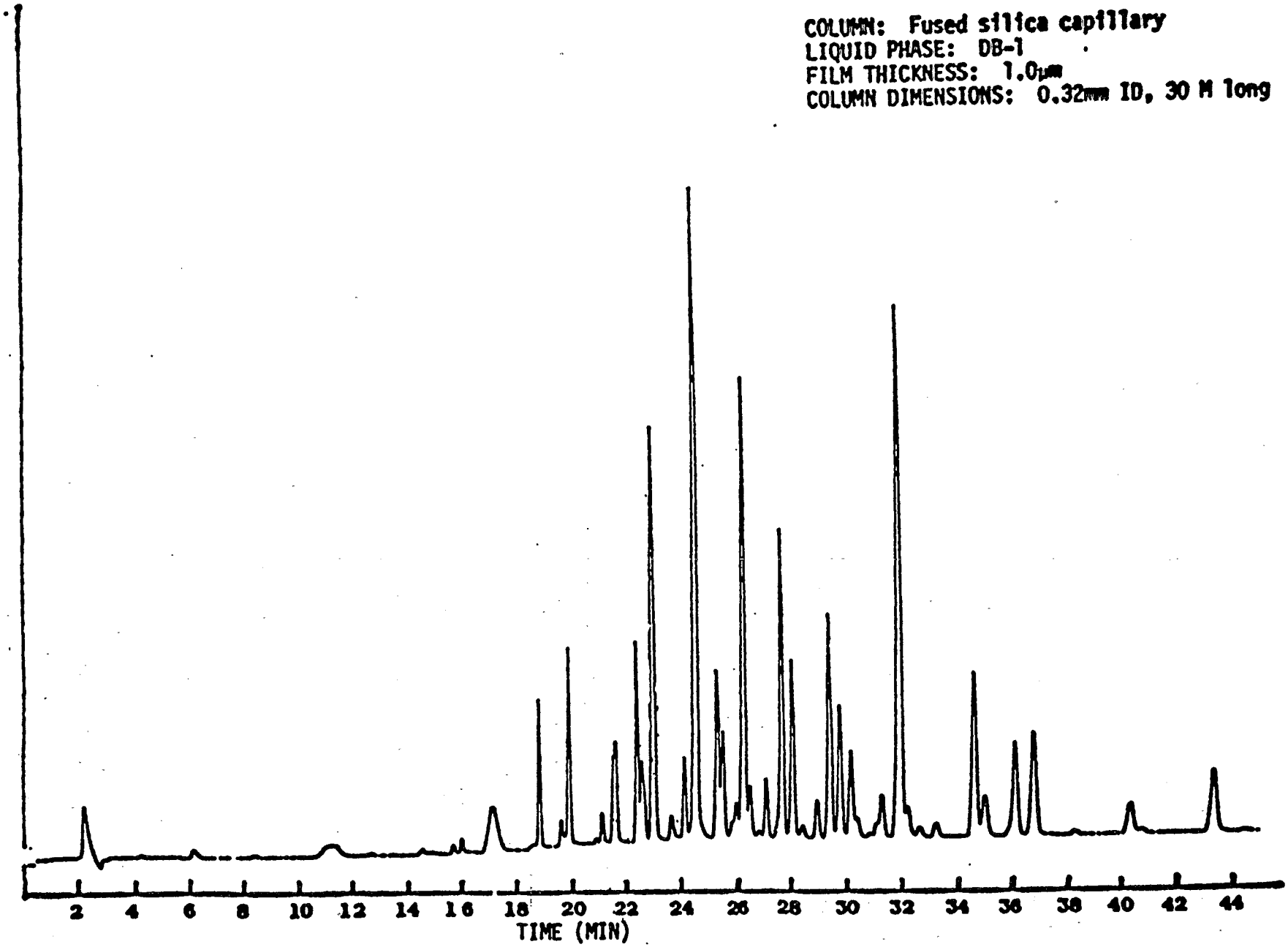

Figure 9. Hexane spiked at 34.3 ug/L with Aroclor 1260.

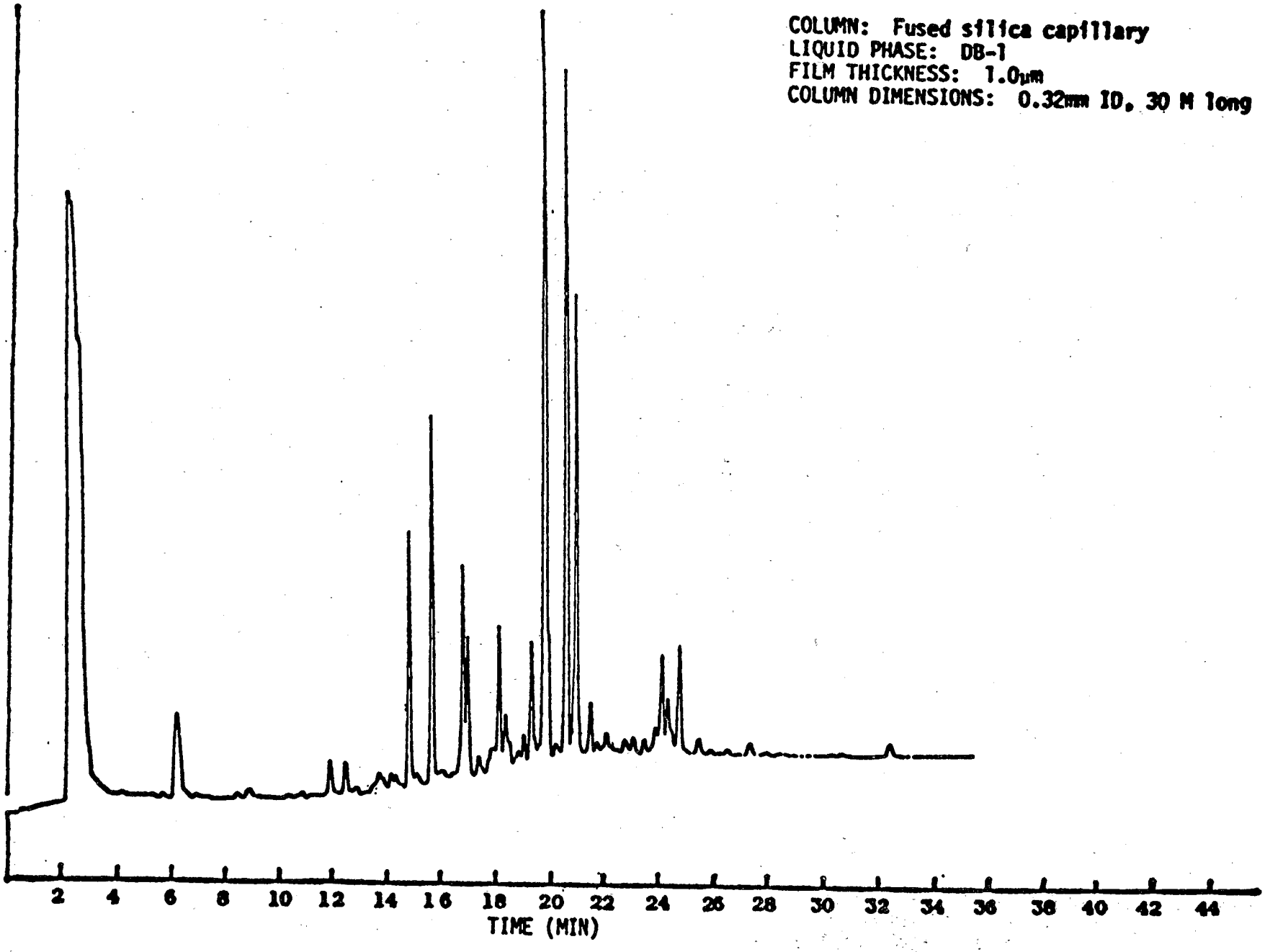

Figure 10. Hexane spiked at 28.6 ug/L with chlordane.

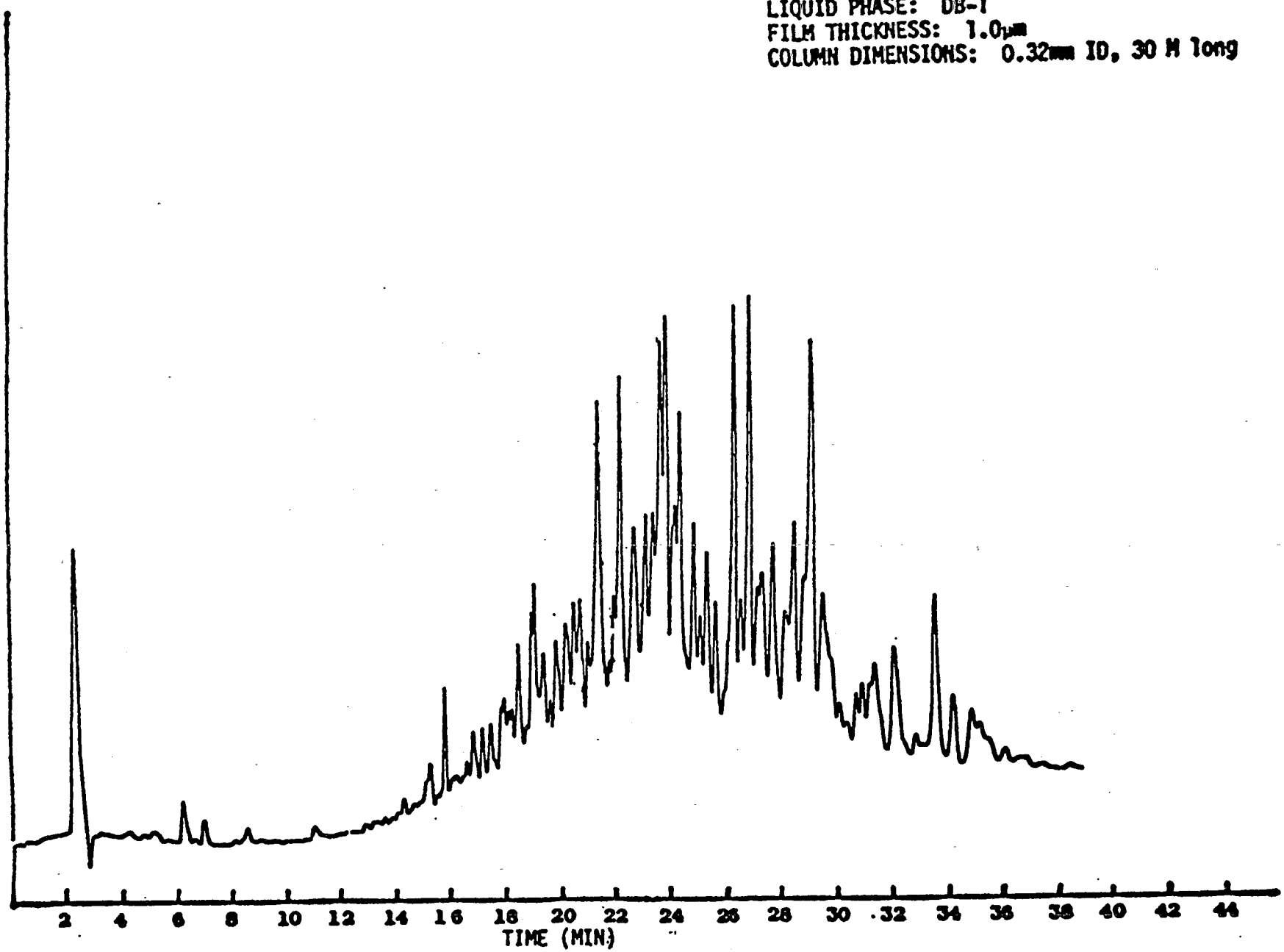

Figure 11. Hexane spiked at 57.1 ug/L with toxaphene.

METHOD 506. Determination of Phthalate and Adipate Esters in Drinking Water by Liquid-Liquid Extraction or Liquid-Solid Extraction and Gas Chromatography with Photoionization Detection

Revision 1.1

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F. K. Kawahara, J. W. Hodgeson - Method 506 Revision 1.0 (1990)

NATIONAL EXPOSURE RESEARCH LABORATORY
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METHOD 506

Determination of Phthalate and Adipate Esters in Drinking Water by Liquid-Liquid Extraction or Liquid-Solid Extraction and Gas Chromatography with Photoionization Detection

1. SCOPE AND APPLICATION

1.1 This method describes a procedure for the determination of certain phthalate and adipate esters in drinking water by liquid/liquid or liquid/solid extraction. The following compounds can be determined by this method:

Analyte	Chemical Abstract Services Registry Number
Bis (2-ethylhexyl) phthalate	117-81-7
Butylbenzyl phthalate	85-68-7
Di-n-butyl phthalate	84-74-2
Diethyl phthalate	84-66-2
Dimethyl phthalate	131-11-3
Bis(2-ethylhexyl) adipate	103-23-1
Di-n-octyl phthalate	117-81-7

1.2 This is a capillary column gas chromatographic (GC) method applicable to the determination of the compounds listed above in ground water and finished drinking water. When this method is used to analyze unfamiliar samples for any or all of the compounds listed above, compound identifications should be supported by at least one additional qualitative technique. Method 525.2 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for all the analytes listed above, using the extract produced by this method.

1.3 This method has been validated in a single laboratory, and method detection limits (MDLs) (1) have been determined for the analytes above (Table 2). Observed detection limits may vary among waters, depending upon the nature of interferences in the sample matrix and the specific instrumentation used.

1.4 This method is restricted to use by or under the supervision of analysts experienced in the use of GC, and in the interpretation of gas chromatograms obtained by a computerized system. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Sect. 10.

2. SUMMARY OF METHOD

2.1 A measured volume of sample, approximately 1-L, is extracted with methylene chloride followed by hexane using a glass separatory funnel. The solvent extract is isolated, dried and concentrated to

a volume of 5 mL or less. The extract is further concentrated by using a gentle stream of nitrogen gas to reduce the sample volume to 1 mL or less.

Alternatively, a measured volume of sample is extracted with a liquid-solid extraction (LSE) cartridge or disk. The LSE media are eluted with acetonitrile followed by methylene chloride (disk extraction) or with methylene chloride only (cartridge extraction). The eluant is concentrated using a gentle stream of nitrogen gas or clean air to reduce the volume to 1 mL or less.

The analytes in the extract are separated by means of capillary gas chromatography using temperature programming. The chromatographically separated phthalate and adipate esters are measured with a photoionization detector, which is operating at 10 eV.

3. DEFINITIONS

3.1 LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.2 FIELD REAGENT BLANK (FRB) -- Reagent water placed in a sample container in the laboratory and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.3 LABORATORY FORTIFIED BLANK (LFB) -- An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

3.4 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.5 STOCK STANDARD SOLUTION -- A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a single analyte prepared in the laboratory

with an assayed reference compound. Stock standard solutions are used to prepare primary dilution standards.

3.6 PRIMARY DILUTION STANDARD SOLUTION -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.7 CALIBRATION STANDARD (CAL) -- a solution prepared from the primary dilution standard solution and stock standard solutions of the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.8 QUALITY CONTROL SAMPLE (QCS) -- a sample matrix containing method analytes or a solution of method analytes in a water miscible solvent which is used to fortify reagent water or environmental samples. The QCS is obtained from a source external to the laboratory, and is used to check laboratory performance with externally prepared test materials.

4. INTERFERENCES

4.1 Method interferences may be caused by contaminants in water, solvents, reagents, glassware, and sample processing hardware. These lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks (Sect. 10.2).

4.1.1 Phthalate esters are contaminants in many products found in the laboratory. It is particularly important to avoid the use of plastics because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Great care must be exercised to prevent contamination. Exhaustive clean up of reagents and glassware must be required to eliminate background phthalate that is not derived from the sample.

4.1.2 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used. Follow by washing with hot water and detergent and thorough rinsing with tap and reagent water. Drain dry and heat in an oven or muffle furnace at 400°C for 1 hour. Do not heat volumetric glassware. Thorough rinsing with acetone may be substituted for the heating. After cooling, the glassware should be sealed with aluminum foil and stored in a clean environment to prevent accumulation of dust and other contaminants.

4.1.3 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in an all glass system may be required. WARNING: When a solvent is purified, stabilizers added by the manufacturer are removed thus potentially making the solvent hazardous. Also, when a solvent is purified, preservatives added by the manufacturer are removed thus potentially reducing the shelf-life.

4.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary from source to source, dependent upon the nature and diversity of the samples. Clean up procedures can be used to overcome many of these interferences.

4.3 It is important that samples and working standards be contained in the same solvent. The solvent for working standards must be the same as the final solvent used in sample preparation. If this is not the case, chromatographic comparability of standards to sample may be affected.

5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound must be treated as a potential health hazard. Accordingly, exposure to these chemicals must be reduced to the lowest possible level. 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 also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified (5-7) for the information of the analyst.

6. EQUIPMENT AND SUPPLIES (All specifications are suggested, catalog numbers are included for illustration only.)

6.1 Sampling Equipment

6.1.1 Grab Sample Bottle--1-L or 1-qt amber glass, fitted with a screw cap lined with Teflon. Protect samples from light if amber bottles are not available. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride and dried before use in order to minimize contamination. (See 4.1.1.)

6.2 Glassware

6.2.1 Separatory Funnel--2-L with Teflon stopcock.

6.2.2 Drying Column--Chromatographic column-300 mm long x 10 mm ID, with Teflon stopcock and coarse frit filter disc at bottom.

6.2.3 Concentrator Tube--Kuderna-Danish, 10 mL, graduated, calibration must be checked at the volumes employed in the test. Tight ground glass stopper is used to prevent evaporation of extracts.

6.2.4 Evaporative Flask--Kuderna-Danish, 500 mL, attach to concentrator tube with springs.

6.2.5 Snyder Column--Kuderna-Danish, three-ball macro size.

6.2.6 Snyder Column--Kuderna-Danish, 2 or 3 ball micro size.

6.2.7 Vials--10 to 15 mL, amber glass with Teflon-lined screw cap.

6.2.8 Boiling Chips--Approximately 10/40 mesh. Heat to 400°C for 30 min. or extract with methylene chloride in a Soxhlet apparatus.

6.2.9 Flask, Erlenmeyer--250 mL.

6.2.10 Chromatography column similar to 6.2.2.

6.2.11 Pasteur Pipets (and Bulb).

6.2.12 Autosampler Vials--Equipped with Teflon-lined septum and threaded or crimp top caps.

6.3 Water Bath--Heated (with concentric ring covers) capable of temperature control (± 2°C). The water bath should be used in a ventilating hood.

6.4 Balance--Analytical, capable of weighing accurately to nearest 0.0001 gm.

6.5 Gas Chromatograph--An analytical system complete with temperature programmable GC fitted with split-splitless injection mode system, suitable for use with capillary columns and all required accessory syringes, analytical columns, gases, detector and stripchart recorder. A data system for processing chromatographic data is recommended.

6.5.1 Column, Fused Silica Capillary--DB-5 or equivalent, 30 m long x 0.32 mm ID with a film thickness of 0.25 micron.

6.5.2 The alternate column, Fused Silica Capillary--30 m long x 0.32 mm ID with a film thickness of 0.25 micron, DB-1 or equivalent.

6.5.3 Detector -- A high temperature photoionization detector equipped for 10 electron volts (nominal voltage) and capable of operating from 250°C to 350°C is required.

6.5.4 An automatic injector system is suggested, but was not used for the development of this method.

6.6 Vacuum source, capable of maintaining a vacuum of 10-15 mm Hg.

7. REAGENTS AND STANDARDS

7.1 Reagent Water -- Reagent water is defined as water in which an interfering substance is not observed at the MDL of the parameters of interest. Reagent water used to generate data in this method was distilled water obtained from the Millipore L/A-7044 system comprised of prefiltration, organic adsorption, deionization and Millipore filtration columnar units. Any system may be used if it generates acceptable reagent water.

7.2 Acetone, hexane, methylene chloride, ethyl acetate, ethyl ether and iso-octane -- Pesticide quality or equivalent to distillation in glass quality.

7.3 Sodium Sulfate--(ACS) Granular, anhydrous. Several levels of purification may be required in order to reduce background phthalate levels towards acceptance: 1) Heat 4 h at 400°C in a shallow tray, 2) Soxhlet extract with methylene chloride for 48 h.

7.4 Florisil--PR grade (60/100 mesh). To prepare for use, place 100 g of Florisil into a 500-mL beaker and heat for approximately 16 h at 40°C. After heating transfer to a 500-mL reagent bottle. Tightly seal and cool to room temperature. When cool, add 3 mL of reagent water. Mix thoroughly by shaking or rolling for 10 min. and let it stand for at least 2 h. Store in the dark in glass containers with ground glass stoppers or foil-lined screw caps.

7.5 Sodium Chloride--(ACS) Granular. Heat 4 h at 400°C in a shallow tray. When cool, keep in tightly sealed glass (not plastic) bottle. This cleaning step is <u>required</u> to minimize background contamination associated with this reagent.

7.6 Ethyl Ether--(ACS) reagent grade.

7.7 Sodium Thiosulfate ($Na_2S_2O_3$)--(ACS) reagent grade.

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

7.9 Liquid-solid extraction (LSE) cartridges. Cartridges are inert non-leaching plastic, for example polypropylene, or glass, and must not contain plasticizers, such as phthalate esters or adipates, that leach into methylene chloride. The cartridges are packed with about 1 gram of silica, or other inert inorganic support, whose surface is modified by chemically bonded octadecyl (C_{18}) groups. The packing must have a narrow size distribution and must not leach organic compounds into methylene chloride. One liter of water should pass through the cartridge in about 2 hrs with the assistance of a slight vacuum of about 13 cm (5 in.) of mercury. The extraction time should not vary unreasonably among LSE cartridges.

7.10 Liquid-solid extraction disks, C-18, 47 mm. Disks are manufactured with Teflon or other inert support and should contain very little contamination.

7.11 Helium carrier gas, as contaminant free as possible.

7.12 Stock standard solutions (1.00 μg/μL) - Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

7.12.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in isooctane 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 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.

7.12.2 Transfer the stock standard solutions into Teflon-sealed 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.

7.12.3 Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem. Butylbenzyl phthalate is especially vulnerable to autoxidation.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Grab samples must be collected in amber glass containers (Sect.6.1). Conventional sampling practices should be followed (8,9); however, the bottle must not be prerinsed with sample before collection.

8.2 SAMPLE PRESERVATION AND STORAGE

8.2.1 For sample dechlorination, add 80 mg sodium thiosulfate to the sample bottle at the sampling site or in the laboratory before shipping to the sampling site.

8.2.2 After the sample is collected, seal the bottle and swirl the sample until the thiosulfate is dissolved.

8.2.3 The samples must be iced or refrigerated at 4°C free from light from the time of collection until extraction. Limited holding studies have indicated that the analytes thus stored are stable up to 14 days or longer. Analyte stability may be affected by the matrix; therefore, the analyst should verify that the preservation technique is applicable to the particular samples under study.

8.3 Extract Storage -- Extracts should be stored at 4°C in absence of light. A 14-day maximum extract storage time is recommended. The analyst should verify appropriate extract holding times applicable to the samples under study.

9. QUALITY CONTROL

9.1 Minimum quality control (QC) requirements are initial demonstration of laboratory capability, analysis of laboratory reagent blanks, laboratory fortified samples, laboratory fortified blanks, and QC samples. A MDL for each analyte must also be determined. Additional quality control practices are recommended.

9.2 Laboratory Reagent Blanks (LRB) Before processing any samples, the analyst must demonstrate that all glassware and reagent interferences are under control. Each time a set of samples is extracted or reagents are changed, a LRB must be analyzed. If within the retention time window of any analyte of interest the LRB produces a peak that would prevent the determination of that analyte using a known standard, determine the source of contamination and eliminate the interference before processing samples.

9.3 Initial Demonstration of Capability.

9.3.1 Select a representative fortified concentration (about 10 times EDL or at a concentration in the middle of the calibration range established in Section 10) for each analyte. Prepare a primary dilution standard (in methanol) containing each analyte at 1000 times selected concentration. With a syringe, add 1 mL of the concentrate to each of four to seven 1-L aliquots of reagent water, and analyze each aliquot according to procedures beginning in Sect. 11.

9.3.2 For each analyte the mean recovery value for these samples must fall in the range of R ± 30% using the values for R for reagent water in Tables 3 or 4. The precision of these measurements, expressed as RSD, must be 20% or less. For

those compounds that meet the acceptance criteria, performance is considered acceptable. For those compounds that fail these criteria, this procedure must be repeated using fresh replicate samples until satisfactory performance has been demonstrated.

9.3.3 For each analyte, determine the MDL. Prepare a minimum of 7 LFBs at a low concentration. Fortification concentration in Table 2 may be used as a guide, or use calibration data obtained in Section 10 to estimate a concentration for each analyte that will produce a peak with a 3-5 times signal to noise response. Extract and analyze each replicate according to Sections 11 and 12. It is recommended that these LFBs be prepared and analyzed over a period of several days, so that day to day variations are reflected in precision measurements. Calculate mean recovery and standard deviation for each analyte. Use the standard deviation and the equation given in Section 13 to calculate the MDL.

9.3.4 The initial demonstration of capability is used primarily to preclude a laboratory from analyzing unknown samples via a new, unfamiliar method prior to obtaining some experience with it. It is expected that as laboratory personnel gain experience with this method the quality of data will improve beyond those required here.

9.4 The analyst is permitted to modify GC columns, GC conditions, concentration techniques (i.e. evaporation techniques), internal standards or surrogate compounds. Each time such method modifications are made, the analyst must repeat the procedures in Sect. 9.3.

9.5 Assessing Laboratory Performance - Laboratory Fortified Blank

9.5.1 The laboratory must analyze at least one laboratory fortified blank (LFB) sample with every twenty samples or one per sample set (all samples extracted within a 24-h period) whichever is greater. Ideally, the fortified concentration of each analyte in the LFB should be the same concentration selected in Section 9.3.1. Calculate accuracy as percent recovery (X_i). If the recovery of any analyte falls outside the control limits (see Sect. 9.5.2), that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

9.5.2 Until sufficient data become available from within their own laboratory, usually a minimum of results from 20 to 30 analyses, the laboratory should assess laboratory performance against the control limits in Sect. 9.3.2 that are derived from the data in Table 2. When sufficient internal performance data becomes available, develop control limits from the mean percent recovery (X) and standard deviation (S)

of the percent recovery. These data are used to establish upper and lower control limits as follows:

UPPER CONTROL LIMIT = X + 3S
LOWER CONTROL LIMIT = X - 3S

After each five to ten new recovery measurements, new control limits should be calculated using only the most recent 20-30 data points. These calculated control limits should <u>not</u> exceed those established in Sect. 9.3.2.

9.6 Assessing Analyte Recovery -- Laboratory Fortified Sample Matrix

9.6.1 The laboratory must fortify each analyte to a minimum of 10% of the routine samples or one fortified sample per set, whichever is greater. The fortified concentration should not be less than the background concentration of the sample selected for fortifying. Ideally, this concentration should be the same as that used for the laboratory fortified blank (Sect. 9.5). Over time, samples from all routine sample sources should be fortified.

9.6.2 Calculate the accuracy as percent recovery, R, for each analyte, corrected for background concentrations measured in the unfortified sample. For each analyte the mean recovery value for these samples must fall in the range of R ± 35% using the values for R for reagent water in Tables 3 or 4.

9.6.3 If the recovery of any such analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control (Sect. 9.5), the recovery problem encountered with the dosed sample is judged to be matrix related, not system related. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

9.7 QUALITY CONTROL SAMPLES (QCS) - Each quarter, the laboratory should analyze one or more QCS (if available). If criteria provided with the QCS are not met, corrective action should be taken and documented.

9.8 The laboratory may adopt additional quality control 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. For example, field or laboratory duplicates may be analyzed to assess the precision of the environmental measurements.

10. <u>CALIBRATION AND STANDARDIZATION</u>

10.1 Establish gas chromatograph operating conditions equivalent to those given in Table 1. The gas chromatographic system is calibrated

using the external standard technique. Calibration standards must be prepared in the same solvent as the final sample extract. This will vary with the extraction option chosen (hexane for LLE, methylene chloride for LSE-cartridge, and acetonitrile for LSE-disk). Sect. 10.2.1 details the hexane option as an example.

10.2 External standard calibration procedure:

10.2.1 Prepare calibration standards at a minimum of three concentration levels for each analyte of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with n-hexane. Guidance on the number of standards is as follows: A minimum of three calibration standards are required to calibrate a range of a factor of 20 in concentration. For a factor of 50 use at least four standards, and for a factor of 100 at least five standards. One calibration standard should contain each analyte of concern at a concentration 2 to 10 times greater than the method detection limit for that compound. The other calibration standards should contain each analyte of concern at concentrations that define the range of the sample analyte concentrations or should define the working range of the detector.

10.2.2 Using injections of 1 to 2 μL, analyze each calibration standard according to Sect. 11.5 and tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to amount injected (calibration factor) is a constant over the working range (<20% relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

10.2.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of a minimum of two calibration check standards, one at the beginning and one at the end of the analysis day. These check standards should be at two different concentration levels to verify the calibration curve. For extended periods of analysis (greater than 8 hrs.), it is strongly recommended that check standards be interspersed with samples at regular intervals during the course of the analyses. If the response for any analyte varies from the predicted response by more than ±20%, the test must be repeated using a fresh calibration standard. If the results still do not agree, generate a new calibration curve. For those analytes that failed the calibration verification, results from field samples analyzed since the last passing calibration should be considered suspect. Reanalyze sample extracts for these analytes after acceptable calibration is restored.

11. PROCEDURE

11.1 LIQUID-LIQUID EXTRACTION

11.1.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-L separatory funnel containing 50 g of NaCl.

11.1.2 Add 60 ml CH_2Cl_2 to the sample bottle. Seal, and shake gently to rinse the inner walls of the bottle. Transfer the solvent to the separatory funnel. Extract the sample by shaking the funnel for 2 min with initial and periodic venting to release excess pressure. Allow the organic layer to separate for a minimum of 10 min from the water phase. 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 technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the solvent extract in a 250-mL Erlenmeyer flask.

11.1.3 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Then extract with 40-mL of hexane, which extract (top phase) is added to the total.

11.1.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D concentrator, provided the concentration factor attained in 11.1.6 - 11.1.8 is achieved without loss of analytes.

11.1.5 Pour the combined extract through a drying column (6.2.2) containing about 10 cm of prerinsed anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

11.1.6 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60 to 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 with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 40 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 approximately 7 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

11.1.7 Increase the temperature of the hot water bath to about 85°C. Remove the Snyder column, rinse the column and the 500-mL evaporative flask with 1 - 2 mL of hexane. Replace with a micro column and evaporative flask. Concentrate the extract as in Sect. 11.1.6 to 0.5 - 1 mL. The elapsed time of concentration should be approximately 15 min.

11.1.8 Remove the micro Snyder column and rinse the column by flushing with hexane using a 5-mL syringe. Concentrate to a volume of 1 ml by purging the liquid surface with a gentle flow of nitrogen or clean air. If an autosampler is to be used, transfer the extract to an autosampler vial with a Pasteur pipet. Seal the vial with a threaded or crimp top cap. Store in refrigerator if further processing will not be performed. If the sample extract requires no further cleanup, proceed with gas chromatographic analysis (Sect. 11.5). If the sample requires further cleanup, proceed to Sect. 11.4.

11.1.9 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11.2 LIQUID-SOLID EXTRACTION - CARTRIDGE OPTION

11.2.1 This method is applicable to a wide range of organic compounds that are efficiently partitioned from the water sample onto a C_{18} organic phase chemically bonded to a solid inorganic matrix, and are sufficiently volatile and thermally stable for gas chromatography (10). See Section 11.3 for the disk option procedure. Particulate bound organic matter will not be partitioned, and more than trace levels of particulates in the water may disrupt the partitioning process. Single laboratory accuracy and precision data have been determined at a single concentration for the analytes listed in Sect. 1.1 fortified into reagent water and raw source water.

11.2.2 Set up the extraction apparatus shown in Figure 1A. An automated extraction system may also be used. The reservoir is not required, but recommended for convenient operation. Water drains from the reservoir through the LSE cartridge and into a syringe needle which is inserted through a rubber stopper into the suction flask. A slight vacuum of 13 cm (5 in.) of mercury is used during all operations with the apparatus. With this extraction apparatus, sample elution requires approximately 2 hours. Acceptable new cartridge and

extraction disk technology have recently become available, which allow significantly faster elution rates.

11.2.3 Mark the water meniscus on the side of the sample bottle (approximately 1 liter) for later determination of sample volume. Pour the water sample into the 2-L separatory funnel with the stopcock closed.

11.2.4 Flush each cartridge with two 10 mL aliquots of methylene chloride, followed by two 10 mL aliquots of methanol, letting the cartridge drain dry after each flush. These solvent flushes may be accomplished by adding the solvents directly to the solvent reservoir in Figure 1A. Add 10-mL of reagent water to the solvent reservoir, but before the reagent water level drops below the top edge of the packing in the LSE cartridge, open the stopcock of the separatory funnel and begin adding sample water to the solvent reservoir. Close the stopcock when an adequate amount of sample is in the reservoir.

11.2.5 Periodically open the stopcock and drain a portion of the sample water into the solvent reservoir. The water sample will drain into the cartridge, and from the exit into the suction flask. Maintain the packing material in the cartridge immersed in water at all times. After all of the sample has passed through the LSE cartridge, wash the separatory funnel and cartridge with 10 mL of reagent water, and draw air through the cartridge for about 10 min.

11.2.6 Transfer the 125-mL solvent reservoir and LSE cartridge (from Figure 1A) to the elution apparatus (Figure 1B). The same 125 mL solvent reservoir is used for both apparatus. Wash the 2-liter separatory funnel with 5 mL of methylene chloride and collect the washings. Close the stopcock on the 100-mL separatory funnel of the elution apparatus, add the washings to the reservoir and enough additional methylene chloride to bring the volume back up to 5 mL and elute the LSE cartridge. Elute the LSE cartridge with an additional 5 mL of methylene chloride (10-mL total). A small amount of nitrogen positive pressure may be used to elute the cartridge. Small amounts of residual water from the LSE cartridge will form an immiscible layer with the methylene chloride in the 100-mL separatory funnel. Open the stopcock and allow the methylene chloride to pass through the drying column packed with anhydrous sodium sulfate (1-in) and into the collection vial. Do not allow the water layer to enter the drying column. Remove the 100 mL separatory funnel and wash the drying column with 2 mL of methylene chloride. Add this to the extract. Concentrate the extract to 1 mL under a gentle stream of nitrogen. The extract is now ready for gas chromatography (Sect. 11.4) or additional cleanup (Sect. 11.3).

11.3 LIQUID-SOLID EXTRACTION - DISK OPTION

11.3.1 Preparation of disks.

11.3.1.1 Insert the disk into the 47 mm filter apparatus. Wash the disk with 5 mL methylene chloride ($MeCl_2$) by adding the $MeCl_2$ to the disk, pulling about half through the disk and allowing it to soak the disk for about a minute, then pulling the remaining $MeCl_2$ through the disk. With the vacuum on, pull air through the disk for a minute.

11.3.1.2 Pre-wet the disk with 5 mL methanol (MeOH) by adding the MeOH to the disk, pulling about half through the disk and allowing it to soak for about a minute, then pulling most of the remaining MeOH through. A layer of MeOH must be left on the surface of the disk, which shouldn't be allowed to go dry from this point until the end of the sample extraction. THIS IS A CRITICAL STEP FOR A UNIFORM FLOW AND GOOD RECOVERY.

11.3.1.3 Rinse the disk with 5 mL reagent water by adding the water to the disk and pulling most through, again leaving a layer on the surface of the disk.

11.3.2 Add 5 mL MeOH per liter of water sample. Mix well.

11.3.3 Add the water sample to the reservoir and turn on the vacuum to begin the filtration. Full aspirator vacuum may be used. Particulate-free water may filter in as little as 10 minutes or less. Filter the entire sample, draining as much water from the sample container as possible.

11.3.4 Remove the filtration top from the vacuum flask, but don't disassemble the reservoir and fritted base. Empty the water from the flask and insert a suitable sample tube to contain the eluant. The only constraint on the sample tube is that it fit around the drip tip of the fritted base. Reassemble the apparatus.

Add 5 mL of acetonitrile (CH_3CN) to rinse the sample bottle. Allow the CH_3CN to settle to the bottom of the bottle and transfer to the disk with a dispo-pipet, rinsing the sides of the glass filtration reservoir in the process. Pull about half of the CH_3CN through the disk, release the vacuum, and allow the disk to soak for a minute. Pull the remaining CH_3CN through the disk.

Repeat the above step twice, using $MeCl_2$ instead of CH_3CN. Pour the combined eluates thru a small funnel with filter paper containing 3 grams of anhydrous sodium sulfate. Rinse

the test tube and sodium sulfate with two 5 mL portions of $MeCl_2$. Collect the filtrate in a concentrator tube.

11.3.5 With the concentrator tube in a 28°C heating block, evaporate the eluate with a stream of N_2 to 0.5 mL.

11.4 EXTRACT CLEANUP - Cleanup procedures may not be necessary for a relatively clean sample matrix, such as most drinking waters. If particular circumstances demand the use of a cleanup procedure, the analyst may use either procedure below or any other appropriate procedure. However, the analyst first must demonstrate that the requirements of Sect. 9 can be met using the method as revised to incorporate the cleanup procedure.

11.4.1 Florisil column cleanup for phthalate esters:

11.4.1.1 Place 10 g of Florisil (see 7.4) into a chromatographic column. Tap the column to settle the Florisil and add 1 cm of anhydrous sodium sulfate to the top.

11.4.1.2 Preelute the column with 40 mL of hexane. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the sample extract (11.1.8 or 11.2.6) onto the column, using an additional 2 mL of hexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 40 mL of hexane and continue the elution of the column. Discard this hexane eluate.

11.4.1.3 Next, elute the column with 100 mL of 20% ethyl ether in hexane (V/V) into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Elute the column at a rate of about 2 mL/min for all fractions. Concentrate the collected fraction as in Section 11.1. No solvent exchange is necessary. Adjust the volume of the cleaned extract to 1 mL in the concentrator tube and analyze by gas chromatography.

11.4.2 Alumina column cleanup for phthalate esters:

11.4.2.1 Place 10 g of alumina into a chromatographic column. Tap the column to settle the alumina and add 1 cm of anhydrous sodium sulfate to the top.

11.4.2.2 Preelute the column with 40 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer

the sample extract (Sect. 11.1.8 or 11.2.6) onto the column, using an additional 2 mL of hexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 35 mL of hexane and continue the elution of the column. Discard this hexane eluate.

11.4.2.3 Next, elute the column with 140 mL of 20% ethyl ether in hexane (V/V) into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Concentrate the collected fraction as in Section 11.1. No solvent exchange is necessary. Adjust the volume of the cleaned extract to 1 mL in the concentrator tube and analyze by gas chromatography.

11.5 GAS CHROMATOGRAPHY

11.5.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included are retention data for the primary and confirmation columns. Other capillary columns, chromatographic conditions may be used if the requirements of Section 9 are met.

11.5.2 Calibrate the system daily as described in Sect. 10.

11.5.3 Inject 1 to 2 µL of the sample extract or standard into the gas chromatograph. Smaller (1.0 µL) volumes may be injected if automatic devices are employed. For optimum reproducibility, an autoinjector is recommended.

11.5.4 Identify the analytes in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.5.5 If the response for a peak exceeds the working range of the system, dilute the extract and reanalyze.

11.5.6 If the measurement of the peak response is prevented by the presence of interferences, further cleanup is required.

11.5.7 The calibration curves should be linear over the range of concentrations in Tables 2-5. Do not extrapolate beyond the calibration range established in Section 10. If analyte response is too high, dilute the extract and reanalyze.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Calculate the amount of material injected from the peak response using the multi-point calibration curve or calibration factor determined in Section 10.2.2. Do not use the daily calibration verification standard to quantitate method analytes in samples. The concentration in the sample can be calculated from Equation 2.

Equation 2.

$$\text{Concentration } (\mu g/L) = \frac{(A)(V_t)}{(V_i)(V_s)}$$

where:

A = Amount of material injected (ng).
V_i = Volume of extract injected (μL).
V_t = Volume of total extract (μL).
V_s = Volume of water extracted (mL).

12.2 Report results in μg/L without correction for recovery data. All QC data obtained should be reported with the sample results.

13. METHOD PERFORMANCE

13.1 Single laboratory accuracy and precision data were obtained by replicate liquid-liquid extraction analyses of reagent water fortified at two sets of concentrations of method analytes. The data are given in Tables 2 and 3. Accuracy and precision data by liquid-solid extraction of reagent water fortified at a single concentration are given in Table 4. Finally, Method validation data obtained by the analyses of fortified tap water and raw source water are given in Tables 5-7.

13.2 Demonstrated MDLs are given in Table 2. To calculate MDLs, the following equations were used:

$$MDL = S\ t_{(n-1,1-alpha\ =\ 0.99)}$$

where:

$t_{(n-1,1-alpha\ =\ 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom

n = number of replicates

S = standard deviation of replicate analyses.

14. POLLUTION PREVENTION

14.1 One option of this method utilizes the new liquid-solid extraction (LSE) technology to remove the analytes from water. It requires the

use of very small volumes of organic solvent and very small quantities of pure analytes, thereby eliminating the potential hazards to both the analyst and the environment. The other option in this method uses significant volumes of organic solvents. It is highly recommended that laboratories use solvent recovery systems to recover used solvent as sample extracts are being concentrated. Recovered solvents should be recycled or properly disposed of.

14.2 For information about pollution prevention that may be applicable to laboratory operations, consult "Less Is Better: Laboratory Chemical Management for Waste Reduction" available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C., 20036.

15. WASTE MANAGEMENT

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions. The laboratory using this method has the responsibility to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations. For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel," also available from the American Chemical Society at the address in Sect. 14.2.

16. REFERENCES

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17. TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. RETENTION DATA AND CHROMATOGRAPHIC CONDITIONS

Parameter	Retention Time (min)	
	Column 1	Column 2
Dimethyl phthalate	17.23	17.89
Diethyl phthalate	20.29	21.13
Di-n-butyl phthalate	27.57	28.67
Butylbenzyl phthalate	34.19	35.34
Bis(2-ethylhexyl) adipate	34.85	36.76
Bis(2-ethylhexyl) phthalate	37.51	39.58
Di-n-octyl phthalate	41.77	44.44

Column 1: DB-5, fused silica capillary, 30 m x 0.32 mm I.D., 0.25 micron film thickness, Helium linear velocity = 30 cm/s.

Column 2: DB-1, fused silica capillary, 30 m x 0.32 mm I.D., 0.25 micron film thickness, Helium linear velocity = 30 cm/s.

Chromatographic Conditions: Injector temperature = 295°C
Detector temperature = 295°C
Program - 1 min hold at 60°C, 6°C/min to 260°C, 10 min hold.
Splitless injection with 45 s delay

TABLE 2. ACCURACY, PRECISION, AND METHOD DETECTION LIMIT DATA FROM SIX LIQUID-LIQUID EXTRACTION ANALYSES OF FORTIFIED REAGENT WATER

Analyte	True Conc. µg/L	Mean Meas. Conc. µg/L	Std. Dev. µg/L	Mean Accuracy % of True Conc.	MDL µg/L
Dimethyl phthalate	2.02	1.42	0.38	70.3	1.14
Diethyl phthalate	1.51	1.16	0.28	76.8	0.84
Di-n-butyl phthalate	2.62	1.78	0.41	67.9	1.23
Butyl benzyl phthalate	6.00	3.27	0.89	54.5	2.67
Bis(2-ethylhexyl) adipate	6.03	3.94	1.44	65.3	11.82
Bis(2-ethylhexyl) phthalate	5.62	2.92	0.75	52.0	2.25
Di-n-octyl phthalate	17.18	7.96	2.14	46.3	6.42

TABLE 3. ACCURACY AND PRECISION DATA FROM SEVEN LIQUID-LIQUID EXTRACTION ANALYSES OF FORTIFIED REAGENT WATER

Analyte	True Concentration µg/L	Mean Accuracy % of True Concentration	Relative Standard Deviation %
Dimethyl phthalate	15	73	16
Diethyl phthalate	15	71	16
Di-n-butyl phthalate	15	68	15
Butyl benzyl phthalate	15	71	15
Bis(2-ethylhexyl) adipate	30	69	18
Bis(2-ethylhexyl) phthalate	30	67	21
Di-n-octyl phthalate	30	62	23

TABLE 4. ACCURACY AND PRECISION DATA FROM SIX LIQUID-SOLID EXTRACTION ANALYSES OF FORTIFIED REAGENT WATER

Analyte	True Concentration µg/L	Mean Accuracy % of True Concentration	Relative Standard Deviation %
Dimethyl phthalate	15	74	11
Diethyl phthalate	15	85	10
Di-n-butyl phthalate	15	74	11
Butyl benzyl phthalate	15	72	14
Bis(2-ethylhexyl) adipate	30	84	11
Bis(2-ethylhexyl) phthalate	30	101	13
Di-n-octyl phthalate	30	85	13

TABLE 5. ACCURACY AND PRECISION DATA FROM SIX LIQUID-LIQUID EXTRACTION ANALYSES OF FORTIFIED TAP WATER

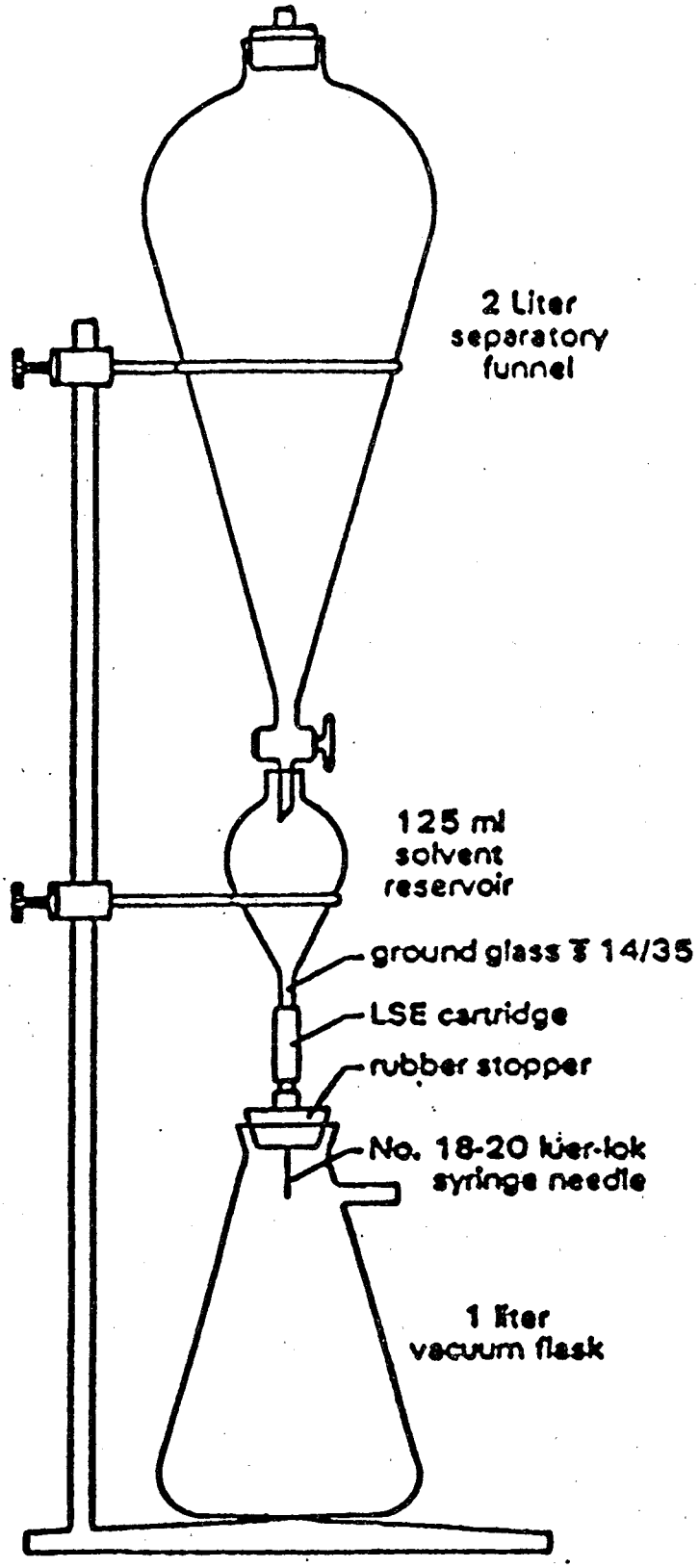
Analyte	True Concentration µg/L	Mean Accuracy % of True Concentration	Relative Standard Deviation %
Dimethyl phthalate	5	103	10.0
Diethyl phthalate	5	106	10.0
Di-n-butyl phthalate	5	94	6.8
Butyl benzyl phthalate	5	93	9.1
Bis(2-ethylhexyl) adipate	5	87	12.0
Bis(2-ethylhexyl) phthalate	5	93	4.9
Di-n-octyl phthalate	5	72	26.0

TABLE 6. ACCURACY AND PRECISION DATA FROM SIX LIQUID-LIQUID EXTRACTION ANALYSES OF FORTIFIED RAW SOURCE WATER

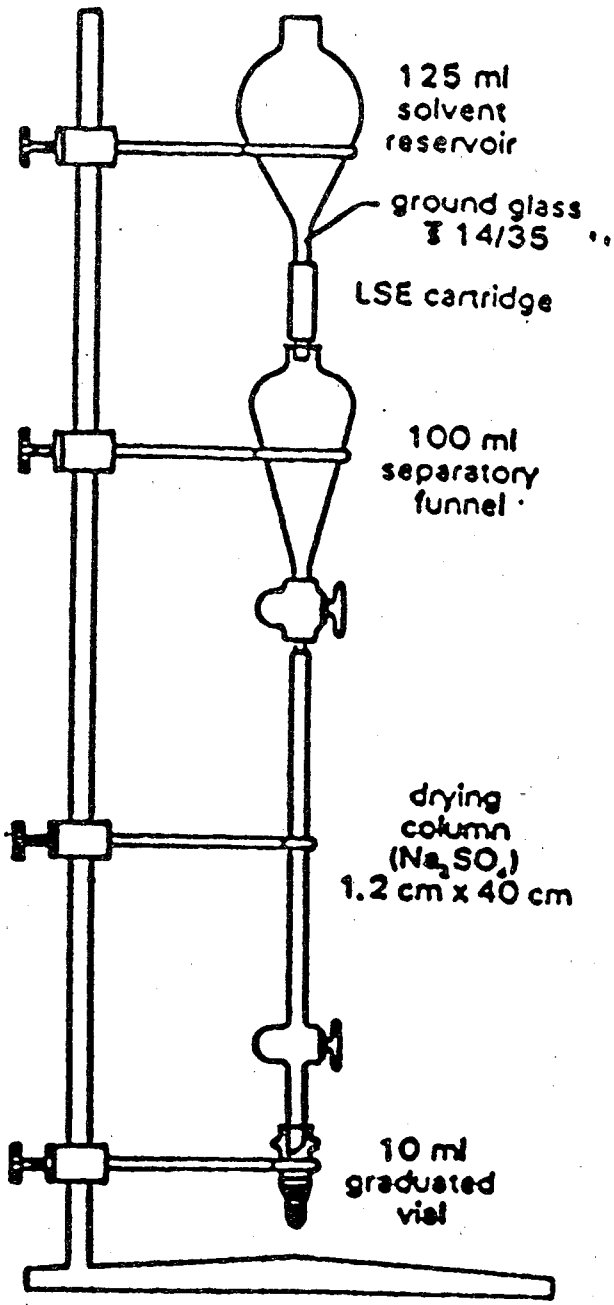
Analyte	True Concentration µg/L	Mean Accuracy % of True Concentration	Relative Standard Deviation %
Dimethyl phthalate	5	59	51
Diethyl phthalate	5	78	45
Di-n-butyl phthalate	5	99	29
Butyl benzyl phthalate	5	72	23
Bis(2-ethylhexyl) adipate	5	115	32
Bis(2-ethylhexyl) phthalate	5	91	35
Di-n-octyl phthalate	5	54	24

TABLE 7. ACCURACY AND PRECISION DATA FROM SIX LIQUID-SOLID EXTRACTION ANALYSES OF FORTIFIED RAW SOURCE WATER

Analyte	True Concentration µg/L	Mean Accuracy % of True Concentration	Relative Standard Deviation %
Dimethyl phthalate	5	110	20
Diethyl phthalate	5	111	32
Di-n-butyl phthalate	5	95	30
Butyl benzyl phthalate	5	82	20
Bis(2-ethylhexyl) adipate	5	65	24
Bis(2-ethylhexyl) phthalate	5	60	21
Di-n-octyl phthalate	5	53	15

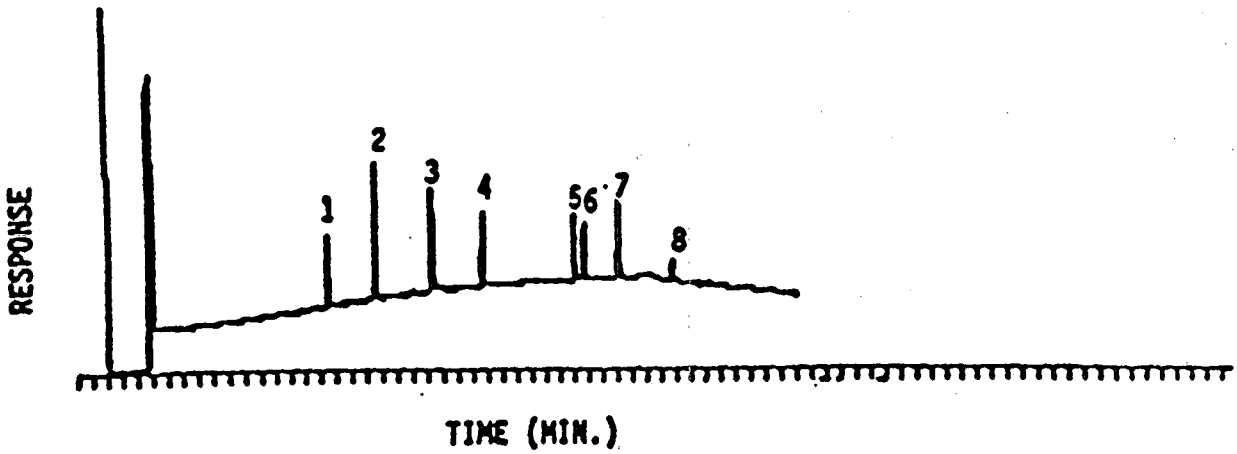


A. Extraction apparatus



B. Elution apparatus

FIGURE 1



Peaks obtained by injecting 5 ng for the 1st, 2nd, 4th and 5th compounds, 10 ng for the 6th, 7th and 8th compounds, and 2.5 ng for the 3rd compound. (Table 1)

FIGURE 2

METHOD 507. DETERMINATION OF NITROGEN- AND PHOSPHORUS-CONTAINING PESTICIDES IN WATER BY GAS CHROMATOGRAPHY WITH A NITROGEN-PHOSPHORUS DETECTOR

Revision 2.1

Edited by J.W. Munch (1995)

T. Engel (Battelle Columbus Laboratories) and D. Munch (U.S. EPA, Office of Water), National Pesticide Survey Method 1, Revision 1.0 (1987)

R. L. Graves - Method 507, Revision 2.0 (1989)

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METHOD 507

DETERMINATION OF NITROGEN-AND PHOSPHORUS-CONTAINING PESTICIDES IN WATER BY GAS CHROMATOGRAPHY WITH A NITROGEN-PHOSPHORUS DETECTOR

1. SCOPE AND APPLICATION

1.1 This is a gas chromatographic (GC) method applicable to the determination of certain nitrogen- and phosphorus-containing pesticides in ground water and finished drinking water. The following compounds can be determined using this method:

Analyte	Chemical Abstract Services Registry Number
Alachlor	15972-60-8
Ametryn	834-12-8
Atraton	1610-17-9
Atrazine	1912-24-9
Bromacil	314-40-9
Butachlor	23184-66-9
Butylate	2008-41-5
Carboxin	5234-68-5
Chlorpropham	101-21-3
Cycloate	1134-23-2
Diazinon(a)*	333-41-5
Dichlorvos	62-73-7
Diphenamid	957-51-7
Disulfoton*	298-04-4
Disulfoton sulfone*	2497-06-5
Disulfoton sulfoxide(a)*	2497-07-6
EPTC	759-94-4
Ethoprop	13194-48-4
Fenamiphos	22224-92-6
Fenarimol	60168-88-9
Fluridone	59756-60-4
Hexazinone	51235-04-2
Merphos*	150-50-5
Methyl paraoxon	950-35-6
Metolachlor	51218-45-2
Metribuzin	21087-64-9
Mevinphos	7786-34-7
MGK 264	113-48-4
Molinate	2212-67-1
Napropamide	15299-99-7
Norflurazon	27314-13-2
Pebulate	1114-71-2
Prometon	1610-18-0
Prometryn	7287-19-6
Pronamide(a)*	23950-58-5
Propazine	139-40-2
Simazine	122-34-9
Simetryn	1014-70-6
Stirofos	22248-79-9
Tebuthiuron	34014-18-1

Terbacil	5902-51-2
Terbufos(a)*	13071-79-9
Terbutryn	886-50-0
Triademefon	43121-43-3
Tricyclazole	41814-78-2
Vernolate	1929-77-7

(a) Compound exhibits aqueous instability. Samples for which this compound is an analyte of interest must be extracted immediately (Sections 11.1 through 11.3).

* These compounds are only qualitatively identified. These compounds are not quantitated because control over precision has not been accomplished.

1.2 This method has been validated in a single laboratory and estimated detection limits (EDLs) and method detection limits (MDLs) have been determined for the analytes above (Sect. 13). Observed detection limits may vary among waters, depending upon the nature of interferences in the sample matrix and the specific instrumentation used.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of GC 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 Sect. 9.

1.4 Analytes that are not separated chromatographically, i.e., analytes which have very similar retention times, cannot be individually identified and measured in the same calibration mixture or water sample unless an alternative technique for identification and quantitation exist (Section 11.5).

1.5 When this method is used to analyze unfamiliar samples for any or all of the analytes above, analyte identifications should be confirmed by at least one additional qualitative technique.

2. SUMMARY OF METHOD

2.1 A measured volume of sample of approximately 1 L is extracted with methylene chloride by shaking in a separatory funnel or mechanical tumbling in a bottle. The methylene chloride extract is isolated, dried and concentrated to a volume of 5 mL during a solvent exchange to methyl tert-butyl ether (MTBE). Chromatographic conditions are described which permit the separation and measurement of the analytes in the extract by Capillary Column GC with a nitrogen-phosphorus detector (NPD).

3. DEFINITIONS

3.1 INTERNAL STANDARD -- A pure analyte(s) added to a solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same solution. The internal standard must be an analyte that is not a sample component.

3.2 SURROGATE ANALYTE -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction and is measured with the same procedures used to measure other sample components. The purpose of a surrogate analyte is to monitor method performance with each sample.

3.3 LABORATORY DUPLICATES (LD1 and LD2) -- Two sample aliquots taken in the analytical laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.4 FIELD DUPLICATES (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.5 LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.6 FIELD REAGENT BLANK (FRB) -- Reagent water placed in a sample container in the laboratory and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.7 LABORATORY PERFORMANCE CHECK SOLUTION (LPC) -- A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.8 LABORATORY FORTIFIED BLANK (LFB) -- An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

3.9 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.10 STOCK STANDARD SOLUTION -- A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a single analyte prepared in the laboratory with an assayed reference compound. Stock standard solutions are used to prepare primary dilution standards.

3.11 PRIMARY DILUTION STANDARD SOLUTION -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.12 CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution and stock standard solutions of the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.13 QUALITY CONTROL SAMPLE (QCS) -- A sample matrix containing method analytes or a solution of method analytes in a water miscible solvent which is used to fortify reagent water or environmental samples. The QCS is obtained from a source external to the laboratory, and is used to check laboratory performance with externally prepared test materials.

4. INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or elevated baselines in gas chromatograms. All reagents and apparatus must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Sect. 9.2.

4.1.1 Glassware must be scrupulously cleaned (1). Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot water and detergent and thorough rinsing with tap and reagent water. Drain dry, and heat in an oven or muffle furnace at 400°C for 1 hour. Do not heat volumetric ware. Thermally stable materials might not be eliminated by this treatment. Thorough rinsing with acetone may be substituted for the heating. After drying and cooling, seal and store glassware in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

4.1.2 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. WARNING: When a solvent is purified, stabilizers added by the manufacturer may be removed thus potentially making the solvent hazardous. Also, when a solvent is purified, preservatives added by the manufacturer are removed thus potentially reducing the shelf-life.

4.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. Between-sample rinsing of the sample syringe and associated equipment with MTBE can minimize sample cross contamination. After analysis of a sample containing high concentrations of analytes, one or more injections of MTBE should be made to ensure that accurate values are obtained for the next sample.

4.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. Also, note that all the analytes listed in the scope and application section are not resolved from each other on any one column, i.e., one analyte of interest may be an interferant for another analyte of interest. The extent of matrix interferences will vary considerably from source to source, depending upon the water sampled. Further processing of sample extracts may be necessary. Positive identifications should be confirmed (Sect. 11.5).

4.4 It is important that samples and working standards be contained in the same solvent. The solvent for working standards must be the same as the final solvent used in sample preparation. If this is not the case, chromatographic comparability of standards to sample may be affected.

5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound must be treated as a potential health hazard. Accordingly, exposure to these chemicals must be reduced to the lowest possible level. 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 also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified (2-4) for the information of the analyst.

5.2 WARNING: When a solvent is purified, stabilizers added by the manufacturer may be removed thus potentially making the solvent hazardous.

6. EQUIPMENT AND SUPPLIES (All specifications are suggested. Catalog numbers are included for illustration only.)

6.1 Sample bottle -- Borosilicate, 1-L volume with graduations (Wheaton Media/Lab bottle 219820 or equivalent), fitted with screw caps lined with TFE-fluorocarbon. Protect samples from light. Amber bottles may be used. The container must be washed and dried as described in Sect. 4.1.1 before use to minimize contamination. Cap liners are cut to fit from sheets (Pierce Catalog No. 012736 or equivalent) and extracted with methanol overnight prior to use.

6.2 GLASSWARE

6.2.1 Separatory funnel -- 2000-mL, with TFE-fluorocarbon stopcock, ground glass or TFE-fluorocarbon stopper.

6.2.2 Tumbler bottle -- 1.7-L (Wheaton Roller Culture Vessel or equivalent), with TFE-fluorocarbon lined screw cap. Cap liners are cut to fit from sheets (Pierce Catalog No. 012736) and extracted with methanol overnight prior to use.

6.2.3 Flask, Erlenmeyer -- 500-mL.

6.2.4 Concentrator tube, Kuderna-Danish (K-D) -- 10- or 25-mL, graduated (Kontes K-570050-2525 or K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stoppers are used to prevent evaporation of extracts.

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

6.2.6 Snyder column, K-D -- Three-ball macro (Kontes K-503000-0121 or equivalent).

6.2.7 Snyder column, K-D -- Two-ball micro (Kontes K-569001-0219 or equivalent).

6.2.8 Vials -- glass, 5- to 10-mL capacity with TFE-fluorocarbon lined screw cap.

6.3 Separatory funnel shaker (Optional) -- Capable of holding 2-L separatory funnels and shaking them with rocking motion to achieve thorough mixing of separatory funnel contents (available from Eberbach Co. in Ann Arbor, MI or other suppliers).

6.4 Tumbler -- Capable of holding tumbler bottles and tumbling them end-over-end at 30 turns/min (Associated Design and Mfg. Co., Alexandria, VA. or other suppliers).

6.5 Boiling stones -- Carborundum, #12 granules (Arthur H. Thomas Co. #1590-033 or equivalent). Heat at 400°C for 30 min prior to use. Cool and store in desiccator.

6.6 Water bath -- Heated, capable of temperature control (± 2°C). The bath should be used in a hood.

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

6.8 GAS CHROMATOGRAPH -- Analytical system complete with temperature programmable GC suitable for use with capillary columns and all required accessories including syringes, analytical columns, gases, detector and stripchart recorder. A data system is recommended for measuring peak areas. Table 1 lists retention times observed for method analytes using the columns and analytical conditions described below.

6.8.1 Column 1 (Primary column) -- 30 m long x 0.25 mm I.D. DB-5 bonded fused silica column, 0.25 μm film thickness (J&W Scientific) or equivalent. Helium carrier gas flow is established at 30 cm/sec linear velocity and oven temperature is programmed from 60°C to 300°C at 4°C/min. Data presented in this method were obtained using this column. The injection volume was 2 μL in splitless mode with a 45 s delay. The injector temperature was 250°C and the detector temperature was 300°C. Alternative columns may be used in accordance with the provisions described in Sect. 9.4.

6.8.2 Column 2 (Confirmation column) -- 30 m long x 0.25 mm I.D.DB-1701 bonded fused silica column, 0.25 μm film thickness (J&W Scientific) or equivalent. Helium carrier gas flow is established at 30 cm/sec linear velocity and oven temperature is programmed from 60C to 300°C at 4°C/min.

6.8.3 Detector -- Nitrogen-phosphorus (NPD).

7. <u>REAGENTS AND STANDARDS</u> -- WARNING: When a solvent is purified, stabilizers added by the manufacturer are removed thus potentially making the solvent hazardous. Also, when a solvent is purified, preservatives added by the manufacturer are removed thus potentially reducing the shelflife.

7.1 Acetone, methylene chloride, methyl tert.-butyl ether (MTBE) -- Distilled-in-glass quality or equivalent.

7.2 Phosphate buffer, pH 7 -- Prepare by mixing 29.6 mL 0.1 N HCl and 50 mL 0.1 M dipotassium phosphate.

7.3 Sodium chloride (NaCl), crystal, ACS grade -- Heat treat in a shallow tray at 400°C for a minimum of 4 hours to remove interfering organic substances. Store in a glass bottle (not plastic) to avoid phthalate contamination.

7.4 Sodium sulfate, granular, anhydrous, ACS grade -- Heat treat in a shallow tray at 400°C for a minimum of 4 hours to remove interfering organic substances. Store in a glass bottle (not plastic) to avoid phthalate contamination.

7.5 Sodium thiosulfate, granular, anhydrous, ACS grade.

7.6 Triphenylphosphate (TPP) -- 98% purity, for use as internal standard (available from Aldrich Chemical Co.).

7.7 1,3-Dimethyl-2-nitrobenzene -- 98% purity, for use as surrogate standard (available from Aldrich Chemical Co.).

7.8 Mercuric Chloride -- ACS grade (Aldrich Chemical Co.) - for use as a bactericide (optional- see Sect. 8).

7.9 Reagent water -- Reagent water is defined as a water that is reasonably free of contamination that would prevent the determination of any analyte of interest. Reagent water used to

generate the validation data in this method was distilled water obtained from the Magnetic Springs Water Co., Columbus, Ohio.

7.10 STOCK STANDARD SOLUTIONS (1.00 μg/μL) -- Stock standard solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedure:

7.10.1 Prepare stock standard solutions by accurately weighing approximately 0.0100 g of pure material. Dissolve the material in MTBE and dilute to volume in a 10-mL volumetric flask. The stock solution for simazine should be prepared in methanol. 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. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.10.2 Transfer the stock standard solutions into TFE-fluorocarbon-sealed screw cap amber vials. Store at room temperature and protect from light.

7.10.3 Stock standard solutions should be replaced after two months or sooner if comparison with laboratory fortified blanks, or QC samples indicate a problem.

7.11 INTERNAL STANDARD SOLUTION -- Prepare the internal standard solution by accurately weighing approximately 0.0500 g of pure TPP. Dissolve the TPP in MTBE and dilute to volume in a 100-mL volumetric flask. Transfer the internal standard solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Addition of 50 μL of the internal standard solution to 5 mL of sample extract results in a final TPP concentration of 5.0 μg/mL. This solution should be replaced when ongoing QC (Sect. 9) indicates a problem. Note that TPP has been shown to be an effective internal standard for the method analytes, but other compounds may be used if the quality control requirements in Sect. 9 are met.

7.12 SURROGATE STANDARD SOLUTION -- Prepare the surrogate standard solution by accurately weighing approximately 0.0250 g of pure 1,3-dimethyl-2-nitrobenzene. Dissolve the 1,3-dimethyl-2-nitrobenzene in MTBE and dilute to volume in a 100-mL volumetric flask. Transfer the surrogate standard solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Addition of 50 μL of the surrogate standard solution to a 1-L sample prior to extraction results in a 1,3-dimethyl-2-nitrobenzene concentration in the sample of 12.5 μg/L. Solution should be replaced when ongoing QC (Sect. 9) indicates a problem. Note that 1,3-dimethyl-2-nitrobenzene has been shown to be an effective surrogate standard for the method analytes, but other compounds may be used if the quality control requirements in Sect. 9 are met.

7.13 LABORATORY PERFORMANCE CHECK SOLUTION -- Prepare the laboratory performance check solution by adding 5 μL of the vernolate stock

solution, 0.5 mL of the bromacil stock solution, 30 µL of the prometon stock solution, 15 µL of the atrazine stock solution, 1.0 mL of the surrogate solution, and 500 µL of the internal standard solution to a 100-mL volumetric flask. Dilute to volume with MTBE and thoroughly mix the solution. Transfer to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Solution should be replaced when ongoing QC (Sect. 9) indicates a problem.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Grab samples must be collected in glass containers. Conventional sampling practices (5) should be followed; however, the bottle must not be prerinsed with sample before collection.

8.2 SAMPLE PRESERVATION AND STORAGE

8.2.1 If residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample to the sample bottle prior to collecting the sample.

8.2.2 After the sample is collected in a bottle containing sodium thiosulfate, seal the bottle and shake until dissolved.

8.2.3 The samples must be iced or refrigerated at 4°C away from light from the time of collection until extraction. Preservation study results indicated that most method analytes present in samples were stable for 14 days when stored under these conditions. The analytes disulfoton sulfoxide, diazinon, pronamide, and terbufos exhibited significant aqueous instability, and samples to be analyzed for these compounds must be extracted immediately. The analytes carboxin, EPTC, fluridone, metolachlor, napropamide, tebuthiuron, and terbacil exhibited recoveries of less than 60% after 14 days. Analyte stability may be affected by the matrix; therefore, the analyst should verify that the preservation technique is applicable to the samples under study.

8.2.4 All performance data presented in this method are from samples preserved with mercuric chloride. No suitable preservation agent (biocide) has been found other than mercuric chloride. However the use of mercuric chloride is not required due to its toxicity and potential harm to the environment.

8.2.5 In some circumstances where biological degradation of target pesticides might be expected, use of mercuric chloride may be appropriate to minimize the possibility of false-negative results. If mercuric chloride is to be used, add it (See 7.8) to the sample bottle in amounts to produce a concentration of 10 mg/L. Add 1 mL of a solution containing 10 mg/mL of mercuric chloride in reagent water to the sample bottle at the sampling site or in the laboratory before shipping to the sampling site. A major disadvantage of mercuric chloride is that it is a highly toxic chemical;

mercuric chloride must be handled with caution, and samples containing mercuric chloride must be disposed of properly.

8.3 Extract Storage -- Extracts should be stored at 4°C away from light. Preservation study results indicate that most analytes are stable for 28 days; however, a 14-day maximum extract storage time is recommended. The analyst should verify appropriate extract holding times applicable to the samples under study.

9. QUALITY CONTROL

9.1 Minimum quality control (QC) requirements are initial demonstration of laboratory capability, determination of surrogate compound recoveries in each sample and blank, monitoring internal standard peak area or height in each sample and blank (when internal standard calibration procedures are being employed), analysis of laboratory reagent blanks, laboratory fortified samples, laboratory fortified blanks, and QC samples. A method detection limit (MDL) must also be determined for each analyte.

9.2 Laboratory Reagent Blanks. Before processing any samples, the analyst must demonstrate that all glassware and reagent interferences are under control. Each time a set of samples is extracted or reagents are changed, a LRB must be analyzed. If within the retention time window of any analyte of interest the LRB produces a peak that would prevent the determination of that analyte, determine the source of contamination and eliminate the interference before processing samples.

9.3 Initial Demonstration of Capability.

9.3.1 Select a representative fortified concentration (about 10 times EDL or at a concentration in the middle of the calibration range established in Sect. 10) for each analyte. Prepare a standard concentrate containing each analyte at 1000 times the selected concentration. With a syringe, add 1 mL of the concentrate to each of four to seven 1-L aliquots of reagent water, and analyze each aliquot according to procedures beginning in Sect. 11.

9.3.2 For each analyte, the mean recovery value for these samples must fall in the range of R ± 30% using the values for R for reagent water in Table 2. The RSD for these measurements must be 20% or less. For those compounds that meet the acceptance criteria, performance is considered acceptable. For those compounds that fail these criteria, this procedure must be repeated using fresh replicate samples until satisfactory performance has been demonstrated.

9.3.3 For each analyte, determine the MDL. Prepare a minimum of 7 LFBs at a low concentration. The fortification concentration in Table 3 may be used as a guide, or use calibration data obtained in Section 10 to estimate a concentration for each analyte that will produce a peak with a 3-5 times signal to noise response. Extract and analyze each replicate according to Sections 11 and 12. It is recommended that these LFBs be

prepared and analyzed over a period of several days, so that day to day variations are reflected in the precision measurement. Calculate mean recovery and standard deviation for each analyte. Use the equation given in Table 3 to calculate the MDL.

9.3.3 The initial demonstration of capability is used primarily to preclude a laboratory from analyzing unknown samples via a new, unfamiliar method prior to obtaining some experience with it. It is expected that as laboratory personnel gain experience with this method the quality of data will improve beyond those required here.

9.4 The analyst is permitted to modify GC columns, GC conditions, concentration techniques (i.e. evaporation techniques), internal standards or surrogate compounds. Each time such method modifications are made, the analyst must repeat the procedures in Sect. 9.3.

9.5 Assessing Surrogate Recovery

9.5.1 When surrogate recovery from a sample or method blank is <70% or >130%, check calculations to locate possible errors, fortifying solutions for degradation, contamination, and instrument performance. If those steps do not reveal the cause of the problem, reanalyze the extract.

9.5.2 If a LRB extract reanalysis fails the 70-130% recovery criterion, the problem must be identified and corrected before continuing.

9.5.3 If sample extract reanalysis meets the surrogate recovery criterion, report only data for the reanalyzed extract. If sample extract reanalysis continues to fail the recovery criterion, report all data for that sample as suspect.

9.6 Assessing the Internal Standard

9.6.1 When using the internal standard calibration procedure, the analyst is expected to monitor the IS response (peak area or peak height) of all samples during each analysis day. The IS response for any sample chromatogram should not deviate from the daily calibration check standard's IS response by more than 30%.

9.6.2 If >30% deviation occurs with an individual extract, optimize instrument performance and inject a second aliquot of that extract.

9.6.2.1 If the reinjected aliquot produces an acceptable internal standard response report results for that aliquot.

9.6.2.2 If a deviation of greater than 30% is obtained for the reinjected extract, analysis of the sample should be repeated beginning with Sect. 11, provided

the sample is still available. Otherwise, report results obtained from the reinjected extract, but annotate as suspect.

9.6.3 If consecutive samples fail the IS response acceptance criterion, immediately analyze a calibration check standard.

9.6.3.1 If the check standard provides a response factor (RF) within 20% of the predicted value, then follow procedures itemized in Sect. 9.6.2 for each sample failing the IS response criterion.

9.6.3.2 If the check standard provides a response factor which deviates more than 20% of the predicted value, then the analyst must recalibrate, as specified in Sect. 9.

9.7 Assessing Laboratory Performance - Laboratory Fortified Blank

9.7.1 The laboratory must analyze at least one laboratory fortified blank (LFB) sample with every twenty samples or one per sample set (all samples extracted within a 24-h period) whichever is greater. Ideally, the fortified concentration of each analyte in the LFB should be the same concentration selected in Section 9.3.1. Calculate accuracy as percent recovery (X_i). If the recovery of any analyte falls outside the control limits (see Sect. 9.7.2), that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

9.7.2 Until sufficient data become available from within their own laboratory, usually a minimum of results from 20 to 30 analyses, the laboratory should assess laboratory performance against the control limits in Sect. 9.3.2 that are derived from the data in Table 2. When sufficient internal performance data becomes available, develop control limits from the mean percent recovery (X) and standard deviation (S) of the percent recovery. These data are used to establish upper and lower control limits as follows:

$$\text{UPPER CONTROL LIMIT} = X + 3S$$

$$\text{LOWER CONTROL LIMIT} = X - 3S$$

After each five to ten new recovery measurements, new control limits should be calculated using only the most recent 20-30 data points. These calculated control limits must <u>not</u> exceed the fixed limits listed in Sect. 9.3.2.

9.7.5 It is recommended that the laboratory periodically determine and document its detection limit capabilities for analytes of interest.

9.7.6 At least quarterly, analyze a QC sample from an outside source.

9.8 Assessing Analyte Recovery - Laboratory Fortified Sample Matrix

9.8.1 The laboratory must add a known concentration to a minimum of 5% of the routine samples or one sample per set, whichever is greater. The fortified concentration should not be less than the background concentration of the sample selected for fortification. Ideally, the concentration should be the same as that used for the laboratory fortified blank (Sect. 9.7). Over time, samples from all routine sample sources should be fortified.

9.8.2 Calculate the percent recovery, P, of the concentration for each analyte, after correcting the analytical result, X, from the fortified sample for the background concentration, b, measured in the unfortified sample, i.e.,:

$$P = 100\ (X - b)\ /\ \text{fortifying concentration},$$

and compare these values to reagent water recoveries listed in Table 2. The calculated value of P must fall in the range of R ± 35%. If P exceeds this control limit the results for that analyte in the unfortified matrix must be listed as suspect due to matrix interference.

9.9 ASSESSING INSTRUMENT SYSTEM - LABORATORY PERFORMANCE CHECK (LPC) - After initial demonstration of capability, instrument performance should be monitored on a daily basis by analysis of the LPC sample. The LPC sample contains compounds designed to monitor instrument sensitivity, column performance (primary column) and chromatographic performance. LPC sample components and performance criteria are listed in Table 4. Inability to demonstrate acceptable instrument performance indicates the need for reevaluation of the instrument system. The sensitivity requirements are set based on the EDLs published in this method. The purpose of the sensitivity requirement is to monitor the stability of instrument sensitivity, not as an absolute sensitivity requirement. If laboratory EDLs differ from those listed in this method, concentrations of the LPC standard compounds must be adjusted to be compatible with the laboratory EDLs.

9.10 The laboratory may adopt additional quality control 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. For example, field or laboratory duplicates may be analyzed to assess the precision of the environmental measurements or field reagent blanks may be used to assess contamination of samples under site conditions, transportation and storage.

10. CALIBRATION

10.1 Establish GC operating parameters equivalent to those indicated in Sect. 6.8. The GC system may be calibrated using either the internal standard technique (Sect. 10.2) or the external standard technique (Sect. 10.3). Be aware that NPDs may exhibit instability (i.e., fail to hold calibration curves over time). The analyst may, when analyzing samples for target analytes which are very rarely

found, prefer to analyze on a daily basis a low level (e.g. 5 to 10 times detection limit or 1/2 times the regulatory limit, whichever is less), sample (containing all analytes of interest) and require some minimum sensitivity (e.g. 1/2 full scale deflection) to show that if the analyte were present it would be detected. The analyst may then quantitate using single point calibration (Sect. 10.2.5 or 10.3.4). NOTE: Calibration standard solutions must be prepared such that no unresolved analytes are mixed together.

10.2 INTERNAL STANDARD CALIBRATION PROCEDURE -- To use this approach, the analyst must select one or more internal standards compatible 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. TPP has been identified as a suitable internal standard.

10.2.1 Prepare calibration standards at a minimum of three (recommend five) concentration levels for each analyte of interest by adding volumes of one or more stock standards to a volumetric flask. Guidance on the number of standards is as follows: A minimum of three calibration standards are required to calibrate a range of a factor of 20 in concentration. For a factor of 50 use at least four standards, and for a factor of 100 at least five standards. The lowest standard should represent analyte concentrations near, but above, their respective EDLs. The remaining standards should bracket the analyte concentrations expected in the sample extracts, or should define the working range of the detector. If Merphos is to be determined, calibrate with DEF (S,S,S-tributylphosphoro-trithioate). Merphos is converted to S,S,S-tributylphosphoro-trithioate (DEF) in the hot GC injection port; DEF is actually detected using the analysis conditions in this method. To each calibration standard, add a known constant amount of one or more of the internal standards, and dilute to volume with MTBE.

10.2.2 Analyze each calibration standard according to the procedure described in Sect. 11.4. Tabulate response (peak height or area) against concentration for each compound and internal standard. Calculate the response factor (RF) for each analyte and surrogate using Equation 1. RF is a unitless value.

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)} \qquad \text{Equation 1}$$

where :

A_s = Response for the analyte.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard µg/L.

C_s = Concentration of the analyte to be measured µg/L.

10.2.3 If the RF value over the working range is constant (20% RSD or less) the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios (A_s/A_{is}) vs. C_s.

10.2.4 The working calibration curve or calibration factor must be verified on each working day by the measurement of a minimum of two calibration check standards, one at the beginning and one at the end of the analysis day. These check standards should be at two different concentration levels to verify the calibration curve. For extended periods of analysis (greater than 8 hrs.), it is strongly recommended that check standards be interspersed with samples at regular intervals during the course of the analyses. If the response for any analyte varies from the predicted response by more than ±20%, the test must be repeated using a fresh calibration standard. If the results still do not agree, generate a new calibration curve. For those analytes that failed the calibration verification, results from field samples analyzed since the last passing calibration should be considered suspect. Reanalyze sample extracts for these analytes after acceptable calibration is restored.

10.2.5 Verify calibration standards periodically (at least quarterly), by analyzing a QCS.

10.3 EXTERNAL STANDARD CALIBRATION PROCEDURE

10.3.1 Prepare calibration standards as in Section 10.2.1, omitting the use of the internal standard.

10.3.2 Starting with the standard of lowest concentration, analyze each calibration standard according to Sect. 11.4 and tabulate response (peak height or area) versus the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (20% RSD or less), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

10.3.3 The working calibration curve or calibration factor must be verified on each working day by the procedures described in Section 10.2.4.

10.3.4 Verify calibration standards periodically (at least quarterly), by analyzing a QCS.

11. PROCEDURE

11.1 EXTRACTION (MANUAL METHOD)

11.1.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume (Sect. 11.1.6). Add preservative (Section 8) to LRBs and LFBs. Fortify the

sample with 50 µL of the surrogate standard solution. Pour the entire sample into a 2-L separatory funnel.

11.1.2 Adjust the sample to pH 7 by adding 50 mL of phosphate buffer. Check pH. Add acid or base if necessary to obtain pH 7.

11.1.3 Add 100 g NaCl to the sample, seal, and shake to dissolve salt.

11.1.4 Add 60 mL methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner walls. Transfer the solvent to the separatory funnel 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 technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 500-mL Erlenmeyer flask.

11.1.5 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

11.1.6 Determine the original sample volume by refilling the sample bottle to the mark and transferring the water to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11.2 EXTRACTION (AUTOMATED METHOD) -- Data presented in this method were generated using the automated extraction procedure with the mechanical tumbler.

11.2.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume (Sect. 11.2.6). Add preservative to LRBs and LFBs. Fortify the sample with 50 µL of the surrogate standard solution. If the mechanical separatory funnel shaker is used, pour the entire sample into a 2-L separatory funnel. If the mechanical tumbler is used, pour the entire sample into a tumbler bottle.

11.2.2 Adjust the sample to pH 7 by adding 50 mL of phosphate buffer. Check pH. Add acid or base if necessary to obtain pH 7.

11.2.3 Add 100 g NaCl to the sample, seal, and shake to dissolve salt.

11.2.4 Add 300 mL methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner walls. Transfer the solvent to the sample contained in the separatory funnel or tumbler

bottle, seal, and shake for 10 s, venting periodically. Repeat shaking and venting until pressure release is not observed. Reseal and place sample container in appropriate mechanical mixing device (separatory funnel shaker or tumbler). Shake or tumble the sample for 1 hour. Complete mixing of the organic and aqueous phases should be observed within about 2 min after starting the mixing device.

11.2.5 Remove the sample container from the mixing device. If the tumbler is used, pour contents of tumbler bottle into a 2-L separatory funnel. 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 technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 500-mL Erlenmeyer flask.

11.2.6 Determine the original sample volume by refilling the sample bottle to the mark and transferring the water to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11.3 EXTRACT CONCENTRATION

11.3.1 Assemble a K-D concentrator by attaching a 25-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D if the requirements of Sect. 9.3 are met.

11.3.2 Dry the extract by pouring it through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate. Collect the extract in the K-D concentrator, and rinse the column with 20-30 mL methylene chloride. Alternatively, add about 5 g anhydrous sodium sulfate to the extract in the Erlenmeyer flask; swirl flask to dry extract and allow to sit for 15 min. Decant the methylene chloride extract into the K-D concentrator. Rinse the remaining sodium sulfate with two 25-mL portions of methylene chloride and decant the rinses into the K-D concentrator.

11.3.3 Add 1 to 2 clean boiling stones to the evaporative flask and attach a macro 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, 65 to 70°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 15 to 20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 2 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

11.3.4 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of MTBE. Add 5-10 mL of MTBE and a fresh boiling stone. Attach a micro-Snyder column to the concentrator tube and prewet the column by adding about 0.5 mL of MTBE 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 to 10 min. When the apparent volume of liquid reaches 2 mL, remove the micro K-D from the bath and allow it to drain and cool. Add 5-10 mL MTBE to the micro K-D and reconcentrate to 2 mL. Remove the micro K-D from the bath and allow it to drain and cool. Remove the micro Snyder column, and rinse the walls of the concentrator tube while adjusting the volume to 5.0 mL with MTBE. NOTE: If methylene chloride is not completely removed from the final extract, it may cause detector problems. If the internal standard calibration procedure is used, add 50 µL of the internal standard solution to the sample extract, seal, and shake to distribute the internal standard.

11.3.5 Transfer extract to an appropriate- sized TFE-fluorocarbon-sealed screw-cap vial and store, refrigerated at 4°C, until analysis by GC-NPD.

11.4 GAS CHROMATOGRAPHY

11.4.1 Sect. 6.8 summarizes the recommended operating conditions for the gas chromatograph. Included in Table 1 are retention times observed using this method. Other GC columns or chromatographic conditions may be used if the requirements of Sect. 9 are met.

11.4.2 Verify the calibration the system daily as described in Sect. 10.2.4 or 10.3.3. The standards and extracts must be in MTBE.

11.4.3 Inject 2 µL of the sample extract. Record the resulting peak size in area units.

11.4.4 If the response for the peak exceeds the working range of the system, dilute the extract and reanalyze. If using IS calibration, add an appropriate amount of IS so that the extract concentration will match the calibration standards.

11.5 IDENTIFICATION OF ANALYTES

11.5.1 Identify a sample component by comparison of its retention time to the retention time of a reference chromatogram. If the retention time of an unknown compound corresponds, within limits, to the retention time of a standard compound, then identification is considered positive.

11.5.2 The width of the retention time window used to make identifications should be based upon 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.

11.5.3 Identification requires expert judgement when sample components are not resolved chromatographically. When peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), or any time doubt exists over the identification of a peak on a chromatogram, appropriate alternative techniques to help confirm peak identification, need be employed. For example, more positive identification may be made by the use of an alternative detector which operates on a chemical/physical principle different from that originally used, e.g., mass spectrometry (6), or the use of a second chromatography column. A suggested alternative column is described in Sect. 6.8.

12. CALCULATIONS

12.1 Calculate analyte concentrations in the sample from the response for the analyte using the procedure for multi-point calibration described in Sect. 10. Do not use the daily calibration verification standard to calculate analye amounts in samples.

12.2 If the internal standard calibration procedure is used, calculate the concentration (C) in the sample using the response factor (RF) determined in Sect. 10.2.2 and Equation 2, or determine sample concentration from the calibration curve.

$$C\ (\mu g/L) = \frac{(A_s)(I_s)}{(A_{is})(RF)(Vo)} \qquad \text{Equation 2}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

I_s = Amount of internal standard added to each extract (μg).

Vo = Volume of water extracted (L).

12.3 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor determined in Sect. 10.3.2. The concentration (C) in the sample can be calculated from Equation 3.

$$C\ (\mu g/L) = \frac{(A)(V_t)}{(V_i)(V_s)} \qquad \text{Equation 3}$$

where:

A = Amount of material injected (ng).

V_i = Volume of extract injected (μL).

V_t = Volume of total extract (μL).

V_s = Volume of water extracted (mL).

13. PRECISION AND ACCURACY

13.1 In a single laboratory, analyte recoveries from reagent water were used to determine analyte MDLs, EDLs (Table 3) and demonstrate method range. Analytes were divided into five groups for recovery studies. Analyte recoveries and standard deviation about the percent recoveries at one concentration are given in Table 2.

13.2 In a single laboratory, analyte recoveries from two standard synthetic ground waters were determined at one concentration level. Results were used to demonstrate applicability of the method to different ground water matrices. Analyte recoveries from the two synthetic matrices are given in Table 2.

14. POLLUTION PREVENTION

14.1 This method uses significant volumes of organic solvents. It is highly recommended that laboratories use solvent recovery systems to recover used solvent as sample extracts are being concentrated. Recovered solvents should be recycled or properly disposed of.

14.2 For information about pollution prevention that may be applicable to laboratory operations, consult "Less is Better: Laboratory Chemical Management for Waste Reduction" available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

15. WASTE MANAGEMENT

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions. The laboratory using this method has the responsibility to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations. For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel," also available from the American Chemical Society at the address in Sect. 14.2.

16. REFERENCES

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Preservation," American Society for Testing and Materials, Philadelphia, PA, 1986.

2. "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, Aug. 1977.

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6. Munch, J. W., "Method 525.2-Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Chromatography/ Mass Spectrometry" in Methods for the Determination of Organic Compounds in Drinking Water; Supplement 3 (1995). USEPA, National Exposure Research Laboratory, Cincinnati, Ohio 45268.

TABLE 1. RETENTION TIMES FOR METHOD ANALYTES

Analyte	Retention Time[a] Col. 1	Col. 2
1,3-Dimethyl-2-nitrobenzene(surrogate)	14.48	(b)
Dichlorvos	16.54	15.35
Disulfoton sulfoxide	19.08	(b)
EPTC	20.07	16.57
Butylate	22.47	18.47
Mevinphos	22.51	21.92
Vernolate	22.94	19.25
Pebulate	23.41	19.73
Tebuthiuron	25.15	42.77
Molinate	25.66	22.47
Ethoprop	28.58	26.42
Cycloate	28.58	29.67
Chlorpropham	29.09	(b)
Atraton	31.26	29.97
Simazine	31.49	31.32
Prometon	31.58	30.00
Atrazine	31.77	31.23
Propazine	32.01	31.13
Terbufos	32.57	(b)
Pronamide	32.76	32.63
Diazinon	33.23	(b)
Disulfoton	33.42	30.90
Terbacil	33.79	(b)
Metribuzin	35.20	34.73
Methyl paraoxon	35.58	34.10
Simetryn	35.72	34.55
Alachlor	35.96	34.10
Ametryn	36.00	34.52
Prometryn	36.14	34.23
Terbutryn	36.80	34.80
Bromacil	37.22	40.00
Metolachlor	37.74	35.70
Triademefon	38.12	37.00
MGK 264 (c)	38.73	36.73
Diphenamid	38.87	37.97
Stirofos	41.27	39.65
Disulfoton sulfone	41.31	42.42
Butachlor	41.45	39.00
Fenamiphos	41.78	41.00
Napropamide	41.83	(b)
Tricyclazole	42.25	44.33
Merphos (d)	42.35	39.28
Carboxin	42.77	42.05
Norflurazon	45.92	47.58
Triphenyl phosphate (int. std.)	47	45.40

TABLE 1 (CONTINUED)

Analyte	Retention Time[a] Col.1	Col.2
Hexazinone	46.58	47.80
Fenarimol	51.32	50.02
Fluridone	56.68	59.07

[a] Columns and analytical conditions are described in Sect. 6.8.1 and 6.8.2.

[b] Data not available

[c] MGK 264 gives two peaks; peak identified in this table used for quantification.

[d] Merphos is converted to S,S,S-tributylphosphoro-trithioate (DEF) in the hot GC injection port; DEF is actually detected using these analyses conditions.

TABLE 2. SINGLE LABORATORY ACCURACY AND PRECISION FOR ANALYTES FROM REAGENT WATER AND SYNTHETIC GROUNDWATERS[a]

Analyte	Conc. µg/L	Reagent Water R[b]	Reagent Water S_R[c]	Synthetic Water 1[d] R	Synthetic Water 1[d] S_R	Synthetic Water 2[e] R	Synthetic Water 2[e] S_R
Alachlor	3.8	95	11	82	6	90	8
Ametryn	20	91	10	102	11	96	4
Atraton	6	91	11	84	7	91	8
Atrazine	1.3	92	8	89	6	92	5
Bromacil	25	91	9	81	5	88	8
Butachlo	3.8	96	4	93	15	84	5
Butylate	1.5	97	21	36	8	83	8
Carboxin	6	102	4	98	13	87	5
Chlorpropham	5	93	11	82	7	93	8
Cycloate	2.5	89	9	97	14	93	3
Diazinon	2.5	115	7	83	8	84	3
Dichlorvos	25	97	6	86	6	106	16
Diphenamid	6	93	8	88	4	93	5
Disulfoton	3	89	10	107	12	95	5
Disulfoton sulfone	7.5	98	10	92	5	96	3
Disulfoton sulfoxide	3.8	87	11	88	22	54	19
EPTC	2.5	85	9	83	5	86	4
Ethoprop	1.9	103	5	91	7	79	3
Fenamiphos	10	90	8	87	5	89	2
Fenarimol	3.8	99	5	89	6	89	6
Fluridone	38	87	9	91	11	86	10
Hexazinone	7.6	90	7	86	6	95	9
Merphos	2.5	96	8	90	4	92	4
Methyl paraoxon	25	98	10	97	8	94	4
Metolachlor	7.5	93	4	92	10	84	4
Metribuzin	1.5	101	5	99	10	86	4
Mevinphos	50	95	11	93	6	92	4
MGK 264	5	100	4	91	11	83	6
Molinate	1.5	98	18	83	8	89	9
Napropamide	2.5	101	6	89	5	104	18
Norflurazon	5.	94	5	101	15	87	4
Pebulate	1.3	94	9	80	6	98	15
Prometon	3	78	9	89	5	63	2
Prometryn	1.9	93	8	91	8	93	4
Pronamide	7.6	91	10	84	7	92	8
Propazine	1.3	92	8	89	6	92	5
Simazine	0.75	100	7	86	5	103	14
Simetryn	2.5	99	5	88	4	103	14
Stirofos	7.6	98	6	84	6	95	10
Tebuthiuron	13	84	9	85	10	98	13
Terbacil	45	97	6	86	5	102	12
Terbufos	5	97	4	80	6	77	7
Terbutryn	2.5	94	9	91	8	92	4

TABLE 2. (CONTINUED)

Analyte	Conc. µg/L	Reagent Water R[b]	Reagent Water S_R[c]	Synthetic Water 1[d] R	Synthetic Water 1[d] S_R	Synthetic Water 2[e] R	Synthetic Water 2[e] S_R
Triademefon	6.5	93	8	94	5	95	5
Tricyclazole	10	86	7	90	6	90	11
Vernolate	1.3	93	6	79	9	81	2

[a] Data corrected for blank and represent the analysis of 7-8 samples using mechanical tumbling and internal standard calibration.

[b] R = average percent recovery.

[c] S = standard deviation of the percent recovery.

[d] Corrected for amount found in blank; Absopure Nature Artesian Spring Water Obtained from the Absopure Water Company in Plymouth, Michigan.

[e] Corrected for amount found in blank; reagent water fortified with fulvic acid at the 1 mg/L concentration level. A well-characterized fulvic acid, available from the International Humic Substances Society (associated with the United States Geological Survey in Denver, Colorado), was used.

TABLE 3. SINGLE LABORATORY ACCURACY, PRECISION, METHOD DETECTION LIMITS (MDLs) AND ESTIMATED DETECTION LIMITS (EDLs) FOR ANALYTES FROM REAGENT WATER

Analyte	Fortified Conc. µg/L	N[a]	Recovery µg/L	RSD %	MDL[b] µg/L	EDL[c] µg/L
Alachlor	0.38	8	119	10	0.14	0.38
Ametryn	2.0	8	100	3	0.20	2.0
Atraton	0.60	8	120	8	0.17	0.6
Atrazine	0.13	8	101	4	0.015	0.13
Bromacil	2.5	8	113	8	0.69	2.5
Butachlor	0.38	8	99	11	0.12	0.38
Butylate	0.15	8	93	13	0.053	0.15
Carboxin	0.60	8	101	10	0.18	0.60
Chlorpropham	0.50	8	124	11	0.20	0.50
Cycloate	0.25	8	101	3	0.022	0.25
Diazinon	0.25	8	94	18	0.13	0.25
Dichlorvos	2.5	8	78	5	0.28	2.5
Diphenamid	0.60	8	84	5	0.082	0.60
Disulfoton	0.30	8	100	3	0.029	0.30
Disulfoton sulfone	3.8	7	94	6	0.63	3.8
Disulfoton sulfoxide	0.38	7	110	6	0.082	0.38
EPTC	0.25	8	87	12	0.080	0.25
Ethoprop	0.19	8	108	3	0.021	0.19
Fenamiphos	1.0	8	91	4	0.12	1.0
Fenarimol	0.38	8	92	19	0.20	0.38
Fluridone	3.8	7	78	30	2.8	3.8
Hexazinone	0.76	8	127	5	0.15	0.76
Merphos	0.25	8	101	5	0.040	0.25
Methyl paraoxon	2.5	8	100	4	0.30	2.5
Metolachlor	0.75	8	94	9	0.19	0.75
Metribuzin	0.15	8	114	6	0.029	0.15
Mevinphos	5.0	8	92	6	0.87	5.0
MGK 264	0.50	8	101	12	0.19	0.50
Molinate	0.15	8	117	12	0.061	0.15
Napropamide	0.25	8	97	9	0.069	0.25
Norflurazon	0.50	8	86	8	0.098	0.50
Pebulate	0.13	8	84	7	0.022	0.13
Prometon	0.30	7	48	9	0.041	0.30
Prometryn	0.19	8	88	5	0.024	0.19
Pronamide	0.76	8	123	10	0.28	0.76
Propazine	0.13	8	93	4	0.014	0.13
Simazine	0.075	8	99	6	0.014	0.075
Simetryn	0.25	8	97	5	0.035	0.25
Stirofos	0.76	8	121	7	0.18	0.76
Tebuthiuron	1.3	8	101	15	0.58	1.3
Terbacil	4.5	8	100	4	0.56	4.5
Terbufos	0.5	8	91	4	0.054	0.50
Terbutryn	0.25	8	91	4	0.031	0.25

TABLE 3. (CONTINUED)

Analyte	MDL Conc. µg/L	N[a]	Recovery µg/L	RSD %	MDL[b] µg/L	EDL[c] µg/L
Triademefon	0.65	8	95	5	0.093	0.65
Tricyclazole	1.0	8	216	3	0.21	1.0
Vernolate	0.13	8	100	14	0.055	0.13

[a] N = Number of Replicates

[b] With these data, the method detection limits (MDL) in the tables were calculated using the formula:

$$MDL = S\ t_{(n-1,1-alpha = 0.99)}$$

where:

$t_{(n-1,1-alpha = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom

n = number of replicates

S = standard deviation of replicate analyses.

[c] EDL = estimated detection limit; defined as either MDL (Appendix B to 40 CFR Part 136 - Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11) or a level of compound in a sample yielding a peak in the final extract with signal-to-noise ratio of approximately 5, whichever value is higher. The concentration used in determining the EDL is not the same as the concentration presented in this table.

TABLE 4. LABORATORY PERFORMANCE CHECK SOLUTION

Test	Analyte	Conc. µg/mL	Requirements
Sensitivity	Vernolate	0.05	Detection of analyte; S/N > 3
Chromatographic performance	Bromacil	5.0	0.80 < PGF < 1.20 (a)
Column performance	Prometon Atrazine	0.30 0.15	Resolution > 0.7 (b)

[a] PGF - peak Gaussian factor. Calculated using the equation:

$$PGF = \frac{1.83 \times W(1/2)}{W(1/10)}$$

where W(1/2) is the peak width at half height in secs. and W(1/10) is the peak width in secs. at tenth height.

[b] Resolution between the two peaks as defined by the equation:

$$R = \frac{t}{W}$$

where t is the difference in elution times between the two peaks and W is the average peak width, at the baseline, of the two peaks.

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METHOD 508. DETERMINATION OF CHLORINATED PESTICIDES IN WATER BY GAS CHROMATOGRAPHY WITH AN ELECTRON CAPTURE DETECTOR

Revision 3.1

Edited by J.W. Munch (1995)

J. J. Lichtenberg, J. E. Longbottom, T. A. Bellar, J. W. Eichelberger, and R. C. Dressman - EPA 600/4-81-053, Revision 1.0 (1981)

D. J. Munch (USEPA, Office of Water) and T. Engel (Battelle Columbus Laboratories) - National Pesticide Survey Method 2, Revision 2.0 (1987)

R. L. Graves - Method 508, Revision 3.0 (1989)

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METHOD 508

DETERMINATION OF CHLORINATED PESTICIDES IN WATER BY GAS CHROMATOGRAPHY WITH AN ELECTRON CAPTURE DETECTOR

1. SCOPE AND APPLICATION

1.1 This is a gas chromatographic (GC) method applicable to the determination of certain chlorinated pesticides in groundwater and finished drinking water. The following compounds can be determined using this method:

Analyte	Chemical Abstract Service Registry Number
Aldrin	309-00-2
Chlordane-alpha	5103-71-9
Chlordane-gamma	5103-74-2
Chlorneb	2675-77-6
Chlorobenzilate(a)	501-15-6
Chlorothalonil	2921-88-2
DCPA	1861-32-1
4,4'-DDD	72-54-8
4,4'-DDE	72-55-9
4,4'-DDT	50-29-3
Dieldrin	60-57-1
Endosulfan I	959-98-8
Endosulfan II	33213-65-9
Endosulfan sulfate	1031-07-8
Endrin	72-20-8
Endrin aldehyde	7421-93-4
Etridiazole	2593-15-9
HCH-alpha	319-84-6
HCH-beta	319-85-7
HCH-delta(a)	319-86-8
HCH-gamma (Lindane)	58-89-9
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
Hexachlorobenzene	118-74-1
Methoxychlor	72-43-5
cis-Permethrin	52645-53-1
trans-Permethrin	52645-53-1
Propachlor	1918-16-7
Trifluralin	1582-09-8
Aroclor 1016*	12674-11-2
Aroclor 1221*	11104-28-2
Aroclor 1232*	11141-16-5
Aroclor 1242*	53469-21-9
Aroclor 1248*	12672-29-6
Aroclor 1254*	11097-69-1
Aroclor 1260*	11096-82-5

Toxaphene*	8001-35-2
Chlordane*	57-74-9

* The extraction conditions of this method are comparable to USEPA Method 608, which does measure the multicomponent constituents: commercial polychlorinated biphenyl (PCB) mixtures (Aroclors), toxaphene, and chlordane. The extract derived from this procedure may be analyzed for these constituents by using the GC conditions prescribed in either Method 608 (packed column) or Methods 505, 508.1 or 525.2 (capillary column)(1). The columns used in this method may well be adequate, however, no data were collected for these constituents during methods development.

(a) Chlorbenzilate and HCH-delta are only qualitatively identified and are not quantitated because control over precision has not been accomplished.

1.2 This method has been validated in a single laboratory and estimated detection limits (EDLs) and method detection limits (MDLs) have been determined for the analytes above (Sect. 13). Observed detection limits may vary between waters, depending upon the nature of interferences in the sample matrix and the specific instrumentation used.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of GC 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 Sect. 9.3.

1.4 Analytes that are not separated chromatographically, i.e., analytes which have very similar retention times, cannot be individually identified and measured in the same calibration mixture or water sample unless an alternative technique for identification and quantitation exist (Sect. 11.5).

1.5 When this method is used to analyze unfamiliar samples for any or all of the analytes above, analyte identifications must be confirmed by at least one additional qualitative technique.

2. SUMMARY OF METHOD

2.1 A measured volume of sample of approximately 1 L is solvent extracted with methylene chloride by shaking in a separatory funnel or mechanical tumbling in a bottle. The methylene chloride extract is isolated, dried and concentrated to a volume of 5 mL after solvent substitution with methyl tert-butyl ether (MTBE). Chromatographic conditions are described which permit the separation and measurement of the analytes in the extract by capillary column GC with an electron capture detector (ECD).

3. DEFINITIONS

3.1 INTERNAL STANDARD -- A pure analyte(s) added to a solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same solution. The internal standard must be an analyte that is not a sample component.

3.2 SURROGATE ANALYTE -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction and is measured with the same procedures used to measure other sample components. The purpose of a surrogate analyte is to monitor method performance with each sample.

3.3 LABORATORY DUPLICATES (LD1 and LD2) -- Two sample aliquots taken in the analytical laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.4 FIELD DUPLICATES (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.5 LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.6 FIELD REAGENT BLANK (FRB) -- Reagent water placed in a sample container in the laboratory and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.7 LABORATORY PERFORMANCE CHECK SOLUTION (LPC) -- A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.8 LABORATORY FORTIFIED BLANK (LFB) -- An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and

whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

3.9 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.10 STOCK STANDARD SOLUTION -- A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a single analyte prepared in the laboratory with an assayed reference compound. Stock standard solutions are used to prepare primary dilution standards.

3.11 PRIMARY DILUTION STANDARD SOLUTION -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.12 CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution and stock standard solutions of the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.13 QUALITY CONTROL SAMPLE (QCS) -- a sample matrix containing method analytes or a solution of method analytes in a water miscible solvent which is used to fortify reagent water or environmental samples. The QCS is obtained from a source external to the laboratory, and is used to check laboratory performance with externally prepared test materials.

4. INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or elevated baselines in gas chromatograms. All reagents and apparatus must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Sect. 9.2.

4.1.1 Glassware must be scrupulously cleaned (2). Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot water and detergent and thorough rinsing with tap and reagent water. Drain dry, and heat in an oven or muffle furnace at 400°C for 1 hour. Do not heat volumetric glassware. Thermally stable materials such as PCBs might not be

eliminated by this treatment. Thorough rinsing with acetone may be substituted for the heating. After drying and cooling, seal and store glassware in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

4.1.2 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. WARNING: When a solvent is purified, stabilizers added by the manufacturer are removed thus potentially making the solvent hazardous. Also, when a solvent is purified, preservatives added by the manufacturer are removed thus potentially reducing the shelf-life.

4.2 Interferences by phthalate esters can pose a major problem in pesticide analysis when using the electron capture detector. These compounds generally appear in the chromatogram as large peaks. Common flexible plastics contain varying amounts of phthalates that are easily extracted or leached 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 phthalates can best be minimized by avoiding the use of plastics in the laboratory. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.

4.3 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. Between-sample rinsing of the sample syringe and associated equipment with MTBE can minimize sample cross contamination. After analysis of a sample containing high concentrations of analytes, one or more injections of MTBE should be made to ensure that accurate values are obtained for the next sample.

4.4 Matrix interferences may be caused by contaminants that are coextracted from the sample. Also, note that all the analytes listed in the Scope and Application Section are not resolved from each other on any one column, i.e., one analyte of interest may be an interferant for another analyte of interest. The extent of matrix interferences will vary considerably from source to source, depending upon the water sampled. Analyte identifications should be confirmed (Sect. 11.5).

4.5 It is important that samples and standards be contained in the same solvent, i.e., the solvent for final working standards must be the same as the final solvent used in sample preparation. If this is not the case, chromatographic comparability of standards to sample may be affected.

5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound must be treated as a potential health hazard. Accordingly, exposure to these chemicals must be reduced to the lowest possible level. 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 also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified (3-5) for the information of the analyst.

5.2 WARNING: When a solvent is purified stabilizers added by the manufacturer are removed thus potentially making the solvent hazardous.

6. EQUIPMENT AND SUPPLIES (All specifications are suggested. Catalog numbers are included for illustration only.)

6.1 SAMPLE BOTTLE -- Borosilicate, 1-L volume with graduations (Wheaton Media/Lab bottle 219820 or equivalent), fitted with screw caps lined with TFE-fluorocarbon. Protect samples from light. Amber bottles may be used. The container must be washed and dried as described in Sect. 4.1.1 before use to minimize contamination. Cap liners are cut to fit from sheets (Pierce Catalog No. 012736) and extracted with methanol overnight prior to use.

6.2 GLASSWARE

6.2.1 Separatory funnel -- 2000-mL, with TFE-fluorocarbon stopcock, ground glass or TFE-fluorocarbon stopper.

6.2.2 Tumbler bottle 1.7-L (Wheaton Roller Culture Vessel or equivalent), with TFE-fluorocarbon lined screw cap. Cap liners are cut to fit from sheets (Pierce Catalog No. 012736) and extracted with methanol overnight prior to use.

6.2.3 Flask, Erlenmeyer -- 500-mL.

6.2.4 Concentrator tube, Kuderna-Danish (K-D) 10- or 25-mL, graduated (Kontes K-570050-1025 or K-570050-2525 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stoppers are used to prevent evaporation of extracts.

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

6.2.6 Snyder column, K-D three-ball macro (Kontes K-503000-0121 or equivalent).

6.2.7 Snyder column, K-D two-ball micro (Kontes K-569001-0219 or equivalent).

6.2.8 Vials -- Glass, 5- to 10-mL capacity with TFE-fluorocarbon lined screw cap.

6.3 SEPARATORY FUNNEL SHAKER -- Capable of holding 2-L separatory funnels and shaking them with rocking motion to achieve thorough mixing of separatory funnel contents (available from Eberbach Co. in Ann Arbor, MI or other suppliers).

6.4 TUMBLER -- Capable of holding tumbler bottles and tumbling them end-over-end at 30 turns/min (Associated Design and Mfg. Co., Alexandria, VA or other suppliers.).

6.5 BOILING STONES CARBORUNDUM, #12 granules (Arthur H. Thomas Co. #1590-033 or equivalent). Heat at 400°C for 30 min prior to use. Cool and store in a desiccator.

6.6 WATER BATH -- Heated, capable of temperature control (± 2°C). The bath should be used in a hood.

6.7 BALANCE -- Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.8 GAS CHROMATOGRAPH -- Analytical system complete with temperature programmable GC suitable for use with capillary columns and all required accessories including syringes, analytical columns, gases, detector and stripchart recorder. A data system is recommended for measuring peak areas. Table 1 lists retention times observed for method analytes using the columns and analytical conditions described below.

6.8.1 Column 1 (Primary column) -- 30 m long x 0.25 mm I.D. DB-5 bonded fused silica column, 0.25 µm film thickness (J&W Scientific). Helium carrier gas flow is established at 30 cm/sec linear velocity and oven temperature is programmed from 60°C to 300°C at 4°C/min. Data presented in this method were obtained using this column. The injection volume was 2 µL splitless mode with a 45 sec. delay. The injector temperature was 250°C and the detector temperature was 320°C. Column performance criteria are presented in Table 4 (See Section 9.9). Alternative columns may be used in accordance with the provisions described in Sect. 9.4.

6.8.2 Column 2 (Alternative column) -- 30 m long x 0.25 mm I.D.DB-1701 bonded fused silica column, 0.25 µm film thickness (J&W Scientific). Helium carrier gas flow is established at 30 cm/sec linear velocity and oven temperature is programmed from 60°C to 300°C at 4°C/min.

6.8.3 Detector -- Electron capture. This detector has proven effective in the analysis of fortified reagent and artificial ground waters.

7. **REAGENTS AND STANDARDS** - - WARNING: When a solvent is purified, stabilizers added by the manufacturer are removed thus potentially making the solvent hazardous. Also, when a solvent is purified, preservatives added by the manufacturer are removed thus potentially reducing the shelf-life.

7.1 ACETONE, methylene chloride, MTBE -- Distilled-in-glass quality or equivalent.

7.2 PHOSPHATE BUFFER, pH 7 Prepare by mixing 29.6 mL 0.1 N HCl and 50 mL 0.1 M dipotassium phosphate.

7.3 SODIUM CHLORIDE, crystal, ACS grade. Heat treat in a shallow tray at 400°C for a minimum of 4 hours to remove interfering organic substances. Store in a glass bottle (not plastic) to avoid phthalate contamination.

7.4 SODIUM SULFATE, granular, anhydrous, ACS grade. Heat treat in a shallow tray at 450°C for a minimum of 4 hours to remove interfering organic substances. Store in a glass bottle (not plastic) to avoid phthalate contamination.

7.5 SODIUM THIOSULFATE, granular, anhydrous, ACS grade.

7.6 PENTACHLORONITROBENZENE (PCNB) 98% purity, for use as internal standard.

7.7 DECACHLOROBIPHENYL (DCB) 96% purity, for use as surrogate standard (available from Chemicals Procurement Inc.).

7.8 MERCURIC CHLORIDE -- ACS grade -- for use as a bactericide (optional).

7.9 REAGENT WATER -- Reagent water is defined as water that is reasonably free of contamination that would prevent the determination of any analyte of interest. Reagent water used to generate the validation data in this method was distilled water obtained from the Magnetic Springs Water Co., Columbus, Ohio.

7.10 STOCK STANDARD SOLUTIONS (1.00 $\mu g/\mu L$) -- Stock standard solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedure:

7.10.1 Prepare stock standard solutions by accurately weighing approximately 0.0100 g of pure material. Dissolve the material in MTBE and dilute to volume in a 10-mL volumetric flask. 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. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.10.2 Transfer the stock standard solutions into TFE-fluorocarbon-sealed screw cap amber vials. Store at room temperature and protect from light.

7.10.3 Stock standard solutions should be replaced after two months or sooner if comparison with laboratory fortified blanks, or QC samples indicate a problem.

7.11 INTERNAL STANDARD SOLUTION -- Prepare an internal standard fortifying solution by accurately weighing approximately 0.0010 g of pure PCNB. Dissolve the PCNB in MTBE and dilute to volume in a 10-mL volumetric flask. Transfer the internal standard solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Addition of 5 µL of the internal standard fortifying solution to 5 mL of sample extract results in a final internal standard concentration of 0.1 µg/mL. Solution should be replaced when ongoing QC (Sect. 9) indicates a problem. Note that PCNB has been shown to be an effective internal standard for the method analytes, but other compounds may be used if the quality control requirements in Section 9 are met.

7.12 SURROGATE STANDARD SOLUTION -- Prepare a surrogate standard fortifying solution by accurately weighing approximately 0.0050 g of pure DCB. Dissolve the DCB in MTBE and dilute to volume in a 10-mL volumetric flask. Transfer the surrogate standard fortifying solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Addition of 50 µL of the surrogate standard fortifying solution to a 1-L sample prior to extraction results in a surrogate standard concentration in the sample of 25 µg/L and, assuming quantitative recovery of DCB, a surrogate standard concentration in the final extract of 5.0 µg/mL. Solution should be replaced when ongoing QC (Sect. 9) indicates a problem. Note DCB has been shown to be an effective surrogate standard for the method analytes, but other compounds may be used if the quality control requirements in Section 9 are met.

7.13 LABORATORY PERFORMANCE CHECK SOLUTION -- Prepare by accurately weighing 0.0010 g each of chlorothalonil, chlorpyrifos, DCPA, and HCH-delta. Dissolve each analyte in MTBE and dilute to volume in individual 10-mL volumetric flasks. Combine 2 µL of the chloropyrifos stock solution, 50 µL of the DCPA stock solution, 50 µL of the chlorothalonil stock solution, and 40 µL of the HCH-delta stock solution to a 100-mL volumetric flask and dilute to volume with MTBE. Transfer to a TFE-fluorcarbon-sealed screw cap bottle and store at room temperature. Solution should be replaced when ongoing QC indicates a problem.

7.14 GC DEGRADATION CHECK SOLUTION -- Prepare a solution in MTBE containing endrin and 4,4'-DDT each at a concentration of 1 µg/mL. This solution will be injected to check for undesirable degradation of these compounds in the injection port by looking for endrin aldehyde and endrin ketone or for 4,4'- DDE and 4,4'- DDD.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Grab samples must be collected in glass containers. Conventional sampling practices (6) should be followed; however, the bottle must not be prerinsed with sample before collection.

8.2 SAMPLE PRESERVATION

8.2.1 If residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample to the sample bottle prior to collecting the sample.

8.2.2 After adding the sample to the bottle containing sodium thiosulfate, seal the sample bottle and shake until dissolved.

8.2.3 Samples must be iced or refrigerated at 4°C from the time of collection until extraction. Preservation study results indicate that most of the target analytes present in the samples are stable for 7 days when stored under these conditions. Preservation data for the analytes chlorthalonil, alpha-HCH, delta-HCH, gamma-HCH, cis-permethrin, trans-permethrin, and trifluralin are nondefinitive, and therefore if these are analytes of interest, it is recommended that the samples be analyzed immediately. Analyte stability may be affected by the matrix; therefore, the analyst should verify that the preservation technique is applicable to the samples under study.

8.2.4 All performance data presented in this method are from samples preserved with mercuric chloride. No suitable preservation agent (biocide) has been found other than mercuric chloride. However, the use of mercuric chloride is not required due to its toxicity and potential harm to the environment.

8.2.5 In some circumstances where biological degradation of target pesticides might be expected, use of mercuric chloride may be appropriate to minimize the possibility of false-negative results. If mercuric chloride is to be used, add it to the sample bottle in amounts to produce a concentration of 10 mg/L. Add 1 mL of a solution containing 10 mg/mL of mercuric chloride in reagent water to the sample bottle at the sampling site or in the laboratory before shipping to the sampling site. A major disadvantage of mercuric chloride is

that it is a highly toxic chemical; mercuric chloride must be handled with caution, and samples containing mercuric chloride must be disposed of properly.

8.3 EXTRACT STORAGE

8.3.1 Sample extracts should be stored at 4°C away from light. A 14-day maximum extract storage time is recommended. However, analyte stability may be affected by the matrix; therefore, the analyst should verify appropriate extract holding times applicable to the samples under study.

9. QUALITY CONTROL

9.1 Minimum quality control (QC) requirements are initial demonstration of laboratory capability, determination of surrogate compound recoveries in each sample and blank, monitoring internal standard peak area or height in each sample and blank (when internal standard calibration procedures are being employed), analysis of laboratory reagent blanks, laboratory fortified samples, laboratory fortified blanks, and QC samples. An MDL for each analyte must also be determined.

9.2 Laboratory Reagent Blanks -- Before processing any samples, the analyst must demonstrate that all glassware and reagent interferences are under control. Each time a set of samples is extracted or reagents are changed, a laboratory reagent blank (LRB) must be analyzed. If within the retention time window of any analyte of interest the LRB produces a peak that would prevent the determination of that analyte, determine the source of contamination and eliminate the interference before processing samples.

9.3 INITIAL DEMONSTRATION OF CAPABILITY

9.3.1 Select a representative fortified concentration (about 10 times EDL or at a concentration that represents a mid-point of the calibration range for each analyte. Prepare a primary dilution standard (in methanol) containing each analyte at 1000 times selected concentration. With a syringe, add 1 mL of the concentrate to each of four to seven 1-L aliquots of reagent water, and analyze each of these LFBs according to procedures beginning in Section 11.

9.3.2 For each analyte, the recovery value for all replicates must fall in the range of R ± 30% using the value for R demonstrated for reagent water in Table 2. The precision of the measurements, calculated as relative standard deviation (RSD), must be 20% or less. For those compounds that fail these criteria, this procedure must be repeated using four fresh samples until satisfactory performance has been demonstrated.

9.3.3 For each analyte, determine the MDL. Prepare a minimum of 7 LFBs at a low concentration. Fortification concentration in Table 3 may be used as a guide, or use calibration data obtained in Section 10 to estimate a concentration for each analyte that will produce a peak with a 3-5 times signal to noise response. Extract and analyze each replicate according to Sections 11 and 12. It is recommended that these LFBs be prepared and analyzed over a period of several days, so that day to day variations are reflected in the precision data. Calculate mean recovery and standard deviation for each analyte. Use the equation given in Table 3 to calculate the MDL.

9.3.4 The initial demonstration of capability is used primarily to preclude a laboratory from analyzing unknown samples via a new, unfamiliar method prior to obtaining some experience with it. It is expected that as laboratory personnel gain experience with this method the quality of data will improve beyond those required here.

9.4 The analyst is permitted to modify GC columns, GC conditions, concentration techniques (i.e. evaporation techniques), internal standards or surrogate compounds. Each time such method modifications are made, the analyst must repeat the procedures in Section 9.3.

9.5 ASSESSING SURROGATE RECOVERY

9.5.1 When surrogate recovery from a sample or method blank is <70% or >130%, check calculations to locate possible errors, fortifying solutions for degradation, contamination or other obvious abnormalities, and instrument performance. If those steps do not reveal the cause of the problem, reanalyze the extract.

9.5.2 If a LRB extract reanalysis fails the 70-130% recovery criterion, the problem must be identified and corrected before continuing.

9.5.3 If sample extract reanalysis meets the surrogate recovery criterion, report only data for the reanalyzed extract. If sample extract reanalysis continues to fail the surrogate recovery criterion, report all data for that sample as suspect.

9.6 ASSESSING THE INTERNAL STANDARD

9.6.1 When using the internal standard calibration procedure, the analyst must monitor the IS response (peak area or peak height) of all samples during each analysis day. The IS response for any sample chromatogram should not deviate from

the daily calibration check standards IS response by more than 30%.

9.6.2 If >30% deviation occurs with an individual extract, optimize instrument performance and inject a second aliquot of that extract.

9.6.2.1 If the reinjected aliquot produces an acceptable internal standard response report results for that aliquot.

9.6.2.2 If a deviation of greater than 30% is obtained for the re-injected extract, analysis of the sample should be repeated beginning with Section 11, provided the sample is still available. Otherwise, report results obtained from the re-injected extract, but annotate as suspect.

9.6.3 If consecutive samples fail the IS response acceptance criterion, immediately analyze a calibration check standard.

9.6.3.1 If the check standard provides a response factor (RF) within 20% of the predicted value, then follow procedures itemized in Section 9.6.2 for each sample failing the IS response criterion.

9.6.3.2 If the check standard provides a response factor which deviates more than 20% of the predicted value, then the analyst must recalibrate, as specified in Section 10. After calibration is restored, reanalyze sample extracts that failed Sect 9.6.2 criteria.

9.7 ASSESSING LABORATORY PERFORMANCE - LABORATORY FORTIFIED BLANK

9.7.1 The laboratory must analyze at least one laboratory fortified blank (LFB) sample with every twenty samples or one per sample set (all samples extracted within a 24-h period) whichever is greater. The fortified concentration of each analyte in the LFB should be 10 times EDL or a concentration that represents a mid-point of the calibration range. Calculate accuracy as percent recovery (X_i). If the recovery of any analyte falls outside the control limits (see Sect. 9.7.2), that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

Note: It is suggested that one multi-component analyte (toxaphene, chlordane or an Aroclor) LFB also be analyzed with each sample set. By selecting a different multi-component analyte for this LFB each work shift, LFB data can

be obtained for all of these analytes over the course of several days.

9.7.2 Until sufficient data becomes available from within their own laboratory, usually a minimum of results from 20 to 30 analyses, the laboratory should assess laboratory performance against the control limits in Sect. 9.3.2 that are derived from the data in Table 2. When sufficient internal performance data becomes available, develop control limits from the mean percent recovery ($\bar{X}$) and standard deviation (S) of the percent recovery. These data are used to establish upper and lower control limits as follows:

$$\text{UPPER CONTROL LIMIT} = \bar{X} + 3S$$
$$\text{LOWER CONTROL LIMIT} = \bar{X} - 3S$$

After each five to ten new recovery measurements, new control limits should be calculated using only the most recent 20-30 data points. These calculated control limits should <u>not</u> exceed those established in Sect. 9.3.2.

9.7.3 It is recommended that the laboratory periodically document and determine its detection limit capabilities for the analytes of interest.

9.7.4 At least quarterly, analyze a QC sample from an outside source.

9.8 ASSESSING METHOD PERFORMANCE - LABORATORY FORTIFIED SAMPLE MATRIX

9.8.1 The laboratory must add a known concentration to a minimum of 10% of the routine samples or one sample per set, whichever is greater. The added concentration should not be less then the background concentration of the sample selected for fortification. Ideally, the fortified analyte concentrations should be the same as that used for the LFB (Section 9.7). Over time, samples from all routine sample sources should be fortified.

9.8.2 Calculate the percent recovery, P, of the concentration for each analyte, after correcting the analytical result, X, from the fortified sample for the background concentration, b, measured in the unfortified sample, i.e.,:

$$P = 100\ (X - b)\ /\ \text{fortifying concentration},$$

and compare these values to reagent water recoveries listed in Table 2. The calculated value of P must fall in the range of R ± 35%. If P exceeds this control limit, and the laboratory performance for that analyte is shown to be in control (Sect. 9.7), the recovery problem encountered with the dosed sample is judged to be matrix related, not system

related. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

9.9 ASSESSING INSTRUMENT SYSTEM - LABORATORY PERFORMANCE CHECK (LPC)

9.9.1 Laboratory performance check (LPC). After initial demonstration of capability, instrument performance should be monitored on a daily basis by analysis of the LPC sample. The LPC sample contains compounds designed to monitor instrument sensitivity, column performance (primary column) and chromatographic performance. LPC sample components and performance criteria are listed in Table 4. Inability to demonstrate acceptable instrument performance indicates the need for reevaluation of the instrument system. The sensitivity requirements are set based on the EDLs published in this method. If laboratory EDLs differ from those listed in this method, concentrations of the LPC standard compounds must be adjusted to be compatible with the laboratory EDLs.

9.9.2 Degradation of DDT and endrin caused by active sites in the injection port and GC columns may occur. This should be checked on a daily basis by injecting the GC degradation check solution. Look for the degradation products of 4,4'-DDT (4,4'-DDE and 4,4'-DDD) and the degradation products of endrin (endrin aldehyde, EA and endrin ketone, EK). For 4,4'-DDT, these products will elute just before the parent, and for endrin, the products will elute just after the parent. If degradation of either DDT or endrin exceeds 20%, resilanize the injection port liner and/or break off a meter from the front of the column. The degradation check solution is required each day in which analyses are performed.

$$\text{\% degrade of 4,4'DDT} = \frac{\text{Total DDT degradation peak area (DDE+DDD)}}{\text{Total DDT peak area (DDT+DDE+DDD)}} \times 100$$

$$\text{\% degrade of endrin} = \frac{\text{Total EA + EK peak area}}{\text{Total endrin+EA+EK area}} \times 100$$

NOTE: If the analyst can verify that 4,4 DDT, endrin, their breakdown products, and the analytes in the IPC solution are all resolved, the IPC solution and the GC degradation check solution may be prepared and analyzed as a single solution.

9.10 The laboratory may adopt additional quality control 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. For example, field or laboratory duplicates may be analyzed to assess the precision of the environmental measurements or field reagent blanks may be used to asses contamination of samples under site conditions, transportation and storage.

10. CALIBRATION

10.1 Establish GC operating parameters equivalent to those indicated in Sect. 6.8. The GC system must be calibrated using the internal standard technique (Sect. 10.2) or the external standard technique (Sect. 10.3). Perform the endrin and DDT degradation check described in Sect. 9.9.2. If degradation of either DDT or endrin exceeds 20%, take corrective action before proceeding with calibration.

10.2 INTERNAL STANDARD CALIBRATION PROCEDURE -- To use this approach, the analyst must select one or more internal standards compatible 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. PCNB has been identified as a suitable internal standard. Data presented in this method were generated using the internal standard calibration procedure.

10.2.1 Prepare calibration standards at a minimum of three (recommend five) concentration levels for each analyte of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more of the internal standards, and dilute to volume with MTBE. Guidance on the number of standards is as follows: A minimum of three calibration standards are required to calibrate a range of a factor of 20 in concentration. For a factor of 50, use at least four standards, and for a factor of 100, at least five standards. The lowest standard should represent analyte concentrations near, but above, their respective EDLs. The remaining standards should bracket the analyte concentrations expected in the sample extracts, or should define the working range of the detector. The calibration standards must bracket the analyte concentration found in the sample extracts. NOTE: Calibration standard solutions must be prepared such that no unresolved analytes are mixed together, and calibration standards for toxaphene, chlordane and each of the Aroclors must be prepared individually.

10.2.2 Analyze each calibration standard according to the procedure (Sect. 11.4). Tabulate response (peak height or area) against concentration for each compound and internal standard. Calculate the response factor (RF) for each analyte and surrogate using Equation 1. RF is a unitless value.

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)} \qquad \text{Equation 1}$$

where :

A_s = Response for the analyte to be measured.
A_{is} = Response for the internal standard.
C_{is} = Concentration of the internal standard (µg/L).
C_s = Concentration of the analyte to be measured (µg/L).

Note: For options on calculating response factors for multi-component analytes refer to Sect. 12.4.

10.2.3 If the RF value over the working range is constant (20% RSD or less) the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios (A_s/A_{is}) vs. C_s.

10.2.4 The working calibration curve or calibration factor must be verified on each working day by the measurement of a minimum of two calibration check standards, one at the beginning and one at the end of the analysis day. These check standards should be at two different concentration levels to verify the calibration curve. For extended periods of analysis (greater than 8 hrs.), it is strongly recommended that check standards be interspersed with samples at regular intervals during the course of the analyses. If the response for any analyte varies from the predicted response by more than ±20%, the test must be repeated using a fresh calibration standard. If the results still do not agree, generate a new calibration curve. For those analytes that failed the calibration verification, results from field samples analyzed since the last passing calibration should be considered suspect. Reanalyze sample extracts for these analytes after acceptable calibration is restored. WARNING: A dirty injector insert will cause poor sensitivity for the late eluting analytes.

NOTE: It is suggested that a calibration verification standard of one multi-component analyte also be analyzed each day or work shift. By alternating the selection of the multi-component analyte chosen, continuing calibration data can be obtained for all of these analytes over a period of several days.

10.2.5 Verify calibration standards periodically, recommend at least quarterly, by analyzing a standard prepared from reference material obtained from an independent source (QCS). Results from these analyses must be within the limits used to routinely check calibration (Sect. 10.2.4).

10.3 EXTERNAL STANDARD CALIBRATION PROCEDURE

10.3.1 Prepare calibration standards as in Section 10.2.1, omitting the use of the internal standard.

10.3.2 Starting with the standard of lowest concentration, analyze each calibration standard according to Sect. 11.4 and

tabulate response (peak height or area) versus the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (20% RSD or less), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

Note: For options on calulating a calibration factor for multi-component analytes, refer to Sect. 12.4.

10.3.3 The working calibration curve or calibration factor must be verified on each working day by the procedures described in Section 10.2.4. Note: It is suggested that one multi-component analyte calibration be verified each day or work shift. By alternating the selection of the analyte (an Aroclor or toxaphene), calibration verification data can be obtained for all these analytes over a period of several days.

10.3.4 Verify calibration standards periodically (at least quarterly), by analyzing a QCS.

11. PROCEDURE

11.1 EXTRACTION (MANUAL METHOD)

11.1.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume (Sect. 11.1.6). Add preservative to LRBs and LFBs. Fortify the sample with 50 μL of the surrogate standard fortifying solution. Pour the entire sample into a 2-L separatory funnel.

11.1.2 Adjust the sample to pH 7 by adding 50 mL of phosphate buffer. Check pH: add H_2SO_4 or NaOH if necessary.

11.1.3 Add 100 g NaCl to the sample, seal, and shake to dissolve salt.

11.1.4 Add 60 mL methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner walls. Transfer the solvent to the separatory funnel 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 technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool,

centrifugation, or other physical methods. Collect the methylene chloride extract in a 500-mL Erlenmeyer flask.

11.1.5 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

11.1.6 Determine the original sample volume by refilling the sample bottle to the mark and transferring the water to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11.2 AUTOMATED EXTRACTION METHOD -- Data presented in this method were generated using the automated extraction procedure with the mechanical tumbler.

11.2.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume (Sect. 11.2.6). Add preservative to LRBs and LFBs. Fortify the sample with 50 μL of the surrogate standard fortifying solution. If the mechanical separatory funnel shaker is used, pour the entire sample into a 2-L separatory funnel. If the mechanical tumbler is used, pour the entire sample into a tumbler bottle.

11.2.2 Adjust the sample to pH 7 by adding 50 mL of phosphate buffer. Check pH: add H_2SO_4 or NaOH if necessary.

11.2.3 Add 100 g NaCl to the sample, seal, and shake to dissolve salt.

11.2.4 Add 300 mL methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner walls. Transfer the solvent to the sample contained in the separatory funnel or tumbler bottle, seal, and shake for 10 s, venting periodically. Repeat shaking and venting until pressure release is not observed during venting. Reseal and place sample container in appropriate mechanical mixing device (separatory funnel shaker or tumbler). Shake or tumble the sample for 1 hour. Complete mixing of the organic and aqueous phases should be observed within about 2 min after starting the mixing device.

11.2.5 Remove the sample container from the mixing device. If the tumbler is used, pour contents of tumbler bottle into a 2-L separatory funnel. 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 technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other

physical methods. Collect the methylene chloride extract in a 500-mL Erlenmeyer flask.

11.2.6 Determine the original sample volume by refilling the sample bottle to the mark and transferring the water to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11.3 EXTRACT CONCENTRATION

11.3.1 Assemble a K-D concentrator by attaching a 25-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D if the requirements of Sect. 9.3 are met.

11.3.2 Dry the extract by pouring it through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate. Collect the extract in the K-D concentrator, and rinse the column with 20-30 mL methylene chloride. Add this rinse to the extract. Alternatively, add about 5 g anhydrous sodium sulfate to dry the extract in the Erlenmeyer flask; swirl the flask to dry extract and allow to sit for 15 min. Decant the methylene chloride extract into the K-D concentrator. Rinse the remaining sodium sulfate with two 25-mL portions of methylene chloride and decant the rinses into the K-D concentrator.

11.3.3 Add 1 to 2 clean boiling stones to the evaporative flask and attach a macro 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, 65 to 70°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 15 to 20 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 2 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

11.3.4 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of MTBE. Add 5-10 mL of MTBE and a fresh boiling stone. Attach a micro-Snyder column to the concentrator tube and prewet the column by adding about 0.5 mL of MTBE 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 to 10 min. When the apparent volume of liquid reaches 2 mL, remove the micro K-D from the bath and allow it to drain and cool.

Add 5-10 mL MTBE to the micro K-D and reconcentrate to 2 mL. Remove the micro K-D from the bath and allow it to drain and cool. Remove the micro Snyder column, and rinse the walls of the concentrator tube while adjusting the volume to 5.0 mL with MTBE.

11.3.5 Transfer extract to an appropriate-sized TFE-fluorocarbon-sealed screw-cap vial and store, refrigerated at 4°C, until analysis by GC-ECD.

11.4 GAS CHROMATOGRAPHY

11.4.1 Sect. 6.8 summarizes the recommended operating conditions for the gas chromatograph. Included in Table 1 are retention times observed using this method. Other GC columns, chromatographic conditions, or detectors may be used if the requirements of Sect. 9.3 are met.

11.4.2 Calibrate or verify the system calibration daily as described in Sect. 10. The standards and extracts must be in MTBE.

11.4.3 If the internal standard calibration procedure is used, add 5 µL of the internal standard fortifying solution to the sample extract, seal, and shake to distribute the internal standard.

11.4.4 Inject 2 µL of the sample extract. Record the resulting peak size in area units.

11.4.5 If the response for the peak exceeds the working range of the system, dilute the extract and reanalyze. If internal standard calibration has been used, add an appropriate amount of additional internal standard to maintain the a concentration of 0.1 µg/mL.

11.5 IDENTIFICATION OF ANALYTES

11.5.1 Identify a sample component by comparison of its retention time to the retention time of a reference chromatogram. If the retention time of an unknown compound corresponds, within limits, to the retention time of a standard compound, then identification is considered positive.

11.5.2 The width of the retention time window used to make identifications should be based upon 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.

11.5.3 Identification requires expert judgment when sample components are not resolved chromatographically. When GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), or any time doubt exists over the identification of a peak on a chromatogram, appropriate alternate techniques, to help confirm peak identification, need to be employed. For example, more positive identification may be made by the use of an alternative detector which operates on a chemical/physical principle different from that originally used; e.g., mass spectrometry (Method 525.2) (1), or the use of a second chromatography column. A suggested alternative column is described in Sect. 6.8.

Note: Identify multi-component analytes by comparison of the sample chromatogram to the corresponding calibration standard chromatograms of chlordane, toxaphene and the Aroclors. Identification of multi-component analytes is made by pattern recognition, in which the experience of the analyst is an important factor.

12. CALCULATIONS

12.1 Calculate analyte concentrations in the sample from the response for the analyte using one of the multi-point calibration procedures described in Sect. 10. Do not use the daily calibration verification standard to calculate the amount of method analytes in samples.

12.2 If the internal standard calibration procedure is used, calculate the concentration (C) in the sample using the calibration curve or response factor (RF) determined in Sect. 10.2 and Equation 2. RF is a unitless value.

$$C\ (\mu g/L) = \frac{(A_s)(I_s)}{(A_{is})(RF)(V_o)} \qquad \text{Equation 2}$$

where:

A_s = Response for the parameter to be measured.
A_{is} = Response for the internal standard.
I_s = Amount of internal standard added to each extract (μg).
V_o = Volume of water extracted (L).

12.3 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor determined in Section 10.3. The concentration (C) in the sample can be calculated from Equation 3.

$$C\ (\mu g/L) = \frac{(A)(V_t)}{(V_i)(V_s)} \qquad \text{Equation 3}$$

where:

A = Amount of material injected (ng).
V_i = Volume of extract injected (μL).
V_t = Volume of total extract (μL).
V_s = Volume of water extracted (mL).

12.4 To quantitate multi-component analytes, one of the following methods should be used.
Option 1- Calculate an average response factor, calibration factor or linear regression equation for each multi-component analyte using the combined area of all the component peaks in each of the calibration standard chromatograms.
Option 2- Calculate an average response factor, calibration factor or linear regression equation for each multi-component analyte using the combined areas of 3-6 of the most intense and reproducible peaks in each of the calibration standard chromatograms.

When quantifying multi-component analytes in samples, the analyst should use caution to include only those peaks from the sample that are attributable to the multi-component analyte. Option 1 should not be used if there are significant interference peaks within the chlordane, Aroclor or toxaphene pattern.

13. PRECISION AND ACCURACY

13.1 In a single laboratory, analyte recoveries from reagent water were used to determine analyte MDLs, EDLs (Table 3) and demonstrate method range. Analytes were divided into two fortified groups for recovery studies. Analyte recoveries and standard deviation about the percent recoveries at one concentration are given in Tables 2 and 3.

13.2 In a single laboratory, analyte recoveries from two standard synthetic ground waters were determined at one concentration level. Results were used to demonstrate applicability of the method to different ground water matrices. Analyte recoveries from the two synthetic matrices are given in Table 2.

14. POLLUTION PREVENTION

14.1 This method uses significant volumes of organic solvents. It is highly recommended that laboratories use solvent recovery systems to recover used solvent as sample extracts are being concentrated. Recovered solvents should be recycled or properly disposed of.

14.2 For information about pollution prevention that may be applicable to laboratory operations, consult "Less is Better: Laboratory Chemical Management for Waste Reduction" available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

15. WASTE MANAGEMENT

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions. The laboratory using this method has the responsibility to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations. For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel," also available from the American Chemical Society at the address in Sect. 14.2.

16. REFERENCES

1. "Methods for the Determination of Organic Compounds in Drinking Water, Supplement 3", (1995). USEPA, National Exposure Research Laboratory, Cincinnati, Ohio, 45268.

2. ASTM Annual Book of Standards, Part 11, Volume 11.02, D3694-82, "Standard Practice for Preparation of Sample Containers and for Preservation," American Society for Testing and Materials, Philadelphia, PA, 1986.

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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. ASTM Annual Book of Standards, Part 11, Volume 11.01, D3370-82, "Standard Practice for Sampling Water," American Society for Testing and Materials, Philadelphia, PA, 1986.

17. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

TABLE 1. RETENTION TIMES FOR METHOD ANALYTES

	Retention Time[a] (minutes)	
	Primary	Alternative
Etridiazole	23.46	22.78
Chlorneb	25.50	26.18
Propachlor	28.90	30.94
Trifluralin	31.62	(b)
HCH-alpha	31.62	32.98
Hexachlorobenzene	31.96	(b)
HCH-beta	33.32	40.12
HCH-gamma	33.66	35.36
PCNB (internal std.)	34.00	34.00
HCH-delta	35.02	41.48
Chlorthalonil	35.36	39.78
Heptachlor	37.74	36.72
Aldrin	40.12	38.08
Chlorpyrifos	40.6	(b)
DCPA	41.14	41.14
Heptachlor epoxide	42.16	42.16
Chlordane-gamma	43.52	43.86
Endosulfan I	44.20	43.52
Chlordane-alpha	44.54	44.54
4,4'-DDE	45.90	44.88
Dieldrin	45.90	45.90
Endrin	46.92	(b)
Endosulfan II	47.60	51.68
Chlorobenzilate	47.94	48.28
4,4'-DDD	48.28	46.92
Endrin aldehyde	48.62	46.92
Endosulfan sulfate	49.98	49.30
4,4'-DDT	50.32	50.32
Methoxychlor	53.38	53.72
cis-Permethrin	58.48	(b)
trans-Permethrin	58.82	(b)
DCB	64.10	(b)

[a] Columns and analytical conditions are described in Sect. 6.8.1 and 6.8.2.
[b] Data not available.

TABLE 2. SINGLE LABORATORY ACCURACY AND PRECISION FOR ANALYTES FROM REAGENT WATER AND SYNTHETIC GROUNDWATERS[a]

Analyte	Fortified Conc. µg/L	Reagent Water R[b]	Reagent Water S_R[c]	Synthetic Water 1[d] R	Synthetic Water 1[d] S_R	Synthetic Water 2[e] R	Synthetic Water 2[e] S_R
Aldrin	0.15	86	9.5	100	11.0	69	9.0
Chlordane-alpha	0.15	99	11.9	96	12.5	99	7.9
Chlordane-gamma	0.15	99	11.9	96	12.5	99	6.9
Chlorneb	5.0	97	11.6	95	6.7	75	8.3
Chlorobenzilate	10.	108	5.4	98	10.8	102	9.2
Chlorthalonil	0.25	91	8.2	103	10.3	71	9.2
DCPA	0.25	103	12.4	100	13.0	101	6.1
4,4'-DDD	0.25	107	6.4	96	8.6	101	7.1
4,4'-DDE	0.10	99	11.9	96	12.5	99	6.9
4,4'-DDT	0.60	112	16.8	98	11.8	84	8.4
Dieldrin	0.20	87	8.7	103	9.3	82	7.4
Endosulfan I	0.15	87	8.7	102	8.2	84	8.4
Endosulfan sulfate	0.15	102	15.3	94	1.3	72	12.2
Endrin	0.15	88	8.8	98	9.8	104	9.4
Endrin aldehyde	0.25	88	7.9	103	11.3	84	9.2
Endosulfan II	0.15	92	10.1	98	10.8	76	6.8
Etridiazole	0.25	103	6.2	91	6.4	98	3.9
HCH-alpha	0.05	92	10.1	106	7.4	86	7.7
HCH-beta	0.10	95	6.7	92	5.5	100	6.0
HCH-delta	0.10	102	11.2	99	11.9	103	6.2
HCH-gamma	0.15	89	9.8	115	6.9	85	7.7
Heptachlor	0.10	98	11.8	85	11.1	85	7.7
Heptachlor epoxide	0.15	87	8.7	103	7.2	82	9.8
Hexachlorobenzene	0.05	99	21.8	82	9.8	68	4.8
Methoxychlor	0.5	105	13.7	101	10.1	104	6.2
cis-Permethrin	5.0	91	9.1	96	11.5	86	9.5
trans-Permethrin	5.0	111	6.7	97	9.7	102	7.1
Propachlor	5.0	103	9.3	116	4.6	95	7.6
Trifluralin	0.25	103	5.2	86	10.3	87	9.6

TABLE 2. (Continued)

[a] Data corrected for amount detected in blank and represent the mean of 7-8 samples.

[b] R = average percent recovery.

[c] S_R = standard deviation of the percent recovery.

[d] Corrected for amount found in blank; Absopure Nature Artesian Spring Water Obtained from the Absopure Water Company in Plymouth, Michigan.

[e] Corrected for amount found in blank; reagent water fortified with fulvic acid at the 1 mg/L concentration level. A well-characterized fulvic acid, available from the International Humic Substances Society (associated with the United States Geological Survey in Denver, Colorado), was used.

TABLE 3.
SINGLE LABORATORY ACCURACY, PRECISION, METHOD DETECTION LIMITS (MDLs) AND ESTIMATED DETECTION LIMITS (EDLs) FOR ANALYTES FROM REAGENT WATER

	Fortified Conc. µg/L	N[a]	Recovery %	RSD %	MDL[b] µg/L	EDL[c] µg/L
Aldrin	0.075	7	66	9	0.014	0.075
Chlordane-alpha	0.015	7	117	8	0.0041	0.0015
Chlordane-gamma	0.015	7	109	3	0.0016	0.0015
Chlorneb	0.50	7	47	34	0.25	0.5
Chlorobenzilate	5.0	8	99	5	2.2	5.0
Chlorothalonil	0.025	7	119	12	0.011	0.025
DCPA	0.025	7	112	4	0.0032	0.025
4,4'-DDD	0.025	7	115	5	0.0044	0.025
4,4'-DDE	0.010	7	127	6	0.0025	0.01
4,4'-DDT	0.060	7	87	23	0.039	0.06
Dieldrin	0.020	7	77	22	0.011	0.02
Endosulfan I	0.015	7	78	25	0.0092	0.015
Endosulfan sulfate	0.015	7	129	4	0.0024	0.015
Endrin	0.015	7	72	18	0.0062	0.015
Endrin aldehyde	0.025	7	95	15	0.011	0.025
Endosulfan II	0.015	7	148	35	0.024	0.024
Etridiazole	0.025	7	96	17	0.013	0.025
HCH-alpha	0.025	8	94	8	0.0053	0.025
HCH-beta	0.010	7	95	12	0.0036	0.01
HCH-delta	0.010	7	84	7	0.0020	0.01
HCH-gamma	0.015	7	80	16	0.0060	0.015
Heptachlor	0.010	7	67	7	0.0015	0.01
Heptachlor epoxide	0.015	7	71	18	0.0059	0.015
Hexachlorobenzene	0.0050	7	115	43	0.0077	0.0077
Methoxychlor	0.050	7	120	11	0.022	0.05
cis-Permethrin	0.50	7	64	24	0.25	0.50
trans-Permethrin	0.50	7	122	9	0.18	0.50
Propachlor	0.50	7	90	18	0.25	0.50
Trifluralin	0.025	7	108	3	0.0026	0.025

[a] N = Number of replicates

[b] With these data, the method detection limits (MDL) in the tables were calculated using the formula:

$$MDL = S\ t_{(n-1,1-alpha = 0.99)}$$

where:

$t_{(n-1,1-alpha = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom.

n = number of replicates

S = standard deviation of replicate analyses.

[c] EDL = estimated detection limit; defined as either MDL (Appendix B to 40 CFR Part 136 - Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11) or a level of compound in a sample yielding a peak in the final extract with signal-to-noise ratio of approximately 5, whichever value is higher.

TABLE 4. LABORATORY PERFORMANCE CHECK SOLUTION

Test	Analyte	Conc, µg/mL	Requirements
Sensitivity	Chlorpyrifos	0.0020	Detection of analyte; S/N > 3
Chromatographic performance	DCPA	0.0500	PGF between 0.80 and 1.15[a]
Column performance	Chlorothalonil HCH-delta	0.0500 0.0400	Resolution > 0.50[b]

[a] PGF - peak Gaussian factor. Calculated using the equation:

$$PGF = \frac{1.83 \times W(1/2)}{W(1/10)}$$

where W(1/2) is the peak width at half height in secs, and W(1/10) is the peak width in secs. at tenth height.

[b] Resolution between the two peaks as defined by the equation:

$$R = \frac{t}{W}$$

where t is the difference in elution times between the two peaks and W is the average peak width, at the baseline, of the two peaks.

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METHOD 508.1 DETERMINATION OF CHLORINATED PESTICIDES, HERBICIDES, AND ORGANOHALIDES BY LIQUID-SOLID EXTRACTION AND ELECTRON CAPTURE GAS CHROMATOGRAPHY

Revision 2.0

James W. Eichelberger - Revision 1.0, 1994

Jean W. Munch - Revision 2.0, 1995

NATIONAL EXPOSURE RESEARCH LABORATORY
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METHOD 508.1

DETERMINATION OF CHLORINATED PESTICIDES, HERBICIDES, AND ORGANOHALIDES IN WATER USING LIQUID-SOLID EXTRACTION AND ELECTRON CAPTURE GAS CHROMATOGRAPHY

1. SCOPE AND APPLICATION

1.1 This method utilizes disk liquid-solid extraction and gas chromatography with an electron capture detector to determine twenty nine chlorinated pesticides, three herbicides, and four organohalides in drinking water, ground water, and drinking water in any treatment stage. Liquid solid extraction cartridges may also be used to carry out sample extractions. Single laboratory accuracy, precision, and method detection limit data have been determined for the following compounds:

Analyte	Chemical Abstracts Service Registry No.
Alachlor	15972-60-8
Aldrin	309-00-2
Atrazine	1912-24-9
Butachlor	23184-66-9
Chlordane-alpha	5103-71-9
Chlordane-gamma	5103-74-2
Chloroneb	2675-77-6
Chlorbenzilate	510-15-6
Chlorthalonil	1897-45-6
Cyanazine	21725-46-2
DCPA	1861-32-1
4,4'-DDD	72-54-8
4,4'-DDE	72-55-9
4,4'-DDT	50-29-3
Dieldrin	60-57-1
Endosulfan I	959-98-8
Endosulfan II	33213-65-9
Endosulfan sulfate	1031-07-8
Endrin	72-20-8
Endrin aldehyde	7421-93-4
Etridiazole	2593-15-9
HCH-alpha	319-84-6
HCH-beta	319-85-7
HCH-delta	319-86-8
HCH-gamma (lindane)	58-89-9
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
Hexachlorobenzene	118-74-1
Hexachlorocyclopentadiene	77-47-4
Methoxychlor	72-43-5
Metolachlor	51218-45-2
Metribuzin	21087-64-9

Analyte	Chemical Abstracts Service Registry No.
cis-Permethrin	54774-45-7
trans-Permethrin	51877-74-8
Propachlor	1918-16-7
Simazine	122-34-9
Toxaphene	8001-35-2
Trifluralin	1582-09-8
Aroclor 1016	12674-11-1
Aroclor 1221	11104-28-2
Aroclor 1232	11141-16-5
Aroclor 1242	53469-21-9
Aroclor 1248	12672-29-6
Aroclor 1254	11097-69-1
Aroclor 1260	11096-82-5

1.2 This method has been validated in a single laboratory and method detection limits have been determined for each analyte listed above. The method detection limit (MDL) is defined as the statistically calculated minimum amount that can be measured with 99% confidence that the reported value is greater than zero (1). For the listed analytes (except multi-component analytes), MDLs which range from 0.001 µg/L to 0.015 µg/L are listed in Table 3. MDLs for multi-component analytes (Aroclors and toxaphene) range from 0.01 to 0.13 µg/L.

2. SUMMARY OF METHOD

2.1 The analytes are extracted from the water sample by passing 1 L of sample through a preconditioned disk or cartridge containing a solid inorganic matrix coated with a chemically bonded C_{18} organic phase (liquid-solid extraction, LSE). The analytes are eluted from the LSE disk or cartridge with small volumes of ethyl acetate and methylene chloride, and this eluate is concentrated by evaporation of some of the solvent. The sample components are separated, identified, and measured by injecting micro-liter quantities of the eluate into a high resolution fused silica capillary column of a gas chromatograph/electron capture detector (GC/ECD) system.

3. DEFINITIONS

3.1 INTERNAL STANDARD (IS) -- A pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same solution.

3.2 SURROGATE ANALYTE (SA) -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction or other processing, and is measured with the same procedures used to measure other sample components. The purpose of the SA is to monitor method performance with each sample.

3.3 LABORATORY REAGENT BLANK (LRB) -- A aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.4 INSTRUMENT PERFORMANCE CHECK SOLUTION (IPC) -- A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.5 LABORATORY FORTIFIED BLANK (LFB) -- An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.6 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.7 STOCK STANDARD SOLUTION (SSS) -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

3.8 PRIMARY DILUTION STANDARD SOLUTION (PDS) -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.9 QUALITY CONTROL SAMPLE (QCS) -- A solution of method analytes of known concentrations which are used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.10 METHOD DETECTION LIMIT (MDL) -- The statistically calculated minimum amount of an analyte that can be measured with 99% confidence that the reported value is greater than zero (1).

4. INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus that lead to anomalous peaks or elevated baselines in gas chromatograms.

4.2 Interfering contamination may occur when a sample containing low concentrations of compounds is analyzed immediately after a sample containing relatively high concentrations of compounds. Syringes and splitless injection port liners must be cleaned carefully or replaced as needed. After analysis of a sample containing high concentrations of compounds, a laboratory reagent blank should be analyzed to ensure that accurate values are obtained for the next sample.

4.3 It is important that samples and standards be contained in the same solvent, i.e., the solvent for final working standards must be the same as the final solvent used in sample preparation. If this is not the case, chromatographic comparability of standards to sample may be affected.

5. SAFETY

5.1 The toxicity or carcinogenicity of each chemical and reagent used in this method has not been precisely defined. However, each one must be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining a current awareness of OSHA regulations regarding safe handling of the chemicals used in this method. Additional references to laboratory safety are cited (2-4).

5.2 Some method analytes have been tentatively classified as known or suspected human or mammalian carcinogens. Pure standard materials and stock standard solutions of these compounds should be handled with suitable protection to skin, eyes, etc.

6. EQUIPMENT AND SUPPLIES (All specifications are suggested. Catalog numbers and brand names are included for illustration only.)

6.1 All glassware, including sample bottles, must be meticulously cleaned. This may be accomplished by washing with detergent and water, rinsing with tap water, distilled water, or solvent, air-drying, and heating (where appropriate) in a muffle furnace for two hours at 400°C. Volumetric glassware must never be heated in a muffle furnace.

6.2 SAMPLE CONTAINERS -- 1-L or 1-quart amber glass bottles fitted with Teflon-lined screw caps. Amber bottles are highly recommended since some of the method analytes are sensitive to light and are oxidized or decomposed upon exposure.

6.3 VOLUMETRIC FLASKS -- Various sizes.

6.4 MICRO-SYRINGES -- Various sizes.

6.5 VIALS -- Various sizes of amber vials with Teflon-lined screw caps.

6.6 DRYING COLUMN -- The drying tube should contain about 5 to 7 grams of anhydrous sodium sulfate to prohibit residual water from contaminating the extract. Any small tube may be used, such as a

syringe barrel, a glass dropper, etc., as long as no sodium sulfate passes through the column into the extract.

6.7 FUSED SILICA CAPILLARY GAS CHROMATOGRAPHY COLUMN -- Any capillary column that provides adequate resolution, capacity, accuracy, and precision may be used. A 30 m X 0.25 mm ID fused silica capillary column coated with a 0.25 µm bonded film of polyphenylmethylsilicone (J&W DB-5) was used to develop this method. Any column which provides analyte separations equivalent to or better than this column may be used.

6.8 GAS CHROMATOGRAPH -- Must be capable of temperature programming, be equipped for split/splitless injection, and be equipped with an electron capture detector. On-column capillary injection is acceptable if all the quality control specifications in Sect. 9 and Sect. 10 are met. The injection system should not allow the analytes to contact hot stainless steel or other hot metal surfaces that promote decomposition.

6.9 VACUUM MANIFOLD -- A manifold system or a commercially available automatic or robotic sample preparation system designed for disks or cartridges should be utilized in this method. Ensure that all quality control requirements discussed in Sect. 9 are met. A standard all glass or Teflon lined filter apparatus should be used for disk or cartridge extraction when an automatic system is not utilized.

7. REAGENTS AND STANDARDS

7.1 HELIUM CARRIER GAS -- As contaminant free as possible.

7.2 EXTRACTION DISKS AND CARTRIDGES - Containing octadecyl bonded silica uniformly enmeshed in an inert matrix. The disks used to generate the data in this method were 47 mm in diameter and 0.5 mm in thickness. Larger disk sizes are acceptable. The disks should not contain any organic compounds, either from the matrix or the bonded silica, that will leach into the ethyl acetate and methylene chloride eluant. Cartridges should be made of inert, non-leaching plastic or glass, and must not leach plasticizers or other organic compounds into the eluting solvent. Cartridges contain about 1 gram of silica or other inert inorganic support whose surface is modified by chemically bonding octadecyl C_{18} groups.

7.3 SOLVENTS -- Methylene chloride, ethyl acetate, and methanol, high purity pesticide quality or equivalent.

7.4 REAGENT WATER -- Water in which an interferant is not observed at the MDL of the compound of interest. Prepare reagent water by passing tap or distilled water through a filter bed containing activated carbon, or by using a water purification system. If necessary, store reagent water in clean bottles with Teflon-lined screw caps.

7.5 HYDROCHLORIC ACID -- 6N.

7.6 SODIUM SULFATE -- Anhydrous, muffled at 400°C for a minimum of 4 hrs and stored in an air-tight clean glass container at ambient temperature.

7.7 SODIUM SULFITE -- Anhydrous.

7.8 PENTACHLORONITROBENZENE -- ≥ 98% purity, for use as the internal standard.

7.9 4,4-DIBROMOBIPHENYL -- ≥ 96% purity, for use as the surrogate compound.

7.10 STOCK STANDARD SOLUTIONS -- Individual solutions of analytes may be purchased from commercial suppliers or prepared from pure materials. These solutions are usually available at a concentration of 500 µg/mL. These solutions are used to make the primary dilution standard. They should be stored in amber vials in a refrigerator or freezer. Stock standard solutions should be replaced if ongoing quality control checks indicate a problem.

7.11 PRIMARY DILUTION STANDARDS -- Prepare the solution(s) to contain all method analytes, but not the internal standard or surrogate compound, at a concentration of 2.5 µg/mL in ethyl acetate.

7.12 INSTRUMENT PERFORMANCE CHECK SOLUTION -- Prepare by accurately weighing 0.0010 g each of chlorothalonil, chlorpyrifos, DCPA, and HCH-delta. Dissolve each analyte in MTBE and dilute to volume in individual 10-mL volumetric flasks. Combine 2µL of the chlorpyrifos stock solution, 50 µL of the DCPA stock solution, 50µL of the chlorothalonil stock solution, and 40µL of the HCH-delta stock solution to a 100-mL volumetric flask and dilute to volume with ethyl acetate. Transfer to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Solution should be replaced when ongoing QC (Section 9) indicates a problem.

7.13 CALIBRATION SOLUTIONS -- Using the primary dilution standards, prepare calibration solutions at six concentrations in ethyl acetate. The calibration range is dependent upon the instrumentation used, and expected analyte concentrations in the samples to be analyzed. A suggested concentration range of calibration solutions is 0.002-1.0 µg/mL. Note: Calibration standards for toxaphene and each of the Aroclors must be prepared individually.

7.14 INTERNAL STANDARD SOLUTION -- Prepare this solution of pentachloronitrobenzene by itself in ethyl acetate at a concentration of 10 µg/mL.

7.15 SURROGATE COMPOUND SOLUTION -- Prepare this solution of 4,4'-dibromobiphenyl by itself in ethyl acetate at a concentration of 10 µg/mL. Other surrogate compounds may be used if it can be demonstrated that they are not in any samples and are not interfered with by any analyte or other sample component.

7.16 GC DEGRADATION CHECK SOLUTION -- Prepare a solution in ethyl acetate containing endrin and 4,4'-DDT each at a concentration of 1 µg/mL. This solution will be injected to check for undesirable degradation of these compounds in the injection port by looking for endrin aldehyde and endrin ketone or for 4,4'- DDE and 4,4'- DDD.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (generally 1-2 min). Adjust the flow to about 500 mL/min and collect the sample from the flowing stream. Keep sample sealed from collection time until analysis. When sampling from a body of water, fill the sample container with water from a representative area. Sampling equipment, including automatic samplers, must not use plastic tubing, plastic gaskets, or any parts that may leach interfering analytes into the sample. Automatic samplers that composite samples over time should use refrigerated glass sample containers.

8.2 Residual chlorine in the sample should be reduced by adding 50 mg/L of sodium sulfite (this may be added as a solid with stirring or shaking until dissolved, or as a prepared solution).

8.3 Adjust the sample to pH ≤2 by adding 6N HCl. It may require up to 4 mL to accomplish this. It is very important that the sample be dechlorinated (Sect. 8.2) before adding the acid to lower the pH of the sample. Adding sodium sulfite and HCl to the sample bottles prior to shipping the bottles to the sampling site is not permitted. HCl should be added at the sampling site to retard any microbiological degradation of method analytes.

8.4 Samples must be iced or refrigerated at 4°C from the time of collection until extraction. Preservation study results show that the analytes (except cyanazine) are stable for 14 days in samples that are preserved as described in Sect. 8.2 and Sect. 8.3. Refrigerated sample extracts may be stored up to 30 days.

8.5 If cyanazine is to be determined, a separate sample must be collected. Cyanazine degrades in the sample when it is stored under acidic conditions or when sodium sulfite is present in the stored sample. Samples collected for cyanazine determination MUST NOT be dechlorinated or acidified when collected. They should be iced or refrigerated as described above and analyzed within 14 days. However, these samples must be dechlorinated and acidified immediately prior to fortification with the surrogate standard and extraction using the same quantities of acid and sodium sulfite described above.

9. QUALITY CONTROL

9.1 Quality control requirements are the initial demonstration of laboratory capability followed by regular analyses of laboratory reagent blanks, laboratory fortified blanks, and laboratory fortified matrix samples. The laboratory must maintain records to

document the quality of the data generated. Additional quality control practices are recommended. Determination of a MDL is also required.

9.2 Before any samples are analyzed or any time a new supply of disks or cartridges are received from a supplier, it must be demonstrated that a laboratory reagent blank is reasonably free of contamination that would prevent the determination of any analyte of concern. Both disks and cartridges could contain trace quantities of phthalate esters or silicon compounds that could prevent the determination of method analytes at low concentrations. Other sources of background contamination are impure solvents, impure reagents, and contaminated glassware. In general, background from method analytes should be below method detection limits.

9.3 INITIAL DEMONSTRATION OF CAPABILITY

9.3.1 To demonstrate initial laboratory capability, analyze a minimum of four replicate laboratory fortified blanks containing each analyte of concern at a suggested concentration in the range of 0.01-0.5 µg/L. Prepare each reagent water replicate by adding sodium sulfite (Sect. 8.2) and HCl (Sect. 8.3) to each sample, then adding an appropriate aliquot of the primary dilution standard solution(s). Analyze each replicate according to the procedures described in Sect. 11.

9.3.2 Calculate the measured concentration of each analyte in each replicate, the mean concentration of each analyte in all replicates, the mean accuracy (as mean percentage of true value) for each analyte, and the precision (as relative standard deviation, RSD) of the measurements for each analyte.

9.3.3 For each analyte, the mean accuracy, expressed as a percentage of the true value, should be 70-130% and the RSD should be ≤ 30%.

9.3.4 To determine the MDL, analyze a minimum of seven replicate laboratory fortified blanks which have been fortified with all analytes of interest at approximately 0.01 µg/L (Use a higher concentration for multi-component analytes). Calculate the MDL of each analyte using the procedure described in Sect. 13.2 (1). It is recommended that these analyses be carried out over a period of three or four days to produce more realistic limits.

9.3.5 Develop a system of control charts to plot the precision and accuracy of analyte and surrogate compound recoveries as a function of time. Charting of surrogate compound recoveries, which are present in every sample, will form a significant record of data quality. When surrogate recovery from a sample, a LFB, or a LFM is <70% or >130%, check calculations to locate possible errors, the fortifying solution for degradation, and changes in instrument performance. If the

cause cannot be determined, reanalyze the sample. If the surrogate recovery from an LFB is still is <70% or >130%, remedial action (Sect. 10.8) will likely be necessary. If the surrogate recovery from a field sample or LFM is still is <70% or >130%, and LFBs are in control, a matrix effect is suspected.

9.4 Assessing the Internal Standard. The analyst should monitor the internal standard response (peak area units) of all samples and LFBs during each work shift. The IS area should not deviate from the latest continuing calibration check (Sect. 10.7) by more than 30%, or from the initial calibration by more than 50%. If this criteria cannot be met, remedial action (Sect. 10.8) must be taken. When method performance has been restored, reanalyze any extracts that failed Sect. 9.4 criteria.

9.5 With each group or set of samples processed within a 12 hr work shift, analyze a LRB to determine background contamination. Any time a new batch of LSE disks or cartridges are received, or a new supply of reagents are used, repeat Sect. 9.2.

9.6 Assessing Laboratory Performance. With each group or set of samples processed within a 12 hr work shift, analyze a LFB containing each analyte of interest at a concentration of 0.01 to 0.5 µg/L. If more than 20 samples are included in a set, analyze a LFB for every 20 samples. Use the criteria in Sect. 9.3.3 to evaluate the accuracy of the measurements. If acceptable accuracy cannot be achieved, the problem must be located and corrected before additional samples are analyzed. Maintain control charts to document data quality.

Note: It is suggested that one multi-component analyte (an Aroclor or toxaphene) LFB also be analyzed with each sample set. By selecting a different multi-component analyte for this LFB each work shift, LFB data can be obtained for all of these analytes over the course of several days.

9.7 Assessing Sample Matrix Effects. In an attempt to ascertain any detrimental matrix effects, analyze a LFM for each type of matrix (i.e. tap water, ground water, surface water). This need not be done with every group of samples unless matrices are vastly different. The LFM should contain each analyte of interest at a concentration similar to that selected in Sect. 9.6. Results from a LFM should be within 65-135% of the fortified amount. If these criteria are not met, then a matrix interference is suspected and must be documented.

9.8 Assessing Instrument Performance. Instrument performance should be monitored each 12 hr work shift by analysis of the IPC sample and GC degradation check solution.

9.8.1 The IPC sample contains compounds designed to indicate appropriate instrument sensitivity, column performance (primary column) and chromatographic performance. IPC sample components and performance criteria are listed in Table 2.

Inability to demonstrate acceptable instrument performance indicates the need for reevaluation of the instrument system.

9.8.2 Inject the GC degradation check solution. Look for the degradation products of 4,4'-DDT (4,4'-DDE and 4,4'-DDD) and the degradation products of endrin (endrin aldehyde, EA and endrin ketone, EK). For 4,4'-DDT, these products will elute just before the parent, and for endrin, the products will elute just after the parent. If degradation of either DDT or endrin exceeds 20%, resilanize the injection port liner and/or break off a meter from the front of the column. The degradation check solution is required in each 12 hr workshift in which analyses are performed.

$$\text{\% degrade of 4,4'DDT} = \frac{\text{Total DDT degradation peak area (DDE+DDD)}}{\text{Total DDT peak area (DDT+DDE+DDD)}} \times 100$$

$$\text{\% degrade of endrin} = \frac{\text{Total EA + EK peak area}}{\text{Total endrin+EA+EK area}} \times 100$$

NOTE: If the analyst can verify that 4,4 DDT, endrin, their breakdown products, and the analytes in the IPC solution are all resolved, the IPC solution and the GC degradation check solution may be prepared and analyzed as a single solution.

9.9 At least quarterly, analyze a QCS from an external source. If measured analyte concentrations are not of acceptable accuracy as described in Sect. 9.3.3, check the entire analytical procedure to locate and correct the problem.

9.10 Numerous other quality control measures are incorporated into other parts of this method, and serve to alert the analyst to potential problems.

10. CALIBRATION AND STANDARDIZATION

10.1 Demonstration and documentation of acceptable initial calibration are required before any samples are analyzed and is required intermittently throughout sample analysis as dictated by results of continuing calibration checks. After initial calibration has been successfully accomplished, at least one continuing calibration check is required each 12 hr work shift in which analyses are performed.

10.2 Establish GC operating parameters equivalent to those below:

Injector temperature	-- 250°C
Detector temperature	-- 320°C
Injection volume	-- 2 µL, splitless for 45 sec.
Temperature program	-- Inject at 40°C and hold 1 min.
	-- program at 20°C/min. to 160°C hold 3 min.
	-- program at 3°C/min. to 275°C with no hold
	-- program at 20°C/min. to 310°C with no hold

Using the above conditions and the column in Sect. 6.7, the total run time is about 50 min. The last eluting analyte is trans-

permethrin which elutes at 267°C with a retention time of 45.4 min. Table 1 lists all method analytes and their retention times using the above conditions. It should be noted that some method analytes elute very close together. If there are unresolved peaks using the above temperature program, the analyst should modify the program to achieve resolution.

10.3 Analyze the instrument performance check sample and GC degradation check sample, and evaluate as described in Sect. 9.8. If acceptance criteria are met, proceed with calibration. If criteria are not met, take remedial action (Sect. 10.8).

10.4 Prepare calibration solutions containing all analytes of interest according to Sect. 7.13 in ethyl acetate. The calibration standard concentrations should bracket the expected concentration range of each analyte in sample extracts, or define the working range of the detector. Each standard must contain the internal standard, pentachloronitrobenzene, at a concentration of 0.5 µg/mL. The surrogate should also be present in each solution at that concentration.
Note: Calibration standards of multi-component analytes must be prepared and analyzed as separate solutions

10.5 Analyze each calibration standard using the suggested conditions in Sect. 10.2. Tabulate peak area versus concentration for each compound and the internal standard. Calculate the response factor (RF) for each analyte and the surrogate using the following equation.

$$RF = \frac{(A_s)\ (C_{IS})}{(A_{IS})\ (C_s)}$$

where: A_s = response for the analyte to be measured
A_{IS} = response for the internal standard
C_{IS} = concentration of the internal standard (µg/mL)
C_s = concentration of the analyte to be measured (µg/mL).

Note: To calibrate for multi-component analytes, one of the following methods should be used.
Option 1- Calculate an average response factor or linear regression equation for each multi-component analyte using the combined area of all the component peaks in each of the calibration standard chromatograms.
Option 2- Calculate an average response factor or linear regression equation for each multi-component analyte using the combined areas of 3-6 of the most intense and reproducible peaks in each of the calibration standard chromatograms.

10.6 If the RF over the working range is constant (≤30% RSD), the average RF can be used for calculations. Alternatively, use the results to generate a linear regression calibration for each analyte using response ratios (A_s/A_{IS}) vs. C_s.

10.7 The linear regression calibration or RF must be verified on each work shift (not to exceed 12 hrs) by measuring one or more calibration standards. Additional periodic calibration checks are good laboratory practice. It is highly recommended that an additional calibration check be performed at the end of any cycle of continuous instrument operation, so that each set of field samples is bracketed by calibration check standards. Varying the concentration of continuing calibration standards from shift to shift is recommended, to evaluate the accuracy of the calibration at more than one point. Calculate the RF for each analyte from the data measured in the continuing calibration check. The RF for each analyte must be within 30% of the mean value measured in the initial calibration. If a linear regression calibration is being used, the measured amount for each analyte from the calibration verification test must be within 30% of the true value. If these conditions do not exist, remedial action should be taken which may require recalibration. For those analytes that failed the calibration verification, results from field samples analyzed since the last passing calibration should be considered suspect. Reanalyze sample extracts for these analytes after acceptable calibration is restored.

Note: It is suggested that a calibration verification standard of one multi-component analyte (an Aroclor or toxaphene) also be analyzed each work shift. By selecting a different multi-component analyte for this calibration verification each work shift, continuing calibration data can be obtained for all of these analytes over the course of several days.

10.8 The following are suggested remedial actions which may improve method performance:

10.8.1 Check and adjust GC operating conditions and temperature programming parameters.

10.8.2 Clean or replace the splitless injector liner. Silanize a cleaned or new liner.

10.8.3 Break off a short portion of the GC column from the end near the injector, or replace GC column. Breaking off a portion of the column will somewhat shorten the analyte retention times.

10.8.4 Prepare fresh calibration solutions and repeat the initial calibrations.

10.8.5 Replace any components in the GC that permit analytes to come in contact with hot metal surfaces.

11. PROCEDURE

11.1 DISK EXTRACTION

11.1.1 This procedure may be carried out in the manual mode or in the automatic mode using a robotic or automatic sample

preparation device. If an automatic system is used to prepare samples, follow the manufacturer's instructions, but follow this procedure. If the manual mode is used, the setup of the extraction apparatus described in EPA Method 525.2 (5) may be used.
This procedure was developed using the standard 47 mm diameter disks. Larger disks (i.e. 90 mm) may be used if special matrix problems are encountered. If larger disks are used, the washing solvent volume is 15 mL and the elution solvent volumes are two 15 mL aliquots.

11.1.2 Insert the disk into the filter apparatus or sample preparation unit. Wash the disk with 5 mL of a 1:1 mixture of ethyl acetate (EtAC) and methylene chloride ($MeCl_2$) by adding the solvent to the disk, then drawing it through very slowly to ensure adequate contact time between solvent and disk. Soaking the disk may not be desirable when disks other than Teflon are used.

11.1.3 Add 5 mL methanol to the disk and draw some of it through slowly. A layer of methanol must be left on the surface of the disk which must not be allowed to go dry from this point until the end of the sample extraction. THIS IS CRITICAL FOR UNIFORM FLOW AND GOOD ANALYTE RECOVERIES.

11.1.4 Rinse the disk with 5 mL reagent water by adding the water to the disk and drawing most through, again leaving a layer on the surface of the disk.

11.1.5 Add 5 mL methanol to the sample and mix well. Mark the water meniscus on the side of the sample bottle for later determination of sample volume.

11.1.6 Add 50 μL of the surrogate compound solution (Sect. 7.15) and shake well.

11.1.7 Draw the sample through the disk while maintaining sufficient vacuum. One liter of drinking water may pass through the disk in as little as 5 min without reducing analyte recoveries. Drain the entire sample from the container through the disk. Determine the original sample volume by refilling the sample bottle to the mark with tap water and transferring the water to a 1000-mL graduated cylinder. Measure to the nearest 5 mL.

11.1.8 Dry the disk by drawing air or nitrogen through the disk for about 10 min.

11.1.9 Remove the filtration glassware, but do not disassemble the reservoir and fritted base. Insert a collection tube into the vacuum manifold. If a suction flask is being used, empty the water from the flask and insert a suitable collection tube to contain the eluate. The only constraint on the collection tube is that it fit around the drip tip of the fritted base. Reassemble the apparatus.

11.1.10 Rinse the inside walls of the sample bottle with 5 mL EtAC then transfer the solvent to the disk using a syringe or disposable pipet. Rinse the inside walls of the glass filtration reservoir with this EtAC. Draw the solvent through the disk very slowly to allow adequate contact time between disk and solvent for good analyte recoveries.

11.1.11 Repeat the above step (Sect. 11.10) with 5 mL $MeCl_2$.

11.1.12 Using the syringe or disposable pipet, rinse the filtration reservoir with two 3 mL portions of 1:1 EtAc:$MeCl_2$. Pour all combined eluates through the drying tube containing about 5 to 7 grams of anhydrous sodium sulfate. Rinse the drying tube and the sodium sulfate with two 3 mL portions of 1:1 EtAc/$MeCl_2$. Collect all eluate and washings in a concentrator tube.

11.1.13 Concentrate the extract to approximately 0.8 mL under a gentle stream of nitrogen while warming gently in a water bath or heating block. Rinse the inside walls of the concentrator tube two or three times with EtAC during concentration. Fortify the extract with 50 µL of the IS fortifying solution (Section 7.14). Adjust the extract volume to 1.0 mL with EtAc.

11.1.14 Inject a 1 or 2 µL aliquot into the gas chromatograph using the GC conditions used for initial calibration (Sect. 10.2). Table 1 lists retention times for method analytes using these conditions.

11.1.15 Identify a method analyte in the sample extract by comparing its gas chromatographic retention time to the retention time of the known analyte in a reference standard chromatogram, a calibration standard, or a laboratory fortified blank. If the retention time of the sample peak is within the pre-defined retention time window, identification is considered positive. The width of the retention time window used to make identifications should be based on measurements of actual retention time variations of standards during the course of a work shift. It is suggested that three times the standard deviation of the retention times obtained when the system is calibrated be used to calculate the window. The experience of the analyst should be an important factor in the interpretation of a gas chromatogram. Confirmation may be performed by analysis on a second column, or if concentrations are sufficient, by GC/MS.

Note: Identify multi-component analytes by comparison of the sample chromatogram to the corresponding calibration standard chromatograms of toxaphene and the Aroclors. Identification of multi-component analytes is made by pattern recognition, in which the experience of the analyst is an important factor. Figures 1-8 illustrate patterns that can be expected from these analytes at low concentrations. The peaks indicated on the chromatograms are those that were used for

quantitation. Other peaks may be selected at the discretion of the analyst.

11.2 CARTRIDGE EXTRACTION

11.2.1 This procedure may be carried out in the manual mode or in the automatic mode using a robotic or automatic sample preparation device. If an automatic system is used to prepare samples, follow the manufacturer's instructions, but follow this procedure. If the manual mode is used, the setup of the extraction apparatus described in EPA Method 525.2 (5) may be used.

11.2.2 Elute each cartridge with a 5 mL aliquot of ethyl acetate followed by a 5 mL aliquot of methylene chloride. Let the cartridge drain dry after each flush. Then elute the cartridge with a 10 mL aliquot of methanol, but DO NOT allow the methanol to elute below the top of the cartridge packing. Add 10 mL of reagent water to the cartridge and elute, but before the reagent water level drops below the top edge of the packing, begin adding sample to the solvent reservoir.

11.2.3 Pour the water sample into the 2-L separatory funnel with the stopcock closed, add 5 mL methanol and the surrogate standard, and mix well. If a vacuum manifold is used instead of the separatory funnel, the sample may be transferred directly to the cartridge after the methanol and surrogate standard are added to the sample.

11.2.4 Drain the sample into the cartridge being careful not to overflow the cartridge. Maintain the packing material in the cartridge immersed in water at all times. After all the sample has passed through the LSE cartridge, draw air or nitrogen through the cartridge for 10 min.

11.2.5 If the setup in Method 525.2 (5) is being used, transfer the 125 mL solvent reservoir and LSE cartridge to the elution apparatus. The same reservoir is used for both apparatus. Rinse the inside of the separatory funnel and the sample jar with 5 mL ethyl acetate and elute the cartridge with this rinse into the collection tube. Wash the inside of the separatory funnel and the sample jar with 5 mL methylene chloride and elute the cartridge, collecting the rinse in the same collection tube. Small amounts of residual water from the sample container and the LSE cartridge may form am immiscible layer with the eluate. Pass the eluate through the drying column which is packed with approximately 5 to 7 grams of anhydrous sodium sulfate and collect in a second tube. Wash the sodium sulfate with at least 2 mL methylene chloride and collect in the same tube. Proceed according to steps in Sect. 11.1.13, 11.1.14 and Sect. 11.1.15 above.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Calculate the concentration (C) of the analyte in the sample using the response factor (RF) determined in Sect. 10.5 and the equation below.

$$C\ (\mu g/L) = \frac{(A_s)\ (I_s)}{(A_{IS})(RF)(V_o)}$$

where: A_s = peak area for the analyte to be measured
A_{IS} = peak area for the internal standard
I_s = amount of internal standard added (μg)
V_o = volume of water extracted (L)

If a linear regression calibration is used, use the regression equation to calculate the amount of analyte in the sample. All samples containing analytes outside the calibration range must be diluted and reanalyzed. When diluting, add additional internal standard to maintain its concentration at 0.5 μg/mL in the diluted extract.

12.2 To quantitate multi-component analytes, one of the following methods should be used.
Option 1- Calculate an average response factor or linear regression equation for each multi-component analyte using the combined area of all the component peaks in each of the calibration standard chromatograms.
Option 2- Calculate an average response factor or linear regression equation for each multi-component analyte using the combined areas of 3-6 of the most intense and reproducible peaks in each of the calibration standard chromatograms.

When quantifying multi-component analytes in samples, the analyst should use caution to include only those peaks from the sample that are attributable to the multi-component analyte. Option 1 should not be used if there are significant interference peaks within the Aroclor or toxaphene pattern.

13. METHOD PERFORMANCE

13.1 Method performance data was obtained using the GC column and conditions described in Sections 6.7 and 10.2. Retention times are listed in Table 1. All data presented here were obtained with the liquid-solid extraction disk option. Previous method development research has shown no significant performance differences between cartridges and disks. Method 525.2 shows comparative recovery data for Method 508.1 analytes using both cartridges and disks.

13.2 Method detection limits (MDL) for all method analytes (except Aroclors and toxaphene) were determined by analyzing seven reagent water samples which were fortified with the analytes at a concentration of 0.01 μg/L. The mean and standard deviation were calculated for each analyte. The MDL was calculated by multiplying the standard deviation by the students-t value for n-1 and a 99%

confidence interval (1). The students-t value for seven replicates (n-1=6) is 3.143. The mean recoveries and the standard deviations along with the MDLs are listed in Table 3. Aroclor and toxaphene data in Table 3 were calculated using Option 2 in Section 12.2.

13.3 Method accuracy and precision were determined by analyzing two sets of eight reagent water samples fortified with method analytes (except the multi-component analytes) at approximately 5 and 10 times the average MDL. The fortification concentrations for these samples were calculated by averaging the analyte MDLs and multiplying that average by 5 and 10. Thus the concentrations used were 0.03 µg/L and 0.048 µg/L. Results of these analyses are listed in Tables 4 and 5. An additional set of samples was analyzed at approximately 20 times the average MDL (0.096µg/L). This set of samples was extracted from an artificial matrix containing 1mg/L fulvic acid. The fulvic acid served to mimic the naturally occurring organic material found in many water sources. The results of these analyses are listed in Table 6.

13.4 Atrazine, hexachlorocyclopentadiene, and metribuzin appear to be problem analytes. Atrazine displays low peak response when compared to most of the other method analytes, and requires manual peak area integration even at the 0.048 µg/L level.
Hexachlorocyclopentadiene, while displaying relatively high peak response, showed poor recovery. The resulting mean recoveries were 50.8, 52.6, and 21.7 percent respectively for the three levels. It is suspected that the higher volatility of hexachlorocyclopentadiene causes the problem. Very careful, very slow nitrogen blowdown may produce higher recoveries of this compound (5).
It is suspected that Metribuzin was recovered poorly due to breakthrough on C-18 media (5).

14. POLLUTION PREVENTION

14.1 This method utilizes liquid-solid extraction (LSE) technology to remove the analytes from water. It requires the use of very small volumes of organic solvent and very small quantities of pure analytes. This eliminates the potential hazards to both the analyst and the environment that are present when large volumes of solvents are used in conventional liquid-liquid extractions.

14.2 For information about pollution prevention that may be applicable to laboratory operations, consult "Less Is Better: Laboratory Chemical Management for Waste Reduction" available from the American Chemical Society's Department of Governmental Relations and Science Policy, 1155 16th Street N.W., Washington, D.C., 20036.

15. WASTE MANAGEMENT

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions. The laboratory using this method has the responsibility to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations.

Compliance is also required with any sewage discharge permits and regulations. For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel," also available from the American Chemical Society at the address in Sect. 14.2.

16. REFERENCES

1. J.A. Glaser, D.L. Foerst, G.D. McKee, S.A. Quave, and W.L. Budde, "Trace Analyses for Wastewaters," Environ. Sci. Technol. 1981 15, 1426-1435. or 40 CFR, Part 136, Appendix B.

2. "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.

3. "OSHA Safety and Health Standards, General Industry," (29CFR1910), Occupational Safety and Health Administration, OSHA 2206 (Revised January 1976).

4. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

5. Munch, J. W., "Method 525.2-Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Chromatography/ Mass Spectrometry" in Methods for the Determination of Organic Compounds in Drinking Water; Supplement 3 (1995). USEPA, National Exposure Research Laboratory, Cincinnati, Ohio 45268.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. RETENTION TIMES FOR METHOD ANALYTES USING THE GC COLUMN IN SECT. 6.7 AND THE GC CONDITIONS IN SECT. 10.2

ANALYTE	RETENTION TIME (Min)
Hexachlorocyclopentadiene	9.64
Etridiazole	11.41
Chloroneb	12.39
Propachlor	14.69
Trifluralin	16.29
HCH-alpha	17.01
Hexachlorobenzene	17.44
Simazine	17.86
Atrazine	18.23
HCH-Beta	18.33
HCH-Gamma	18.71
HCH-Delta	19.21
Chlorthalonil	20.27
Metribuzin	21.88
Heptachlor	22.78
Alachlor	22.86
Aldrin	24.81
Metolachlor	25.02
Cyanazine	25.21
DCPA	26.49
Heptachlor Epoxide	27.20
Chlordane-Gamma	28.65
Endosulfan I	29.36
Chlordane-alpha	29.58
Dieldrin	30.95
4,4'-DDE	31.97

TABLE 1. RETENTION TIMES FOR METHOD ANALYTES USING THE GC COLUMN IN SECT. 6.7 AND THE GC CONDITIONS IN SECT. 10.2

ANALYTE	RETENTION TIME (Min)
Endrin	32.24
Butachlor[a]	32.65
Endosulfan II	32.81
Chlorbenzilate	32.98
4,4'-DDD	33.49
Endrin Aldehyde	33.96
Endosulfan sulfate	35.43
4,4'-DDT	35.80
Methoxychlor	39.38
cis-Permethrin	44.98
trans-Permethrin	45.42
Toxaphene[a]	33.53, 36.48, 39.12[b]
Aroclor 1016[a]	18.93, 22.55, 24.83[b]
Aroclor 1221[a]	13.67, 18.02, 19.93[b]
Aroclor 1232[a]	18.93, 22.55, 24.83[b]
Aroclor 1242[a]	18.93, 22.55, 24.83[b]
Aroclor 1248[a]	24.15, 24.83, 31.40[b]
Aroclor 1254[a]	31.80, 34.12, 38.88[b]
Aroclor 1260[a]	35.65, 41.38, 43.08[b]
Pentachlorointrobenzene (IS):	19.02 minutes
4,4-Dibromobiphenyl (SUR):	25.64 minutes

[a] Retention time was determined with the following GC conditions:

Injector temperature -- 250°C
Detector temperature -- 320°C
Injection volume -- 2 µL, splitless for 45 sec.
Temperature program -- Inject at 60°C and hold 1 min.
-- program at 20°C/min. to 160°C hold 3 min.
-- program at 3°C/min. to 275°C with no hold
-- program at 20°C/min. to 310°C with no hold

TABLE 1. RETENTION TIMES FOR METHOD ANALYTES USING THE GC COLUMN IN SECT. 6.7 AND THE GC CONDITIONS IN SECT. 10.2

The IS retention time using these conditions is 21.15 min. The SUR retention time using these conditions is 28.18 min.

[b] The retention times listed do not reflect the total number of peaks characteristic of the multi-component analyte. Listed peaks indicate those chosen for quantitation. Quantitative data is in Table 3.

TABLE 2. LABORATORY PERFORMANCE CHECK SOLUTION

Test	Analyte	Conc. µg/mL	Requirements
Sensitivity	Chlorpyrifos	0.0020	Detection ofanalyte;S/N > 3
Chromatographic performance	DCPA	0.0500	PGF between 0.80 and 1.15[a]
Column performance	Chlorothalonil HCH-delta	0.0500 0.0400	Resolution > 0.50[b]

[a] PGF - peak Gaussian factor. Calculated using the equation:

$$PGF = \frac{1.83 \times W(1/2)}{W(1/10)}$$

where W(1/2) is the peak width at half height in secs. and W(1/10) is the peak width in secs. at tenth height.

[b] Resolution between the two peaks as defined by the equation:

$$R = \frac{t}{W}$$

where t is the difference in elution times between the two peaks and W is the average peak width, at the baseline, of the two peaks.

TABLE 3. MDL STATISTICAL RESULTS FOR SEVEN REPLICATES IN REAGENT WATER

ANALYTE	Fortified Conc. (µg/L)	MEAN µg/L	% REC	STD. DEV. µg/L	% RSD	CALC. MDL
Alachlor	0.01	0.008	80	0.0030	37.5	0.009
Aldrin	0.01	0.008	80	0.0030	37.5	0.009
Atrazine	0.01	0.014	140	0.0010	7.14	0.003
Butachlor	0.5	0.43	86	0.023	5.5	0.07
Chlorbenzilate	0.01	0.008	80	0.0007	8.75	0.002
Chlordane-alpha	0.01	0.007	70	0.0012	17.1	0.004
Chlordane-gamma	0.01	0.006	60	0.003	50.0	0.001
Chloroneb	0.01	0.012	120	0.0019	15.8	0.006
Chlorothalonil	0.01	0.007	70	0.0007	10.0	0.002
Cyanazine	0.01	0.010	100	0.0022	22.0	0.007
DCPA	0.01	0.010	100	0.0028	28.0	0.009
4,4'-DDD	0.01	0.009	90	0.0008	8.89	0.003
4,4'-DDE	0.01	0.008	80	0.0009	11.2	0.003
4,4'-DDT	0.01	0.012	120	0.0011	9.17	0.004
4,4'-Dibromobiphenyl (Surrogate)	0.01	0.440	88.0	0.027	6.14	
Dieldrin	0.01	0.007	70	0.0009	12.9	0.003
Endosulfan I	0.01	0.007	70	0.0019	27.1	0.006
Endosulfan II	0.01	0.007	70	0.0003	42.9	0.001
Endosulfan Sulfate	0.01	0.007	70	0.0010	14.3	0.003

TABLE 3. MDL STATISTICAL RESULTS FOR SEVEN REPLICATES IN REAGENT WATER

ANALYTE	Fortified Conc. (µg/L)	MEAN µg/L	% REC	STD. DEV. µg/L	% RSD	CALC. MDL
Endrin	0.01	0.015	150	0.0023	15.3	0.007
Endrin Aldehyde	0.01	0.008	80	0.0012	15.0	0.004
Etridiazole	0.01	0.011	110	0.0045	40.9	0.014
HCH-alpha	0.01	0.007	70	0.0003	42.8	0.001
HCH-beta	0.01	0.009	90	0.0029	32.2	0.009
HCH-delta	0.01	0.008	80	0.0014	17.5	0.004
HCH-gamma	0.01	0.007	70	0.0020	28.6	0.006
Heptachlor	0.01	0.009	90	0.0016	17.8	0.005
Heptachlor Epoxide	0.01	0.006	60	0.0003	5.0	0.001
Hexachlorobenzene	0.01	0.010	100	0.0004	4.0	0.001
Hexachlorocyclopenta diene	0.01	0.004	40	0.0013	32.5	0.004
Methoxychlor	0.01	0.006	60	0.0009	15.0	0.003
Metolochlor	0.01	0.013	130	0.0049	37.7	0.015
Metribuzin	0.01	0.009	90	0.0028	31.1	0.009
cis-Permethrin	0.01	0.007	70	0.0030	42.9	0.009
trans-Permethrin	0.01	0.011	110	0.0022	20.0	0.007
Propachlor	0.01	0.008	80	0.0027	33.8	0.008
Simazine	0.01	0.009	90	0.0025	27.8	0.008
Trifluralin	0.01	0.006	60	0.0003	5.0	0.001

TABLE 3. MDL STATISTICAL RESULTS FOR SEVEN REPLICATES IN REAGENT WATER

ANALYTE	Fortified Conc. (µg/L)	MEAN µg/L	% REC	STD. DEV. µg/L	% RSD	CALC. MDL
Toxaphene	1.0	0.81	81	0.041	5.1	0.13
Aroclor 1016	0.2	0.16	82	0.009	5.7	0.029
Aroclor 1221	0.2	0.17	85	0.012	6.8	0.037
Aroclor 1232	0.2	0.18	90	0.010	5.8	0.033
Aroclor 1242	0.2	0.20	100	0.014	6.9	0.043
Aroclor 1248	0.2	0.18	88	0.014	8.0	0.044
Aroclor 1254	0.2	0.16	82	0.012	7.0	0.036
Aroclor 1260	0.2	0.16	82	0.004	2.4	0.012

TABLE 4. EIGHT REPLICATES IN REAGENT WATER
ANALYTE CONCENTRATIONS 0.03 µg/L

ANALYTE	MEAN µg/L	%REC	STD. DEV. µg/L	% RSD
Alachlor	0.031	103	0.005	16.1
Aldrin	0.025	81.9	0.005	20.2
Atrazine	0.021	70.4	0.002	11.4
Chlorbenzilate	0.024	81.5	0.006	23.1
Chlordane-alpha	0.025	83.4	0.005	18.8
Chlordane-gamma	0.025	82.3	0.007	28.8
Chloroneb	0.026	88.3	0.006	24.3
Chlorothalonil	0.032	106	0.006	19.5
Cyanazine	0.029	95.2	0.004	12.8
DCPA	0.026	85.2	0.004	14.1
4,4'-DDD	0.027	89.1	0.004	16.4
4,4'-DDE	0.023	78.0	0.005	20.0
4,4'-DDT	0.028	93.8	0.005	17.4
4,4'-Dibromobiphenyl (Surrogate)	0.466	93.2	0.032	6.97
Dieldrin	0.027	91.5	0.004	15.8
Endosulfan I	0.028	92.6	0.005	17.8
Endosulfan II	0.026	87.9	0.005	18.6
Endosulfan Sulfate	0.032	106	0.004	11.5
Endrin	0.029	96.5	0.004	13.9

TABLE 4. EIGHT REPLICATES IN REAGENT WATER
ANALYTE CONCENTRATIONS 0.03 µg/L (Cont.)

ANALYTE	MEAN µg/L	%REC	STD. DEV. µg/L	% RSD
Endrin Aldehyde	0.030	98.8	0.004	13.7
Etridiazole	0.028	95.3	0.008	27.1
HCH-alpha	0.026	88.4	0.007	24.9
HCH-beta	0.028	95.0	0.004	13.9
HCH-delta	0.034	114	0.004	11.1
HCH-gamma	0.033	110	0.004	11.3
Heptachlor Epoxide	0.027	90.6	0.005	17.4
Heptachlor	0.026	85.6	0.006	22.1
Hexachlorobenzene	0.032	107	0.006	20
Hexachlorocyclopentadiene	0.015	50.8	0.007	44.8
Methoxychlor	0.024	92.7	0.003	10.7
Metolochlor	0.034	113	0.006	18.2
Metribuzin	0.012	39.5	0.002	15.8
cis-Permethrin	0.033	81.2	0.004	17.8
trans-Permethrin	0.033	111	0.004	13.4
Propachlor	0.028	93.0	0.005	17.4
Simazine	0.020	68.4	0.002	11.5
Trifluralin	0.024	80.5	0.004	18.0

TABLE 5. EIGHT REPLICATES IN REAGENT WATER
ANALYTE CONCENTRATIONS 0.048 µg/L

ANALYTE	MEAN µg/L	%REC	STD. DEV. µg/L	% RSD
Alachlor	0.044	91.1	0.002	3.70
Aldrin	0.034	69.8	0.004	11.5
Atrazine	0.036	74.9	0.002	6.60
Chlorbenzilate	0.051	107	0.004	8.40
Chlordane-alpha	0.047	97.7	0.002	4.80
Chlordane-gamma	0.044	92.6	0.003	5.40
Chloroneb	0.055	155	0.004	6.70
Chlorothalonil	0.059	123	0.004	6.00
Cyanazine	0.045	94.5	0.000	3.60
DCPA	0.042	88.5	0.001	2.90
4,4'-DDD	0.052	108	0.003	5.80
4,4'-DDE	0.046	94.8	0.004	8.30
4,4'-DDT	0.056	116	0.004	7.20
4,4'-Dibromobiphenyl (Surrogate)	0.474	94.7	0.032	6.79
Dieldrin	0.048	101	0.002	4.00
Endosulfan I	0.049	102	0.004	7.50
Endosulfan II	0.051	106	0.004	7.80
Endosulfan Sulfate	0.056	117	0.005	9.30
Endrin	0.053	111	0.004	8.20

TABLE 5. EIGHT REPLICATES IN REAGENT WATER
ANALYTE CONCENTRATIONS 0.048 µg/L (Cont.)

ANALYTE	MEAN µg/L	%REC	STD. DEV. µg/L	% RSD
Endrin Aldehyde	0.047	98.5	0.005	10.7
Etridiazole	0.051	107	0.003	6.46
HCH-alpha	0.052	109	0.005	10.0
HCH-beta	0.044	90.7	0.002	3.60
HCH-delta	0.058	120	0.005	8.80
HCH-gamma	0.053	111	0.007	13.3
Heptachlor	0.040	82.6	0.004	9.80
Heptachlor Epoxide	0.048	100	0.003	6.60
Hexachlorobenzene	0.044	90.7	0.005	11.8
Hexachlorocyclopentadiene	0.025	52.6	0.005	19.1
Methoxychlor	0.052	109	0.005	9.50
Metolochlor	0.060	126	0.002	3.60
Metribuzin	0.033	67.7	0.006	18.1
cis-Permethrin	0.049	102	0.009	18.9
trans-Permethrin	0.056	117	0.007	11.7
Propachlor	0.049	102	0.002	3.33
Simazine	0.039	82.2	0.003	6.69
Trifluralin	0.0043	89.9	0.002	4.71

TABLE 6. EIGHT REPLICATES IN REAGENT WATER CONTAINING FULVIC ACID (1 mg/L)
ANALYTE CONCENTRATIONS 0.096 µg/L

ANALYTE	MEAN µg/L	%REC	STD. DEV. µg/L	% RSD
Alachlor	0.093	96.6	0.012	13.2
Aldrin	0.071	73.6	0.006	8.90
Atrazine	0.069	71.9	0.005	9.30
Chlorbenzilate	0.086	89.9	0.009	10.4
Chlordane-alpha	0.088	91.9	0.004	4.90
Chlordane-gamma	0.072	74.5	0.006	7.50
Chloroneb	0.082	85.4	0.008	9.70
Chlorothalonil	0.079	82.5	0.007	9.20
Cyanazine	0.085	89.0	0.011	12.5
DCPA	0.075	78.6	0.004	4.90
4,4'-DDD	0.091	95.0	0.009	10.3
4,4'-DDE	0.095	96.5	0.005	5.00
4,4'-DDT	0.082	85.0	0.008	9.50
4,4'-Dibromobiphenyl (Surrogate)	0.046	91.2	0.030	6.64
Dieldrin	0.089	92.3	0.009	9.90
Endosulfan I	0.088	91.8	0.008	8.60
Endosulfan II	0.088	92.0	0.006	7.40
Endosulfan Sulfate	0.094	98.3	0.007	7.30
Endrin	0.098	102	0.010	10.3

TABLE 6. EIGHT REPLICATES IN REAGENT WATER CONTAINING FULVIC ACID (1 mg/L)
ANALYTE CONCENTRATIONS 0.096 µg/L (Cont.)

ANALYTE	MEAN µg/L	%REC	STD. DEV. µg/L	% RSD
Endrin Aldehyde	0.067	69.8	0.003	5.20
Etridiazole	0.095	98.9	0.009	9.80
HCH-alpha	0.092	95.4	0.006	6.70
HCH-beta	0.088	91.2	0.007	7.80
HCH-delta	0.094	97.6	0.006	5.90
HCH-gamma	0.102	106	0.007	7.10
Heptachlor	0.068	71.4	0.007	9.80
Heptachlor Epoxide	0.088	91.6	0.007	7.80
Hexachlorobenzene	0.063	65.3	0.006	8.90
Hexachlorocyclopentadiene	0.021	21.7	0.008	40.1
Methoxychlor	0.092	96.1	0.011	12.0
Metolochlor	0.110	115	0.012	11.1
Metribuzin	0.039	40.7	0.004	9.50
cis-Permethrin	0.078	81.3	0.009	11.1
trans-Permethrin	0.082	85.2	0.008	11.1
Propachlor	0.098	102	0.017	17.4
Simazine	0.076	78.8	0.005	6.10
Trifluralin	0.074	77.4	0.010	13.3

Figure 1. Aroclor 1016. Chromatogram of LFB at 0.2 ug/L

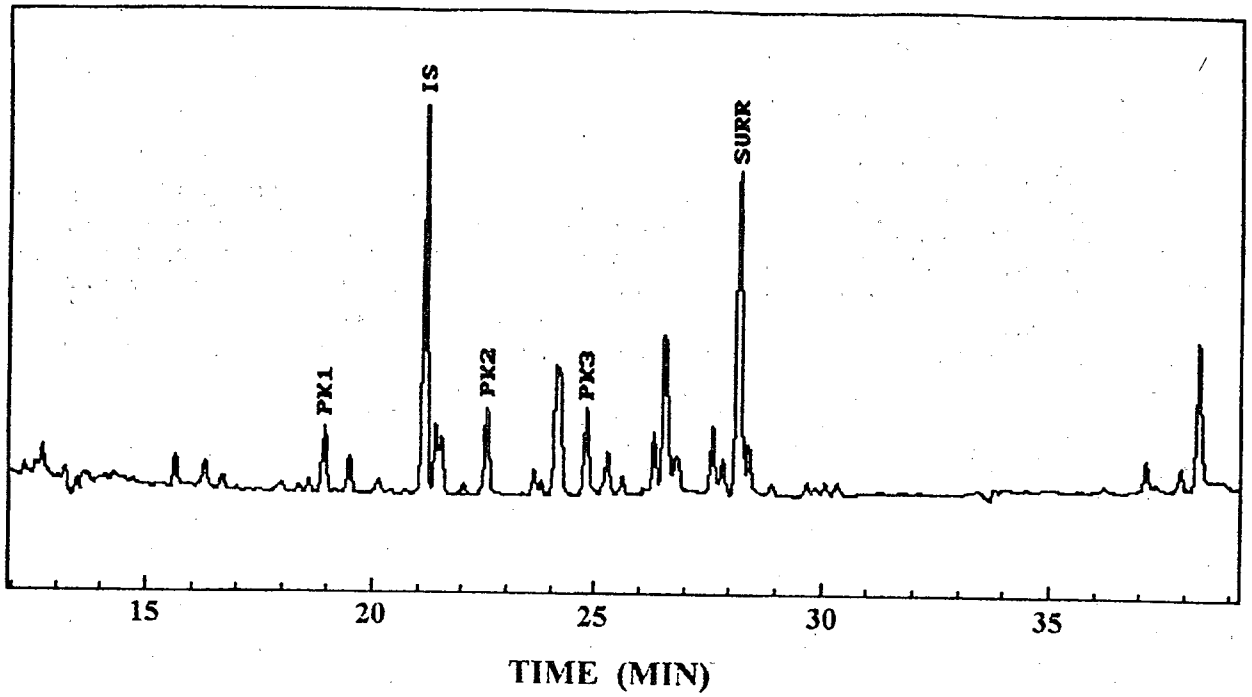


Figure 2. Aroclor 1221. Chromatogram of LFB at 0.2 ug/L

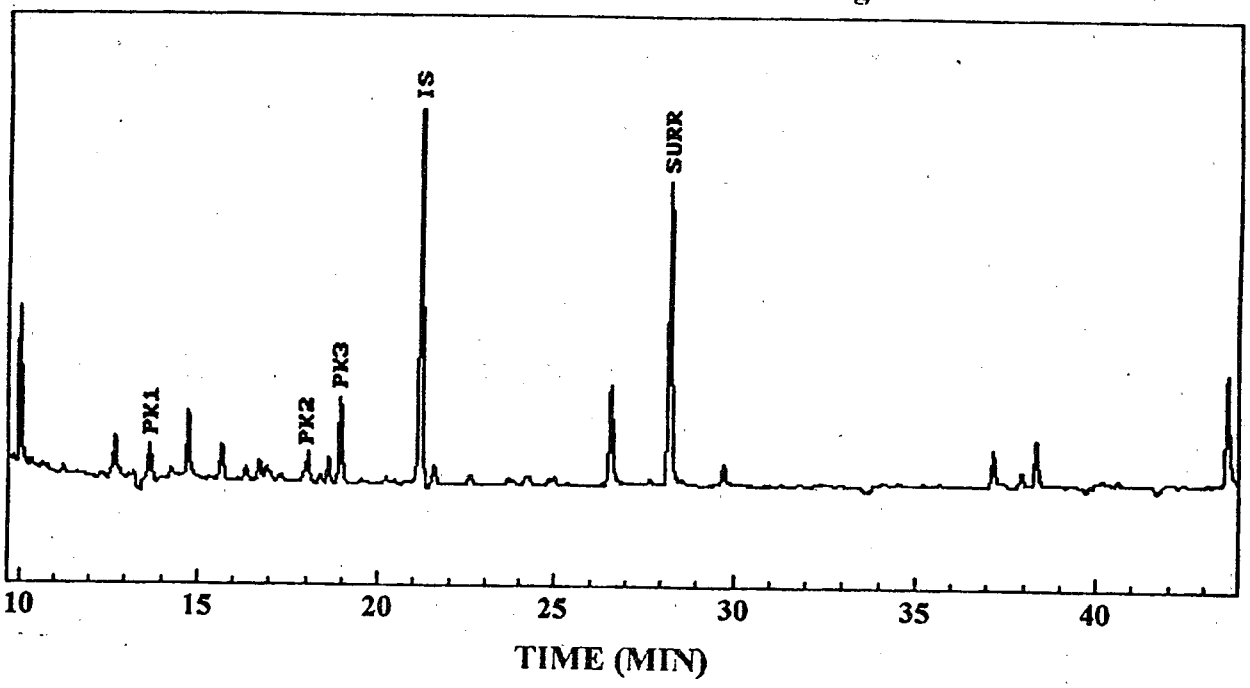


Figure 3. Aroclor 1232. Chromatogram of LFB at 0.2ug/L

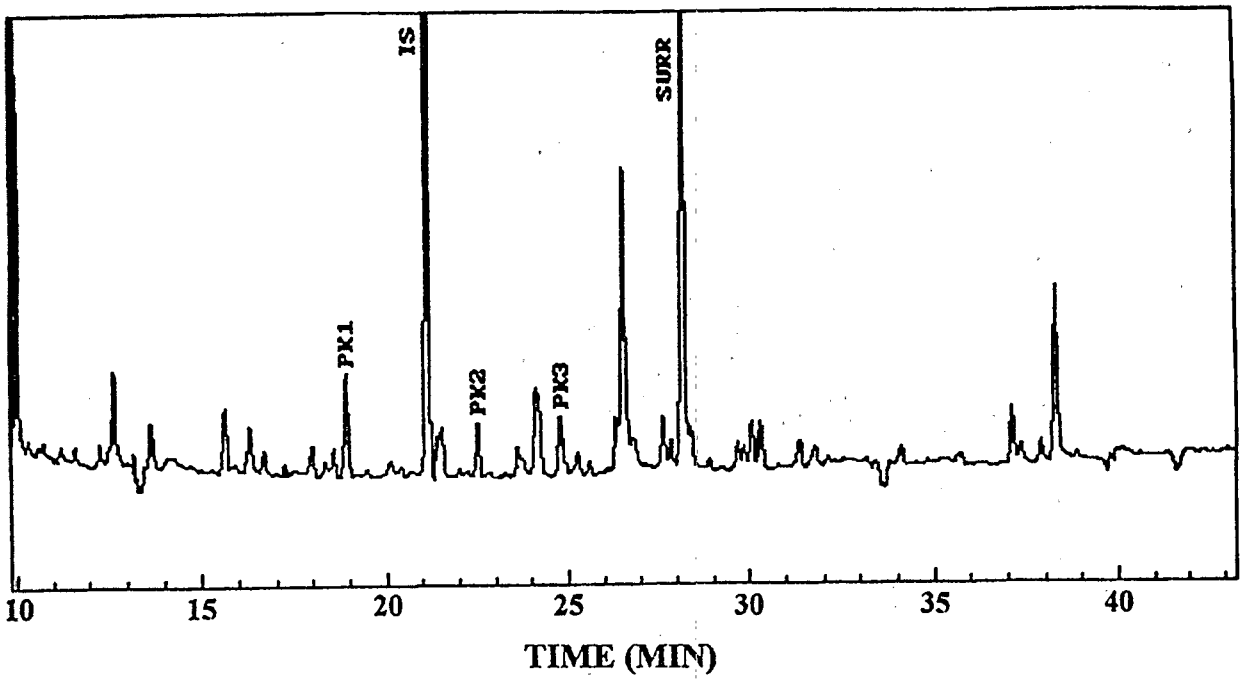


Figure 4. Aroclor 1242. Chromatogram of LFB at 0.2ug/L

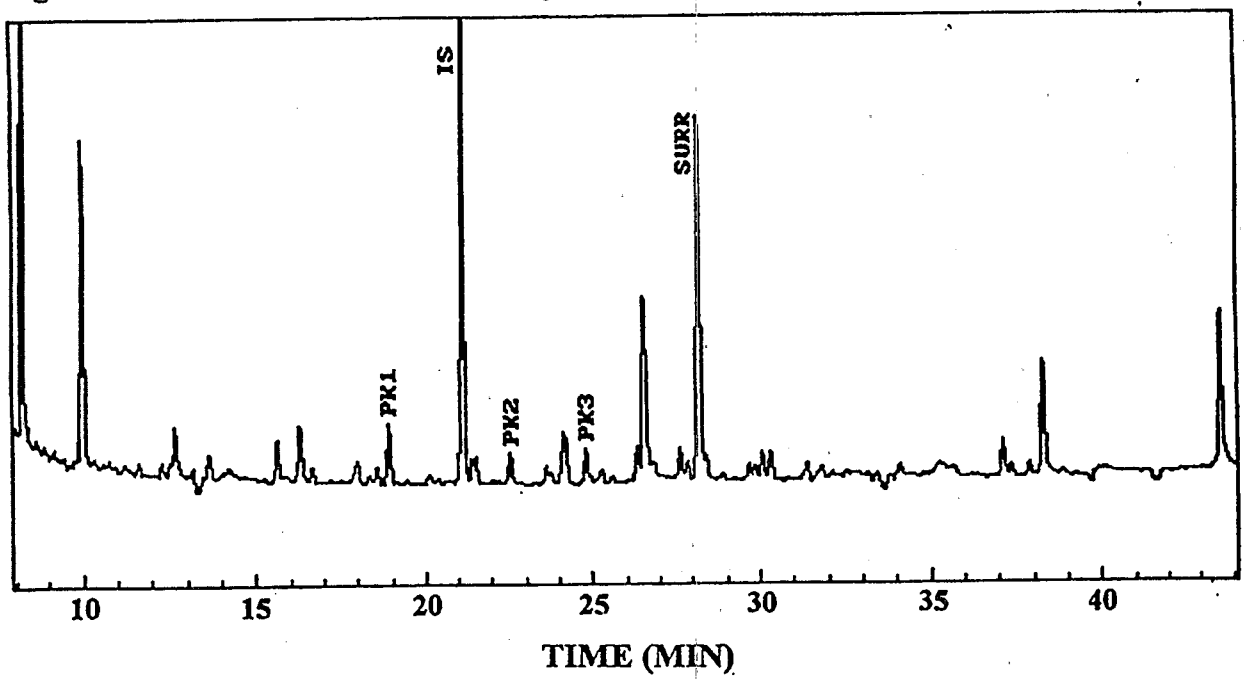


Figure 5. Aroclor 1248. Chromatogram of LFB at 0.2ug/L

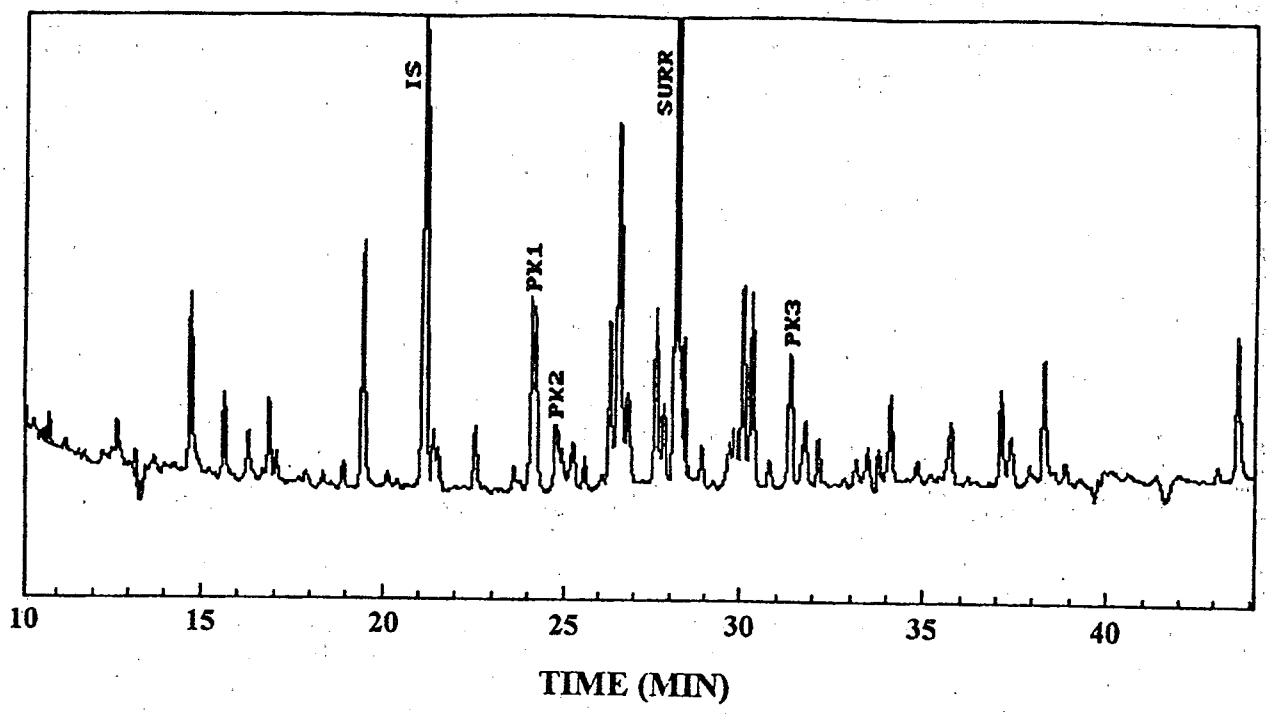


Figure 6. Aroclor 1254. Chromatogram of LFB at 0.2ug/L

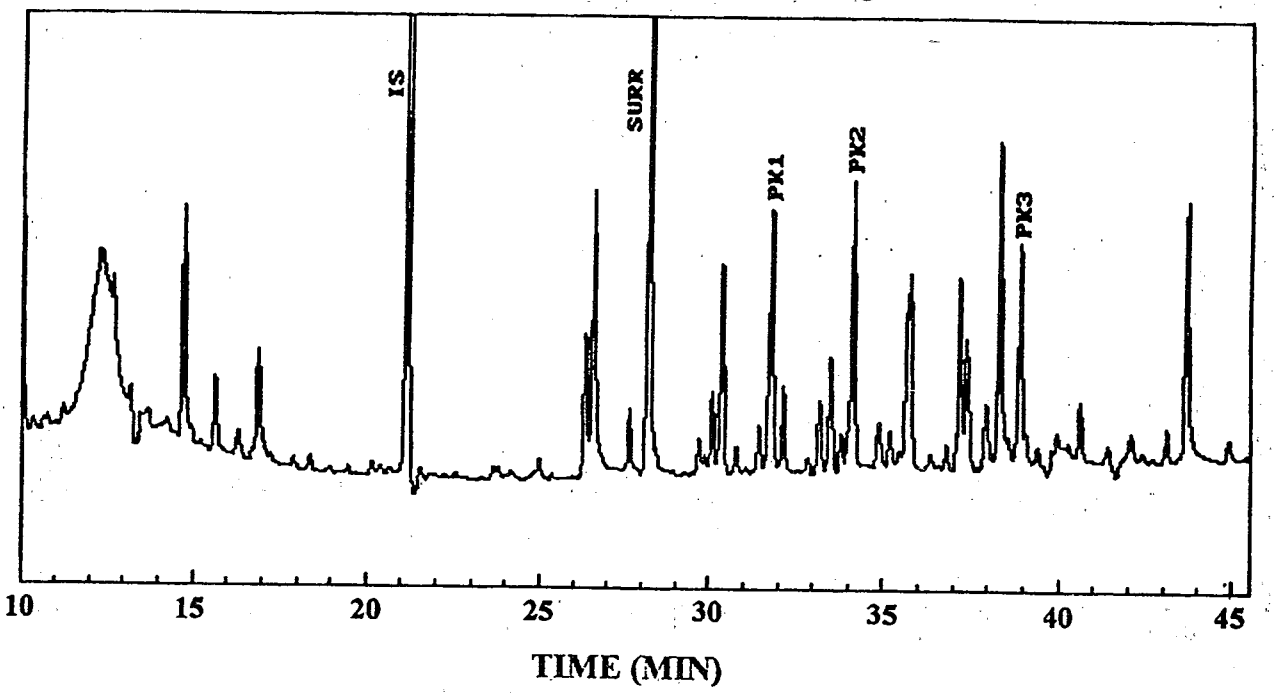


Figure 7. Aroclor 1260. Chromatogram of LFB at 0.2ug/L

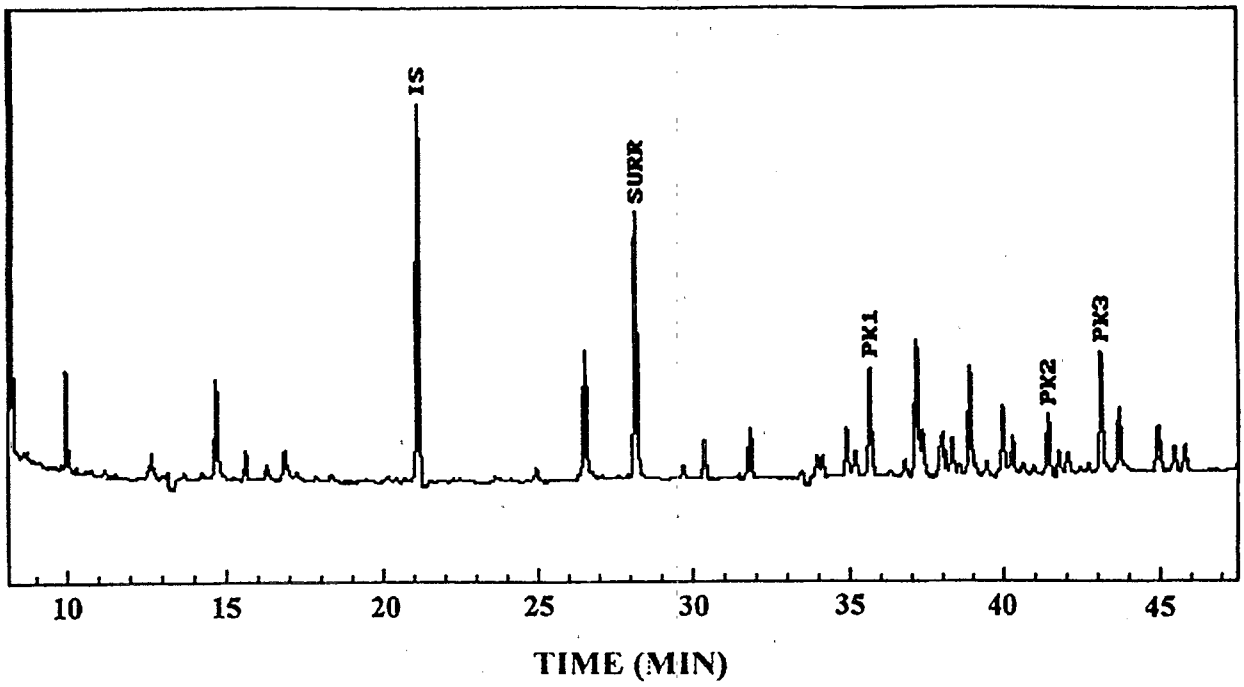
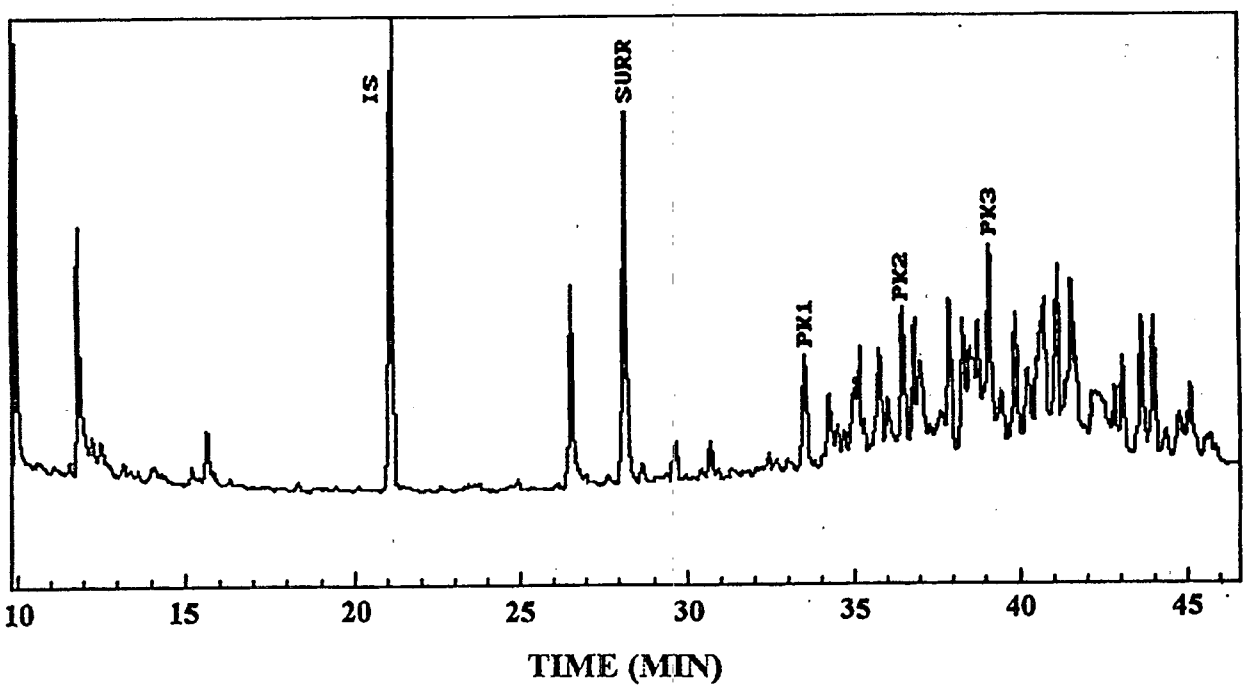


Figure 8. Toxaphene. Chromatogram of LFB at 0.2ug/L



METHOD 509. DETERMINATION OF ETHYLENE THIOUREA (ETU) IN WATER USING GAS CHROMATOGRAPHY WITH A NITROGEN-PHOSPHORUS DETECTOR

Revision 1.1

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J.W. Eichelberger, Method 509 Revision 1.0 (1992)

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METHOD 509

DETERMINATION OF ETHYLENE THIOUREA (ETU) IN WATER USING GAS CHROMATOGRAPHY WITH A NITROGEN-PHOSPHORUS DETECTOR

1. SCOPE AND APPLICATION

1.1 This method utilizes gas chromatography (GC) to determine ethylene thiourea (ETU, Chemical Abstracts Registry No. 96-45-7) in water.

1.2 This method has been validated in a single laboratory during development. The method detection limit (MDL) has been determined in reagent water (1) and is listed in Table 2. Method detection limits may vary among laboratories, depending upon the analytical instrumentation used and the experience of the analyst. In addition to the work done during the development of this method and its use in the National Pesticide Survey, an interlaboratory method validation study of this method has been conducted.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of GC 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 Sect. 9.3.

1.4 When a tentative identification of ETU is made using the recommended primary GC column (Sect. 6.7.1), it must be confirmed by at least one additional qualitative technique. This technique may be the use of the confirmation GC column (Sect. 6.7.2) with the nitrogen-phosphorus detector or analysis using a gas chromatograph/mass spectrometer (GC/MS).

2. SUMMARY OF METHOD

2.1 The ionic strength and pH of a measured 50-mL aliquot of sample are adjusted by addition of ammonium chloride and potassium fluoride. The sample is poured onto a column of kieselguhr diatomaceous earth. ETU is eluted from the column with 400 mL of methylene chloride. A free radical scavenger is then added in excess to the eluate. The methylene chloride eluant is concentrated to a volume of 5 mL after solvent exchange with ethyl acetate. Gas chromatographic conditions are described which permit the separation and measurement of ETU with a nitrogen-phosphorus detector (NPD).

3. DEFINITIONS

3.1 ARTIFICIAL GROUND WATER -- An aqueous matrix designed to mimic a real ground water sample. The artificial ground water should be reproducible for use by others.

3.2 CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3 METHOD DETECTION LIMIT (MDL) -- The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

3.4 INTERNAL STANDARD (IS) -- A pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component.

3.5 FIELD DUPLICATES (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.6 INSTRUMENT PERFORMANCE CHECK SOLUTION (IPC) -- A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.7 LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.8 QUALITY CONTROL SAMPLE (QCS) -- A solution of method analytes of known concentrations which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.9 STOCK STANDARD SOLUTION (SSS) -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

3.10 SURROGATE ANALYTE (SA) -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amounts(s) before extraction or other processing and is measured with the same procedures used to measure other

sample components. The purpose of the SA is to monitor method performance with each sample.

4. INTERFERENCES

4.1 Method interferences from contaminants in solvents, reagents, glassware and other sample processing apparatus may cause discrete artifacts or elevated baselines in gas chromatograms. All reagents and apparatus must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Sect. 9.2.

4.1.1 Glassware must be scrupulously cleaned (2). Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot water and detergent and thorough rinsing with tap and reagent water. Drain dry, and heat in an oven or muffle furnace at 400°C for 1 hr. Do not heat volumetric ware. Thermally stable materials might not be eliminated by this treatment. Thorough rinsing with acetone and methylene chloride may be substituted for the heating. After drying and cooling, seal and store glassware in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

4.1.2 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.

4.2 Interfering contamination may occur when a sample containing a low concentration of ETU is analyzed immediately following a sample containing a relatively high concentration of ETU. Thorough between-sample rinsing of the sample syringe and associated equipment with ethyl acetate can minimize sample cross contamination. After analysis of a sample containing high concentrations of ETU, one or more injections of ethyl acetate should be made to ensure that accurate values are obtained for the next sample.

4.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences may vary considerably from source to source, depending upon the sample. Tentative identifications must be confirmed using the confirmation column (Sect. 6.7.2) and the conditions in Table 1.

4.4 Studies have shown that persistent ETU decomposition is circumstantially linked to free radical mechanism. Addition of a free radical scavenger is necessary to prohibit any free radical reactions.

4.5 It is important that samples and working standards be contained in the same solvent. The solvent for working standards must be the same as the final solvent used in sample preparation. If this is

not the case, chromatographic comparability of standards to sample may be affected.

5. SAFETY

5.1 ETU is a suspected carcinogen and teratogen. Primary standards of ETU should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of ETU. Each 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 (3-5) for the information of the analyst.

6. EQUIPMENT AND SUPPLIES (All specifications are suggested. Catalog numbers are included for illustration only.)

6.1 SAMPLING CONTAINERS -- 60-mL screw cap vials equipped with Teflon-faced silicone septa. Prior to use, wash vials and septa with detergent and rinse with tap and distilled water. Allow the septa to air dry at room temperature, place in a 105°C oven for 1 hr, then remove and allow to cool in an area known to be free of organics. Heat vials at 400°C for 1 hr to remove organics.

6.2 GLASSWARE

6.2.1 Concentrator tube, Kuderna-Danish (K-D) - 10-mL or 25-mL, graduated. Calibration must be checked at the volumes employed in the test. Ground glass stoppers are used to prevent evaporation of extracts.

6.2.2 Evaporative flask, K-D - 500-mL Attach to concentrator tube with springs.

6.2.3 Snyder column, K-D - three-ball macro to which a condenser can be connected to collect solvent.

6.2.4 Vials - Glass, 5 to 10-mL capacity with Teflon lined screw caps.

6.3 Boiling stones - carborundum, #12 granules, heat at 400°C for 30 min prior to use. Cool and store in a desiccator.

6.4 Water bath - Heated, capable of temperature control (±2°C). The bath should be used in a hood.

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

6.6 Tube heater - Capable of holding 8 K-D concentrator tubes and heating the mid-section of the tubes to 35-40°C while applying a nitrogen stream.

6.7 GAS CHROMATOGRAPH - Analytical system complete with GC equipped with a nitrogen-phosphorus detector, split/splitless injector for capillary columns and all required accessories. A data system is recommended for measuring peak areas. An autoinjector is recommended to improve precision of analyses.

6.7.1 Primary column - DB-Wax or equivalent,10 m x 0.25 mm I.D. bonded fused silica column, 0.25 µm film thickness. Validation data presented in this method were obtained using this column. Alternative columns may be used provided equal or better peak separation and peak shape are obtained.

6.7.2 Confirmation column - DB-1701 or equivalent, 5 m x 0.25 mm I.D. bonded fused silica column, 0.25 µm film thickness.

6.7.3 Detector - Nitrogen-phosphorus (NPD). This detector has proven effective in the analysis of ETU in fortified reagent and artificial ground waters.

7. REAGENTS AND STANDARDS

7.1 REAGENT WATER -- Reagent water is defined as water in which an interference is not observed at the retention time for ETU at the method detection limit. A Millipore Super-Q Water System or its equivalent may be used to generate reagent water. Water that has been charcoal filtered may also be suitable.

7.2 Methylene chloride, ethyl acetate -- distilled-in-glass quality or equivalent.

7.3 Nitrogen gas - high purity.

7.4 Extrelut QE Extraction column - Obtained from EM Science (Catalog No. 902050-1) or equivalent. Extrelut QE columns contain a specially modified form of large pore Kieselguhr with a granular structure.

7.5 Ammonium chloride, granular, ACS grade -- for pH and ionic strength adjustment of samples.

7.6 Potassium fluoride, anhydrous, ACS grade -- for ionic strength adjustment of sample.

7.7 Dithiothreitol (DTT) (Cleland's reagent) - for use as a free-radical scavenger (available from Aldrich Chemical Co.).

7.7.1 DTT in ethyl acetate, 1000 µg/mL - May be prepared by adding 1 g DTT to a 1-L volumetric flask and diluting to volume with

ethyl acetate. Smaller amounts may be prepared if only a small number of samples are to be analyzed. Store at room temperature.

7.8 Propylene thiourea (PTU) - For use as a surrogate standard. Prepared from carbon disulfide and 1,2-diaminopropane using the procedure published by Hardtmann, et. al. (Journal of Medicinal Chemistry, 18(5), 447-453, 1975), or purchase from commercial sources.

7.9 3,4,5,6-Tetrahydro-2-pyrimidinethiol (THP) - >98% purity, for use as an internal standard (available from Aldrich Chemical Co.).

7.10 STOCK STANDARD SOLUTION (0.10 µg/µL) - The stock standard solution may be purchased as a certified solution or prepared from pure standard material using the following procedure:

7.10.1 Prepare stock standard solution by accurately weighing 0.0010 g of pure ETU. Dissolve the ETU in ethyl acetate containing 1000 µg/mL of DTT and dilute to volume in a 10-mL volumetric flask. Larger volumes may be used at the convenience of the analyst. If ETU purity is certified at 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.

7.10.2 Transfer the stock standard solution into a Teflon sealed screw cap vial. Store at room temperature and protect from light.

7.10.3 The stock standard solution should be replaced after two weeks or sooner if comparison with laboratory control standards indicates a problem.

7.11 INTERNAL STANDARD FORTIFYING SOLUTION -- Prepare an internal standard fortifying solution by accurately weighing 0.0010 g of pure THP. Dissolve the THP in ethyl acetate containing 1000 µg/mL of DTT and dilute to volume in a 10-mL volumetric flask. Transfer the solution to a Teflon sealed screw cap bottle and store at room temperature. Addition of 50 µL of the internal standard fortifying solution to 5 mL of sample extract results in a final internal standard concentration of 1.0 µg/mL.

7.12 SURROGATE STANDARD FORTIFYING SOLUTION - Prepare a surrogate standard fortifying solution by accurately weighing 0.0010 g of pure PTU. Dissolve the PTU in ethyl acetate containing 1000 µg/mL of DTT and dilute to volume in a 10-mL volumetric flask. Transfer the solution to a Teflon sealed screw cap bottle and store at room temperature. Addition of 5 µL of the surrogate standard fortifying solution to a sample prior to extraction results in a surrogate

standard concentration in the sample of 10 µg/L and, assuming quantitative recovery of PTU, a surrogate standard concentration in the final extract of 0.10 µg/mL.

7.13 INSTRUMENT PERFORMANCE CHECK SOLUTION - Prepare the instrument performance check solution by adding 10 µL of the ETU stock standard solution, 1.0 mL of the internal standard fortifying solution, and 100 µL of the surrogate standard fortifying solution to a 100-mL volumetric flask and diluting to volume with ethyl acetate containing 1000 µg/mL of DTT. Transfer the solution to a Teflon sealed screw cap bottle and store at room temperature.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 SAMPLE COLLECTION -- Grab samples must be collected in 60-mL glass containers fitted with Teflon-lined screw caps (Sect. 6.1). Conventional sampling practices (6) should be followed; however, the bottle must not be prerinsed with sample before collection.

8.2 SAMPLE STORAGE -- The samples must be iced or refrigerated at 4°C and protected from light from the time of collection until extraction. Samples should be extracted as soon as possible after collection to avoid possible degradation of ETU. All samples must be extracted within 14 days of collection. Extracts must be stored under refrigeration and protected from light. Extracts must be analyzed within 28 days of extraction.

8.3 SAMPLE PRESERVATION -- ETU may chemically degrade in some samples even when the sample is refrigerated. When this method was developed, mercuric chloride was used to ensure against biological degradation. No suitable preservation reagent has been found other than mercuric chloride. However, the use of mercuric chloride is not recommended due to its toxicity and potential harm to the environment. Biological degradation may occur only rarely in samples with limited biological activity such as finished drinking waters.

9. QUALITY CONTROL

9.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of the following: an initial demonstration of laboratory capability; measurement of the surrogate compound in each sample; analysis of laboratory reagent blanks, laboratory fortified blanks, laboratory fortified matrix samples, and QC check standards. A MDL for ETU must also be determined.

9.2 LABORATORY REAGENT BLANKS -- Before processing any samples, the analyst must demonstrate that all glassware and reagent interferences are under control. This is accomplished by analyzing a laboratory reagent blank (LRB). A LRB is a 50-mL aliquot of reagent water, fortified with the internal standard and the

surrogate compound, that is analyzed according to Sect. 11 exactly as if it were a sample. Each time a set of samples is analyzed or reagents are changed, it must be demonstrated that the laboratory reagent blank is free of contamination that would prevent the determination of ETU at the MDL. All interfering contaminants must be eliminated before sample analyses are started.

9.3 Initial Demonstration of Capability.

9.3.1 Select a representative fortified concentration (about 10 times MDL or at a concentration in the middle of the calibration range established in Section 10) for ETU. Prepare a 4-7 replicate LFBs containing ETU at the selected concentration, and analyze each LFB according to procedures beginning in Sect. 11.

9.3.2 The mean recovery value for these samples must fall in the range of ± 20% of the fortified amount. The precision of these measurements, expressed as RSD, must be 20% or less. If the data meet these criteria, performance is considered acceptable. If acceptance criteria is not met, this procedure must be repeated using fresh replicate samples until satisfactory performance has been demonstrated.

9.3.3 To determine the MDL, prepare a minimum of 7 LFBs at a low concentration. The fortification concentration in Table 2 may be used as a guide, or use calibration data obtained in Section 10 to estimate a concentration that will produce a peak with a 3-5 times signal to noise response. Extract and analyze each replicate according to Sections 11 and 12. It is recommended that these LFBs be prepared and analyzed over a period of several days, so that day to day variations are reflected in the precision of the measurements. Calculate mean recovery and standard deviation for each analyte. Use the standard deviation and the equation given in Section 13 to calculate the MDL.

9.3.4 The initial demonstration of capability is used primarily to preclude a laboratory from analyzing unknown samples via a new, unfamiliar method prior to obtaining some experience with it. It is expected that as laboratory personnel gain experience with this method the quality of data will improve beyond those required here.

9.4 The analyst is permitted to modify GC columns or GC conditions to improve the separations, identifications, or lower the cost of measurement. Each time a modification is made, the analyst is required to repeat the procedure in Sect. 9.3.

9.5 ASSESSING SURROGATE RECOVERY

9.5.1 All samples and blanks must be fortified with the surrogate compound according to Sect. 11.1 before extraction to monitor preparation and analysis of samples.

9.5.2 Surrogate recovery must be evaluated for acceptance by determining whether the measured surrogate concentration (expressed as percent recovery) falls within the required recovery limits. Performance-based recovery criteria for PTU has been generated from single-laboratory results. Measured recovery of PTU must be between 70 and 130 percent.

9.5.3 If the surrogate recovery for a sample or blank is outside of the required surrogate recovery limits specified in Sect. 9.5.2, the laboratory must take the following actions:

(1) Check calculations to make sure there are no errors.

(2) Check internal standard and surrogate standard solutions for degradation, contamination, or other obvious abnormalities.

(3) Check instrument performance.

Reinject the extract if the above steps fail to reveal the cause of the problem. The problem must be identified and corrected before continuing. Reanalyzing the sample or blank, if possible, may be the only way to solve the problem.

9.6 ASSESSING THE INTERNAL STANDARD

9.6.1 The analyst is must monitor the internal standard peak area in all samples and blanks during each analysis day. The IS response for any sample chromatogram should not deviate from the IS response of the most recent daily calibration check standard by more than 20%.

9.6.2 If >20% deviation occurs with an individual extract, optimize instrument performance and inject a second aliquot of that extract. If the reinjected aliquot produces an acceptable IS response, report results for that injection. If a deviation >30% is obtained for the reinjected extract, reanalyze the sample beginning with Sect. 11, provided the sample is still available. Otherwise, report results obtained from the reinjected extract, but mark them as suspect.

9.6.3 If consecutive samples fail the IS response acceptance criteria, immediately analyze a medium calibration check standard. If the check standard provides a response for the IS within 20% of the predicted value, then follow procedures

itemized in Sect. 9.6.2 for each sample failing the IS response criteria. If the check standard provides a response which deviates more than 20% from the predicted value, then the analyst must recalibrate.

9.7 ASSESSING LABORATORY PERFORMANCE

9.7.1 The laboratory must analyze at least one laboratory fortified blank (LFB) per sample set. The ETU fortifying concentration in the LFB should be 10 times the MDL or at a concentration near the middle of the calibration range demonstrated by the laboratory. Calculate the percent recovery of the ETU. If the recovery falls outside the control limits (see Sect. 9.7.2), the system is judged out of control and the source of the problem must be identified and resolved before continuing analyses.

9.7.2 Until sufficient LFB data become available, usually a minimum of 20 to 30 results, the laboratory should assess its performance against the control limits described in Sect. 9.3.2. When sufficient laboratory performance data become available, develop control limits from the mean percent recovery (R) and standard deviation (S) of the percent recovery. These data are used to establish upper and lower control limits as follows:

$$\text{Upper Control Limit} = R + 3S$$
$$\text{Lower Control Limit} = R - 3S$$

After five to ten new recovery measurements are made, control limits should be recalculated using only the most recent 20 to 30 data points. Control limits must <u>not</u> exceed the fixed acceptance limits in Section 9.3.2.

9.8 Assessing Analyte Recovery - Laboratory Fortified Sample Matrix

9.8.1 The laboratory must add a known concentration to a minimum of 5% of the routine samples or one sample per set, whichever is greater. The fortified concentration should not be less than the background concentration of the sample selected for fortification. Ideally, the concentration should be the same as that used for the laboratory fortified blank (Sect. 9.3.1). Over time, samples from all routine sample sources should be fortified.

9.8.2 Calculate the percent recovery, P of the concentration for each analyte, after correcting the analytical result, X, from the fortified sample for the background concentration, b, measured in the unfortified sample, i.e.,:

$$P = 100\ (X - b)\ /\ \text{fortifying concentration},$$

and compare these values recoveries listed in Table 2. The calculated value of P must fall in the range of ± 25% of the amount fortified. If P exceeds this control limit the results for that analyte in the unfortified matrix must be listed as suspect due to matrix interference.

9.9 ASSESSING INSTRUMENT PERFORMANCE -- Instrument performance should be monitored on a daily basis by analyzing the instrument performance check solution (IPC). The IPC solution contains compounds monitor instrument sensitivity and column performance. The IPC components and performance criteria are listed in Table 4. Inability to demonstrate acceptable instrument performance indicates the need for remedial action on the GC-NPD system. A chromatogram from the analysis of the IPC is shown in Figure 1. The sensitivity requirements are set according the MDL. MDLs will vary somewhat in different laboratories according to instrument capabilities. The laboratory should adjust the amount of ETU in the IPC based on the demonstrated sensitivity of the instrumentation used.

9.10 QC Samples- It is recommended that the laboratory periodically (at least quarterly), analyze one or more standard materials from an outside source to validate performance.

9.11 ADDITIONAL QC -- 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.

10. CALIBRATION AND STANDARDIZATION

10.1 Establish GC operating parameters equivalent to those indicated in Table 1. Ensure that the gas chromatographic system is working properly by injecting the instrument performance check solution (Sect. 7.14) and checking for proper peak shapes, reasonable retention times, and sufficient sensitivity. The GC system is calibrated using the internal standard technique (Sect. 10.2).

10.2 INTERNAL STANDARD CALIBRATION PROCEDURE -- This approach requires the analyst to use at least one internal standard compatible in analytical behavior to the compound of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. In developing this method, THP (3,4,5,6-tetrahydro-2-pyrimidinethiol) was found to be a suitable internal standard.

10.2.1 Prepare ETU calibration standards at five concentration levels by adding volumes of the ETU stock standard solution to five volumetric flasks. To each flask, add a known constant amount of internal standard and dilute to volume with ethyl acetate containing 1000 µg/mL of DTT. One of the standards should be representative of an ETU concentration near, but above, the MDL. The other concentrations should

correspond to the range of concentrations expected in the sample concentrates, or should define the working range of the detector.

10.2.2 Inject each calibration standard and tabulate the relative response for ETU to the internal standard (RR_a) using the equation:

$$RR_a = A_a/A_{is}$$

where: A_a = the peak area of ETU, and
A_{is} = the peak area of the internal standard.

Generate a calibration curve of RR_a versus ETU concentration in the sample in µg/L.

10.2.3 The working calibration curve must be verified on each working day by the measurement of a minimum of two calibration check standards, one at the beginning and one at the end of the analysis day. These check standards should be at two different concentration levels to verify the calibration curve. For extended periods of analysis (greater than 8 hrs.), it is strongly recommended that check standards be interspersed with samples at regular intervals during the course of the analyses. If the ETU response varies from the predicted response by more than 20%, the test should be repeated using a fresh calibration standard. Alternatively, a new ETU calibration curve should be prepared. Any sample extracts analyzed since the last acceptable calibration check should be considered suspect, and should be reanalyzed after calibration is restored.

11. PROCEDURE

11.1 SAMPLE EXTRACTION

11.1.1 Pipet a 50-mL aliquot of water sample into a sample bottle (Sect. 6.1) containing 1.5 g of ammonium chloride and 25 g of potassium fluoride. Seal the bottle and shake vigorously until salts are dissolved. Fortify the sample with 5 µL of the surrogate standard fortifying solution (Sect. 7.13).

11.1.2 Pour contents of the bottle onto the Extrelut (sorbent) column (Sect. 7.4). Allow the column to stand undisturbed for 15 min.

11.1.3 Add 5 mL of 1000 µg/mL DTT in ethyl acetate to a K-D concentrator tube equipped with a 500-mL flask.

11.1.4 Add 400 mL of methylene chloride in 50-75 mL portions to the Extrelut column and collect the eluant in the K-D apparatus (Sect. 11.1.3).

11.2 EXTRACT CONCENTRATION

11.2.1 Conduct the following work in a fume hood which is properly vented. Add 1 or 2 boiling stones to the K-D apparatus and attach a macro Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top. Attach a condenser to the Snyder column to recover the methylene chloride as it escapes the column. Place the K-D apparatus in a 65-70°C water bath so that the K-D tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. 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.

11.2.2 Reduce the liquid volume in the K-D tube to approximately 1 mL by placing the sample in a tube heater at 35-40°C under a stream of nitrogen. The tube heater heats the solvent in the K-D tube at volume markings between 1 and 10 mL.

11.2.3 Dilute sample to 5 mL with ethyl acetate; rinse walls of K-D tube while adding ethyl acetate. Immediately fortify the sample with 50 µL of internal standard fortifying solution (Sect. 7.12). Agitate sample to disperse internal standard. Transfer sample to a GC vial and determine ETU by GC-NPD as described in Sect. 11.3.

11.3 GAS CHROMATOGRAPHY

11.3.1 Table 1 summarizes the recommended GC operating conditions. Included in Table 1 are retention times observed using this method. An example of the separations achieved using these conditions are shown in Figure 1. Other GC columns or chromatographic conditions may be used if the requirements of Sect. 9.3 are met.

11.3.2 Calibrate or verify the system calibration daily as described in Sect. 10. The standards and extracts must be in ethyl acetate.

11.3.3 Inject 2 µL of the sample extract. Record the resulting peak size in area units.

11.3.4 The width of the retention time window used to make identifications should be based upon 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.

11.3.5 Confirmatory techniques such as chromatography with a dissimilar column, or an alternate technique such as particle

beam/HPLC/mass spectrometry (EPA Method 553) may be used for confirmation of ETU in extracts prepared by this method. A suggested confirmation column is described in Table 1.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Calculate the ETU concentration in the sample from the ETU relative response (RR_a) to the internal standard using the multi-point calibration curve described in Sect. 10.2.2. Do not use the daily calibration verification standard to quantitate ETU in samples. Do not extrapolate beyond the linear range established during calibration.

13. METHOD PERFORMANCE

13.1 In a single laboratory, ETU recovery and precision data from reagent water were determined at four concentration levels. Results were used to determine the MDL and demonstrate method range. These data are given in Table 2. The equation used to calculate the MDL are as follows:

$$MDL = S\ t_{(n-1,1-alpha\ =\ 0.99)}$$

where:

$t_{(n-1,1-alpha\ =\ 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom

n = number of replicates

S = standard deviation of replicate analyses.

13.2 In a single laboratory, ETU recovery and precision data from two artificial ground waters were determined at a single concentration level of 10 µg/L. Results were used to demonstrate applicability of the method to different ground water matrices. These data are listed in Table 3.

14. POLLUTION PREVENTION

14.1 Although this method requires 400 mL methylene chloride extracting solvent per sample, no pollution of the environment will occur due to the recovery of the solvent during the extract concentration procedure. Very little solvent will escape the fume hood. No other solvents are utilized in this method except for the very small amount of ethyl acetate needed to make up calibration and fortification standards. These small amounts of solvent pose no threat to the environment.

14.2 For information about pollution prevention that may be applicable to laboratory operations, consult "Less is Better: Laboratory Chemical

Management for Waste Reduction" available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

15. WASTE MANAGEMENT

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules, and land disposal restrictions. The laboratory has the responsibility to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations. For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel," also available from the American Chemical Society at the address in Sect. 14.2.

16. REFERENCES

1. 40 CFR, Part 136, Appendix B

2. ASTM Annual Book of Standards, Part 31, D3694, "Standard Practice for Preparation of Sample Containers and for Preservation," American Society for Testing and Materials, Philadelphia, PA, p. 679, 1980.

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, Aug. 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. ASTM Annual Book of Standards, Part 31, D3370, "Standard Practice for Sampling Water," American Society for Testing and Materials, Philadelphia, PA, p. 76, 1980.

17. TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. PRIMARY AND CONFIRMATION CHROMATOGRAPHIC CONDITIONS

Analyte	Retention Time, min	
	Primary column	Confirmation column
ETU	3.5	4.5
THP (internal standard)	5.1	5.0
PTU (surrogate standard)	2.7	2.2

Primary conditions:

Column:	10 m long x 0.25 mm I.D. DB-Wax bonded fused silica column (J&W), 0.25 m film thickness
Carrier gas:	He @ 30 cm/sec linear velocity
Makeup gas:	He @ 30 mL/min flow
Detector gases:	Air @ 100 mL/min flow; H2 @ 3 mL/min flow
Injector temperature:	220°C
Detector temperature:	230°C
Oven temperature:	220°C isothermal
Sample:	2 µL splitless; 9 sec split delay
Detector:	Nitrogen-phosphorus

Confirmation conditions:

Column:	5 m long x 0.25 mm I.D. DB-1701 bonded fused silica column (J&W), 0.25 m film thickness
Carrier gas:	He @ 30 cm/sec linear velocity
Makeup gas:	He @ 30 mL/min flow
Detector gases:	Air @ 100 m:/min flow; H2 @ 3 mL/min flow
Injector temperature:	150°C
Detector temperature:	270°C
Oven temperature:	150°C isothermal
Sample:	2 µL splitless; 9 sec split delay
Detector:	Nitrogen-phosphorus

TABLE 2. RESULTS FROM MDL AND METHOD RANGE STUDIES (a)

Fortified Level, µg/L	Amt in Blank, µg/L	n(d)	R(e)	S(f)	RSD(g)	MDL
5.0	0.492	7	97 (c)	0.845	17	2.7
10	ND (b)	7	102	0.886	9	-
25	ND	7	94	1.31	6	-
100	ND	7	97	5.96	6	-

(a) Studies conducted in reagent water; average recovery of PTU surrogate from seven fortified reagent water samples was 100% (RSD) was 8.5%.

(b) ND = not detected.

(c) Data corrected for amount detected in blank.

(d) n = number of recovery data points.

(e) R = average percent recovery.

(f) S = standard deviation.

(g) RSD = percent relative standard deviation.

TABLE 3. RESULTS FROM MATRIX EVALUATION STUDIES (a)

Matrix	Amt. in Blank, µg/L	n(e)	R(f)	S(g)	RSD(h)
Hard (b)	ND (d)	7	93	0.372	4
Organic-contaminated (c)	ND	7	93	0.253	3

(a) Samples were fortified at 10 µg/L level with ETU.

(b) Absopure Natural Artesian Spring water obtained from the Absopure Water Company in Plymouth, Michigan.

(c) Reagent water fortified with fulvic acid at the 1 mg/L concentration level. A well-characterized fulvic acid, available from the International Humic Substances Society (associated with the United States Geological Survey in Denver, Colorado), was used.

(d) ND = not detected.

(e) n = number of recovery data points.

(f) R = average percent recovery.

(g) S = standard deviation.

(h) RSD = percent relative standard deviation.

TABLE 4. LABORATORY PERFORMANCE CHECK

Test	Analyte	Conc. µg/mL	Requirements(a)
Sensitivity	Ethylene thiourea (ETU)	0.01	Detection of analyte; S/N > 3
Chromatographic performance	3,4,5,6-Tetrahydro-2-pyrimidinethiol (THP)	1	PSF between 0.95 and 1.05 (a) PGF between 0.93 and 1.07 (b)

(a) PSF = peak symmetry factor. Calculated using the equation.

$$PSF = \frac{w(\frac{1}{2})}{0.5 \times W(\frac{1}{2})}$$

where $w(\frac{1}{2})$ is the width of the front of the peak at half height in secs. and $W(\frac{1}{2})$ is the peak width in secs. at half height.

(b) PGF = peak Gaussian factor. Calculated using the equation.

$$PGF = \frac{1.83 \times w(\frac{1}{2})}{W(1/10)}$$

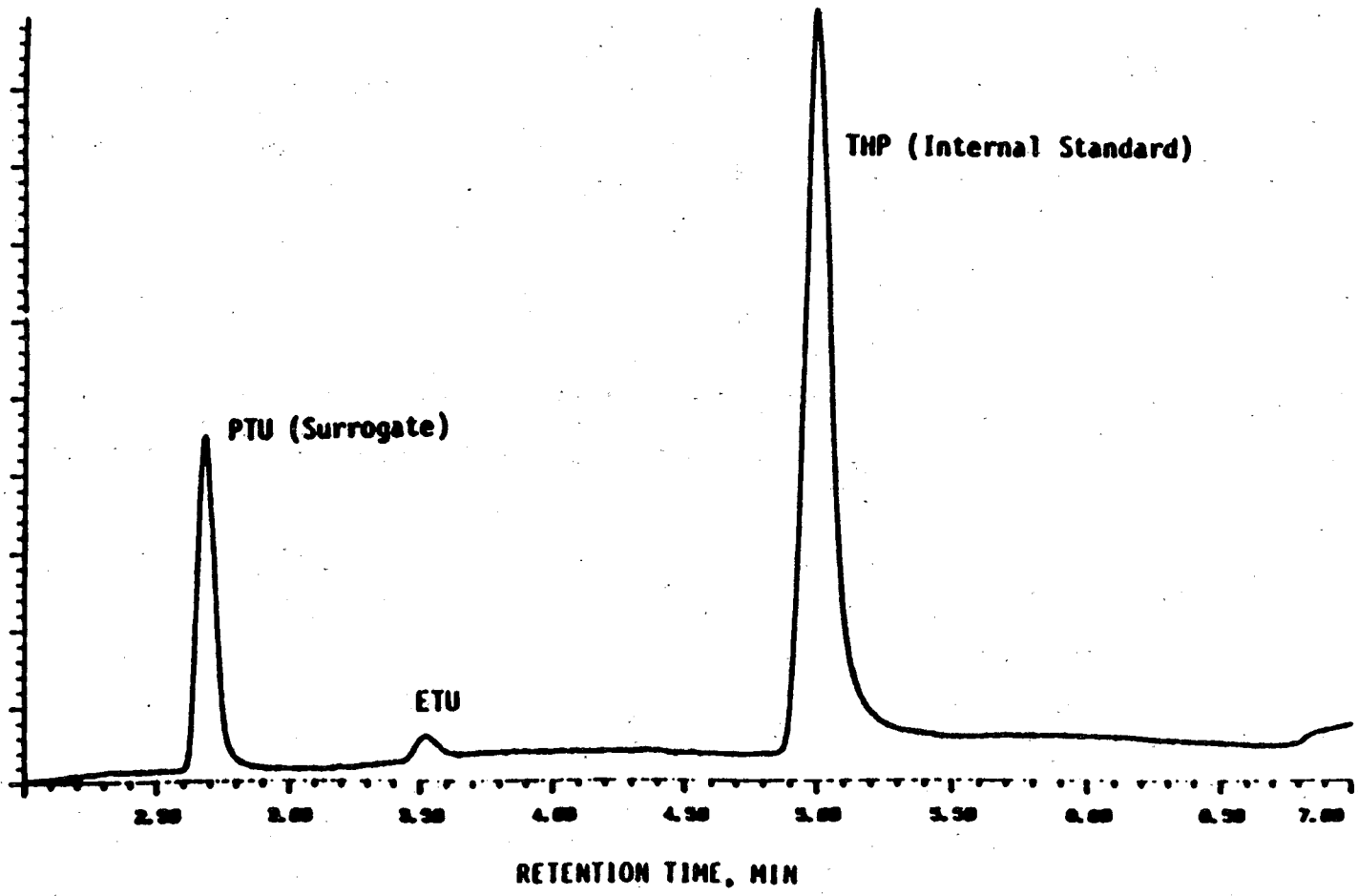

FIGURE 1. GC-NPD CHROMATOGRAM OF QUALITY CONTROL STANDARD

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METHOD 515.1. DETERMINATION OF CHLORINATED ACIDS IN WATER BY GAS CHROMATOGRAPHY WITH AN ELECTRON CAPTURE DETECTOR

Revision 4.1

Edited by J.W. Munch (1995)

R.C. Dressman and J.J. Lichtenberg - EPA 600/4-81-053, Revision 1.0 (1981)

J.W. Hodgeson - Method 515, Revision 2.0 (1986)

D. J. Munch (USEPA, Office of Water) and T. Engel (Battelle Columbus Laboratories) - National Pesticide Survey Method 3, Revision 3.0 (1987)

R.L. Graves - Method 515.1, Revision 4.0 (1989)

NATIONAL EXPOSURE RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
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METHOD 515.1

DETERMINATION OF CHLORINATED ACIDS IN WATER BY GAS CHROMATOGRAPHY WITH AN ELECTRON CAPTURE DETECTOR

1. SCOPE AND APPLICATION

1.1 This is a gas chromatographic (GC) method applicable to the determination of certain chlorinated acids in ground water and finished drinking water. The following compounds can be determined by this method:

Analyte	Chemical Abstract Services Registry Number
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 acid metabolites(a)	
Dicamba	1918-00-9
3,5-Dichlorobenzoic acid	51-36-5
Dichlorprop	120-36-5
Dinoseb	88-85-7
5-Hydroxydicamba	7600-50-2
4-Nitrophenol*	100-02-7
Pentachlorophenol (PCP)	87-86-5
Picloram	1918-02-1
2,4,5-T	93-76-5
2,4,5-TP	93-72-1

(a)DCPA monoacid and diacid metabolites included in method scope; DCPA diacid metabolite used for validation studies.

*These compounds are only qualitatively identified. These compounds are not quantitated because control over precision has not been accomplished.

1.2 This method is also applicable to the determination of salts and esters of analyte acids. The form of each acid is not distinguished by this method. Results are calculated and reported for each listed analyte as the total free acid.

1.3 This method has been validated in a single laboratory and estimated detection limits (EDLs) and method detection limits (MDLs) have been determined for the analytes above (Sect.13). Observed detection limits may vary between ground waters, depending upon the nature of interferences in the sample matrix and the specific instrumentation used.

1.4 This method is restricted to use by or under the supervision of analysts experienced in the use of GC 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 Sect. 9.3.

1.5 Analytes that are not separated chromatographically i.e., which have very similar retention times, cannot be individually identified and measured in the same calibration mixture or water sample unless an alternate technique for identification and quantitation exist (Sect. 11.9).

1.6 When this method is used to analyze unfamiliar samples for any or all of the analytes above, analyte identifications must be confirmed by at least one additional qualitative technique.

2. SUMMARY OF METHOD

2.1 A measured volume of sample of approximately 1 L is adjusted to pH 12 with 6 N sodium hydroxide and shaken for 1 hr to hydrolyze derivatives. (Note: Since many of the herbicides contained in this method are applied as a variety of esters and salts, it is vital to hydrolyze them to the parent acid prior to extraction.) Extraneous organic material is removed by a solvent wash. The sample is acidified, and the chlorinated acids are extracted with ethyl ether by shaking in a separatory funnel or mechanical tumbling in a bottle. The acids are converted to their methyl esters using diazomethane as the derivatizing agent or alternatively, trimethylsilyldiazomethane (TMSD). Excess derivatizing reagent is removed, and the esters are determined by capillary column/GC using an electron capture detector (ECD).

2.2 The method provides aa optional Florisil separation procedure to aid in the elimination of interferences that may be encountered.

3. DEFINITIONS

3.1 INTERNAL STANDARD -- A pure analyte(s) added to a solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same solution. The internal standard must be an analyte that is not a sample component.

3.2 SURROGATE ANALYTE -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction and is measured with the same procedures used to measure other sample components. The purpose of a surrogate analyte is to monitor method performance with each sample.

3.3 LABORATORY DUPLICATES (LD1 and LD2) -- Two sample aliquots taken in the analytical laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 give a measure of the precision

associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.4 FIELD DUPLICATES (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.5 LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.6 FIELD REAGENT BLANK (FRB) -- Reagent water placed in a sample container in the laboratory and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.7 LABORATORY PERFORMANCE CHECK SOLUTION (LPC) -- A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.8 LABORATORY FORTIFIED BLANK (LFB) -- An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

3.9 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.10 STOCK STANDARD SOLUTION -- A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a single analyte prepared in the laboratory with an assayed reference compound. Stock standard solutions are used to prepare primary dilution standards.

3.11 PRIMARY DILUTION STANDARD SOLUTION -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted

as needed to prepare calibration solutions and other needed analyte solutions.

3.12 CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution and stock standard solutions of the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.13 QUALITY CONTROL SAMPLE (QCS) -- A sample matrix containing method analytes or a solution of method analytes in a water miscible solvent which is used to fortify reagent water or environmental samples. The QCS is obtained from a source external to the laboratory, and is used to check laboratory performance with externally prepared test materials.

4. INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or elevated baselines in gas chromatograms. All reagents and apparatus must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Sect. 9.2.

4.1.1 Glassware must be scrupulously cleaned.(1) Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot water and detergent and thorough rinsing with dilute acid, tap and reagent water. Drain dry, and heat in an oven or muffle furnace at 400°C for 1 hr. Do not heat volumetric glassware. Thermally stable materials such as PCBs might not be eliminated by this treatment. Thorough rinsing with acetone may be substituted for the heating. After drying and cooling, seal and store glassware in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

4.1.2 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. WARNING: When a solvent is purified, stabilizers added by the manufacturer are removed, thus potentially making the solvent hazardous. Also, when a solvent is purified, preservatives added by the manufacturer are removed, thus potentially reducing the shelf-life.

4.2 The acid forms of the analytes are strong organic acids which react readily with alkaline substances and can be lost during sample preparation. Glassware and glass wool must be acid-rinsed with 1N hydrochloric acid and the sodium sulfate must be acidified with sulfuric acid prior to use to avoid analyte losses due to adsorption.

4.3 Organic acids and phenols, especially chlorinated compounds, cause the most direct interference with the determination. Alkaline hydrolysis and subsequent extraction of the basic sample removes many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis.

4.4 Interferences by phthalate esters can pose a major problem in pesticide analysis when using the ECD. These compounds generally appear in the chromatogram as large peaks. Common flexible plastics contain varying amounts of phthalates, that are easily extracted or leached 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 phthalates can best be minimized by avoiding the use of plastics in the laboratory. Exhaustive purification of reagents and glassware may be required to eliminate background phthalate contamination.(1)

4.5 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. Between-sample rinsing of the sample syringe and associated equipment with methyl-t-butyl-ether (MTBE) can minimize sample cross contamination. After analysis of a sample containing high concentrations of analytes, one or more injections of MTBE should be made to ensure that accurate values are obtained for the next sample.

4.6 Matrix interferences may be caused by contaminants that are coextracted from the sample. Also, note that all analytes listed in the Scope and Application Section are not resolved from each other on any one column, i.e., one analyte of interest may be an interferant for another analyte of interest. The extent of matrix interferences will vary considerably from source to source, depending upon the water sampled. The procedures in Sect. 11 can be used to overcome many of these interferences. Positive identifications should be confirmed (Sect. 11.9).

4.7 It is important that samples and working standards be contained in the same solvent. The solvent for working standards must be the same as the final solvent used in sample preparation. If this is not the case, chromatographic comparability of standards to sample may be affected.

5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound must be treated as a potential health hazard. Accordingly, exposure to these chemicals must be reduced to the lowest possible level. 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 also be made available to all personnel involved in

the chemical analysis. Additional references to laboratory safety are available and have been identified (2-4) for the information of the analyst.

5.2 DIAZOMETHANE -- A toxic carcinogen which can explode under certain conditions. The following precautions must be followed:

5.2.1 Use only a well ventilated hood -- do not breath vapors.

5.2.2 Use a safety screen.

5.2.3 Use mechanical pipetting aides.

5.2.4 Do not heat above 90°C -- **EXPLOSION** may result.

5.2.5 Avoid grinding surfaces, ground glass joints, sleeve bearings, glass stirrers -- **EXPLOSION** may result.

5.2.6 Store away from alkali metals -- **EXPLOSION** may result.

5.2.7 Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips.

5.2.8 The diazomethane generation apparatus used in the esterification procedures (Sect. 11.4 and 11.5) produces micromolar amounts of diazomethane to minimize safety hazards.

5.3 ETHYL ETHER -- Nanograde, redistilled in glass, if necessary.

5.3.1 Ethyl ether is an extremely flammable solvent. If a mechanical device is used for sample extraction, the device should be equipped with an explosion-proof motor and placed in a hood to avoid possible damage and injury due to an explosion.

5.3.2 Ethyl ether must be free of peroxides as indicated by EM Quant test strips (available from Scientific Products Co., Cat. No. P1126-8, and other suppliers).

5.4 WARNING: When a solvent is purified, stabilizers added by the manufacturer are removed, thus potentially making the solvent hazardous.

6. **EQUIPMENT AND SUPPLIES** (All specifications are suggested. Catalog numbers are included for illustration only.)

6.1 SAMPLE BOTTLE -- Borosilicate, 1-L volume with graduations (Wheaton Media/Lab bottle 219820 or equivalent), fitted with screw caps lined with TFE-fluorocarbon. Protect samples from light. The container must be washed and dried as described in Sect. 4.1.1 before use to minimize contamination. Cap liners are cut to fit from sheets

(Pierce Catalog No. 012736) and extracted with methanol overnight prior to use.

6.2 GLASSWARE

6.2.1 Separatory funnel -- 2000-mL, with TFE-fluorocarbon stopcocks, ground glass or TFE-fluorocarbon stoppers.

6.2.2 Tumbler bottle -- 1.7-L (Wheaton Roller Culture Vessel or equivalent), with TFE-fluorocarbon lined screw cap. Cap liners are cut to fit from sheets (Pierce Catalog No. 012736) and extracted with methanol overnight prior to use.

6.2.3 Concentrator tube, Kuderna-Danish (K-D) -- 10- or 25-mL, graduated (Kontes K-570050-2525 or Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stoppers are used to prevent evaporation of extracts.

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

6.2.5 Snyder column, K-D -- three-ball macro (Kontes K-503000-0121 or equivalent).

6.2.6 Snyder column, K-D -- two-ball micro (Kontes K-569001-0219 or equivalent).

6.2.7 Flask, round-bottom -- 500-mL with 24/40 ground glass joint.

6.2.8 Vials -- glass, 5- to 10-mL capacity with TFE-fluorocarbon lined screw cap.

6.2.9 Disposable pipets -- sterile plugged borosilicate glass, 5-mL capacity (Corning 7078-5N or equivalent).

6.3 SEPARATORY FUNNEL SHAKER -- Capable of holding 2-L separatory funnels and shaking them with rocking motion to achieve thorough mixing of separatory funnel contents (available from Eberbach Co. in Ann Arbor, MI or other suppliers).

6.4 TUMBLER -- Capable of holding tumbler bottles and tumbling them end-over-end at 30 turns/min (Associated Design and Mfg. Co., Alexandria, VA and other suppliers).

6.5 BOILING STONES -- Teflon, Chemware (Norton Performance Plastics No. 015021 and other suppliers).

6.6 WATER BATH -- Heated, capable of temperature control (± 2°C). The bath should be used in a hood.

6.7 BALANCE -- Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.8 DIAZOMETHANE GENERATOR -- Assemble from two 20 x 150 mm test tubes, two Neoprene rubber stoppers, and a source of nitrogen as shown in Figure 1 (available from Aldrich Chemical Co.). When esterification is performed using diazomethane solution, the diazomethane collector is cooled in an approximately 2-L thermos for ice bath or a cryogenically cooled vessel (Thermoelectrics Unlimited Model SK-12 or equivalent).

6.9 GLASS WOOL -- Acid washed (Supelco 2-0383 or equivalent) and heated at 450°C for 4 hr.

6.10 GAS CHROMATOGRAPH -- Analytical system complete with temperature programmable GC suitable for use with capillary columns and all required accessories including syringes, analytical columns, gases, detector and stripchart recorder or computerized data system. A data system is recommended for measuring peak areas. Table 1 lists retention times observed for method analytes using the columns and analytical conditions described below.

6.10.1 Column 1 (Primary column) -- 30 m long x 0.25 mm I.D. DB-5 bonded fused silica column, 0.25 µm film thickness (J&W Scientific). Helium carrier gas flow is established at 30 cm/sec linear velocity and oven temperature is programmed from 60°C to 300°C at 4°C/min. Data presented in this method were obtained using this column. The injection volume was 2 µL splitless mode with 45 second delay. The injector temperature was 250°C and the detector was 320°C. Alternative columns may be used in accordance with the provisions described in Sect. 9.4.

6.10.2 Column 2 (Confirmation column) -- 30 m long x 0.25 mm I.D. DB-1701 bonded fused silica column, 0.25 µm film thickness (J&W Scientific). Helium carrier gas flow is established at 30 cm/sec linear velocity and oven temperature is programmed from 60°C to 300°C at 4°C/min.

6.10.3 Detector -- Electron capture. This detector has proven effective in the analysis of method analytes in fortified reagent and artificial ground waters.

7. **REAGENTS AND STANDARDS** - WARNING: When a solvent is purified, stabilizers added by the manufacturer are removed, thus potentially making the solvent hazardous. Also, when a solvent is purified, preservatives added by the manufacturer are removed, thus potentially reducing the shelf-life.

7.1 ACETONE, METHANOL, METHYLENE CHLORIDE, MTBE -- Pesticide quality or equivalent.

7.2 ETHYL ETHER, UNPRESERVED -- Nanograde, redistilled in glass if necessary. Must be free of peroxides as indicated by EM Quant test strips (available from Scientific Products Co., Cat. No. PI126-8, and other suppliers). Procedures recommended for removal of peroxides are provided with the test strips.

7.3 SODIUM SULFATE, GRANULAR, ANHYDROUS, ACS GRADE -- Heat treat in a shallow tray at 450°C for a minimum of 4 hr to remove interfering organic substances. Acidify by slurrying 100 g sodium sulfate with enough ethyl ether to just cover the solid. Add 0.1 mL concentrated sulfuric acid and mix thoroughly. Remove the ether under vacuum. Mix 1 g of the resulting solid with 5 mL of reagent water and measure the pH of the mixture. The pH must be below pH 4. Store at 130°C.

7.4 SODIUM THIOSULFATE, GRANULAR, ANHYDROUS -- ACS grade.

7.5 SODIUM HYDROXIDE (NAOH), PELLETS -- ACS grade.

7.5.1 NaOH, 6 N -- Dissolve 216 g NaOH in 900 mL reagent water.

7.6 SULFURIC ACID, CONCENTRATED -- ACS grade, sp. gr. 1.84.

7.6.1 Sulfuric acid, 12 N -- Slowly add 335 mL concentrated sulfuric acid to 665 mL of reagent water.

7.7 POTASSIUM HYDROXIDE (KOH), PELLETS -- ACS grade.

7.7.1 KOH, 37% (w/v) -- Dissolve 37 g KOH pellets in reagent water and dilute to 100 mL.

7.8 CARBITOL (DIETHYLENE GLYCOL MONOETHYL ETHER) -- ACS grade. Available from Aldrich Chemical Co.

7.9 DIAZALD, ACS grade -- Available from Aldrich Chemical Co.

7.10 DIAZALD SOLUTION -- Prepare a solution containing 10 g Diazald in 100 mL of a 50:50 by volume mixture of ethyl ether and carbitol. This solution is stable for one month or longer when stored at 4°C in an amber bottle with a Teflon-lined screw cap.

7.11 TRIMETHYLSILYLDIAZOMETHANE (TMSD) -- Available from Aldrich Chemical Co. as a 2 molar solution in hexane. TMSD is stable during storage in this solution.

7.12 SODIUM CHLORIDE (NACL), CRYSTAL, ACS GRADE -- Heat treat in a shallow tray at 450°C for a minimum of 4 hr to remove interfering organic substances.

7.13 4,4'-DIBROMOOCTAFLUOROBIPHENYL (DBOB) -- 99% purity, for use as internal standard (available from Aldrich Chemical Co).

7.14 2,4-DICHLOROPHENYLACETIC ACID (DCAA) -- 99% purity, for use as surrogate standard (available from Aldrich Chemical Co).

7.15 MERCURIC CHLORIDE -- ACS grade (Aldrich Chemical Co.) - for use as a bacteriocide (optional- see Section 8).

7.16 REAGENT WATER -- Reagent water is defined as water that is reasonably free of contamination that would prevent the

determination of any analyte of interest. Reagent water used to generate the validation data in this method was distilled water obtained from the Magnetic Springs Water Co., Columbus, Ohio.

7.17 SILICIC ACID, ACS GRADE.

7.18 FLORISIL -- 60-100/PR mesh (Sigma No. F-9127). Activate by heating in a shallow container at 150°C for at least 24 and not more than 48 hr.

7.19 STOCK STANDARD SOLUTIONS (1.00 μg/μL) -- Stock standard solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedure:

7.19.1 Prepare stock standard solutions by accurately weighing approximately 0.0100 g of pure material. Dissolve the material in MTBE and dilute to volume in a 10-mL volumetric flask. 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. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.19.2 Transfer the stock standard solutions into TFE-fluorocarbon-sealed screw cap amber vials. Store at room temperature and protect from light.

7.19.3 Stock standard solutions should be replaced after two months or sooner if comparison with laboratory fortified blanks, or QC samples indicate a problem.

7.20 INTERNAL STANDARD SOLUTION -- Prepare an internal standard solution by accurately weighing approximately 0.0010 g of pure DBOB. Dissolve the DBOB in MTBE and dilute to volume in a 10-mL volumetric flask. Transfer the internal standard solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Addition of 25 μL of the internal standard solution to 10 mL of sample extract, or 12.5 μL to 5 mL of sample extract, results in a final internal standard concentration of 0.25 μg/mL. Solution should be replaced when ongoing QC (Sect. 9) indicates a problem. Note that DBOB has been shown to be an effective internal standard for the method analytes, but other compounds may be used if the quality control requirements in Sect. 9 are met.

7.21 SURROGATE STANDARD SOLUTION -- Prepare a surrogate standard solution by accurately weighing approximately 0.0010 g of pure DCAA. Dissolve the DCAA in MTBE and dilute to volume in a 10-mL volumetric flask. Transfer the surrogate standard solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Addition of 50 μL of the surrogate standard solution to a 1-L sample prior to extraction results in a surrogate standard concentration in the sample of 5 μg/L and, assuming quantitative recovery of DCAA, a surrogate standard concentration in the final extract of 0.5 μg/mL.

Solution should be replaced when ongoing QC (Sect. 9) indicates a problem. Note DCAA has been shown to be an effective surrogate standard for the method analytes, but other compounds may be used if the quality control requirements in Sect. 9 are met.

7.22 LABORATORY PERFORMANCE CHECK SOLUTIONS -- Prepare a diluted dinoseb solution by adding 10 µL of the 1.0 µg/µL dinoseb stock solution to the MTBE and diluting to volume in a 10-mL volumetric flask. To prepare the check solution, add 40 µL of the diluted dinoseb solution, 16 µL of the 4-nitrophenol stock solution, 6 µL of the 3,5-dichlorobenzoic acid stock solution, 50 µL of the surrogate standard solution, 25 µL of the internal standard solution, and 250 µL of methanol to a 5-mL volumetric flask and dilute to volume with MTBE. Methylate sample as described in Sects. 11.4 or 11.5. Dilute the sample to 10 mL in MTBE. Transfer to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Solution should be replaced when ongoing QC (Sect. 9) indicates a problem.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Grab samples must be collected in glass containers. Conventional sampling practices (5) should be followed; however, the bottle must not be prerinsed with sample before collection.

8.2 SAMPLE PRESERVATION AND STORAGE

8.2.1 If residual chlorine is present, add 80 mg of sodium thiosulfate (or 50 mg sodium sulfite) per liter of sample to the sample bottle prior to collecting the sample.

8.2.2 After the sample is collected in a bottle containing the dechlorinating agent, seal the bottle and shake until dissolved.

8.2.3 The samples must be iced or refrigerated at 4°C away from light from the time of collection until extraction. Preservation study results indicated that most method analytes present in samples were stable for 14 days when stored under these conditions. Analyte stability may be affected by the matrix; therefore, the analyst should verify that the preservation technique is applicable to the samples under study.

8.2.4 All performance data presented in this method are from samples preserved with mercuric chloride. No suitable preservation agent (biocide) has been found other than mercuric chloride. However the use of mercuric chloride is not required due to its toxicity and potential harm to the environment.

8.2.5 In some circumstances where biological degradation of target pesticides might be expected, use of mercuric chloride may be appropriate to minimize the possibility of false-negative results. If mercuric chloride is to be used, add it (Sect.

7.8) to the sample bottle in amounts to produce a concentration of 10 mg/L. Add 1 mL of a solution containing 10 mg/mL of mercuric chloride in reagent water to the sample bottle at the sampling site or in the laboratory before shipping to the sampling site. A major disadvantage of mercuric chloride is that it is a highly toxic chemical; mercuric chloride must be handled with caution, and samples containing mercuric chloride must be disposed of properly.

8.3 EXTRACT STORAGE

8.3.1 Extracts should be stored at 4°C away from light. Preservation study results indicate that most analytes are stable for 28 days; however, the analyst should verify appropriate extract holding times applicable to the samples under study.

9. QUALITY CONTROL

9.1 Minimum quality control (QC) requirements are initial demonstration of laboratory capability, determination of surrogate compound recoveries in each sample and blank, monitoring internal standard peak area or height in each sample and blank (when internal standard calibration procedures are being employed), analysis of laboratory reagent blanks, laboratory fortified samples, laboratory fortified blanks, and QC samples. A MDL for each analyte must also be determined.

9.2 LABORATORY REAGENT BLANKS (LRB). Before processing any samples, the analyst must demonstrate that all glassware and reagent interferences are under control. Each time a set of samples is extracted or reagents are changed, a LRB must be analyzed. If within the retention time window of any analyte the LRB produces a peak that would prevent the determination of that analyte, determine the source of contamination and eliminate the interference before processing samples.

9.3 INITIAL DEMONSTRATION OF CAPABILITY.

9.3.1 Select a representative fortified concentration for each analyte. Suggested concentrations are 10 times the EDL or a concentration that represents a mid-point in the calibration range. Prepare a primary dilution standard (in methanol) containing each analyte at 1000 times selected concentration. With a syringe, add 1 mL of the concentrate to each of four to seven 1-L aliquots of reagent water, and analyze each aliquot according to procedures beginning in Sect. 11.

9.3.2 For each analyte the recovery value for all of these samples must fall in the range of ± 30% of the fortified amount, with the RSD of the measurements 30% or less. For those compounds that meet the acceptable criteria, performance is considered acceptable and sample analysis may begin. For those compounds that fail these criteria, this procedure must be

reported using fresh samples until satisfactory performance has been demonstrated.

9.3.3 For each analyte, determine the MDL. Prepare a minimum of 7 LFBs at a low concentration. Fortification concentrations in Table 3 may be used as a guide, or use calibration data obtained in Section 10 to estimate a concentration for each analyte that will produce a peak with a 3-5 times signal to noise response. Extract and analyze each replicate according to Sections 11 and 12. It is recommended that these LFBs be prepared and analyzed over a period of several days, so that day to day variations are reflected in precision measurements. Calculate mean recovery and standard deviation for each analyte. Use the standard deviation and the equation given in Table 3 to calculate the MDL.

9.3.4 The initial demonstration of capability is used primarily to preclude a laboratory from analyzing unknown samples via a new, unfamiliar method prior to obtaining some experience with it. It is expected that as laboratory personnel gain experience with this method the quality of data will improve beyond those required here.

9.4 The analyst is permitted to modify GC columns, GC conditions, concentration techniques (i.e., evaporation techniques), internal standard or surrogate compounds. Each time such method modifications are made, the analyst must repeat the procedures in Sect. 9.3

9.5 ASSESSING SURROGATE RECOVERY.

9.5.1 When surrogate recovery from a sample or method blank is <70% or >130%, check (1) calculations to locate possible errors, (2) standard solutions for degradation, (3) contamination, and (4) instrument performance. If those steps do not reveal the cause of the problem, reanalyze the extract.

9.5.2 If a LRB extract reanalysis fails the 70-130% recovery criterion, the problem must be identified and corrected before continuing.

9.5.3 If sample extract reanalysis meets the surrogate recovery criterion, report only data for the reanalyzed extract. If sample extract continues to fail the recovery criterion, report all data for that sample as suspect.

9.6 ASSESSING THE INTERNAL STANDARD

9.6.1 When using the internal standard calibration procedure, the analyst must monitor the IS response (peak area or peak height) of all samples during each analysis day. The IS response for any sample chromatogram should not deviate from the daily calibration check standard's IS response by more than 30%.

9.6.2 If >30% deviation occurs with an individual extract, optimize instrument performance and inject a second aliquot of that extract.

9.6.2.1 If the reinjected aliquot produces an acceptable internal standard response, report results for that aliquot.

9.6.2.2 If a deviation of greater than 30% is obtained for the reinjected extract, analysis of the samples should be repeated beginning with Sect. 11, provided the sample is still available. Otherwise, report results obtained from the reinjected extract, but annotate as suspect.

9.6.3 If consecutive samples fail the IS response acceptance criterion, immediately analyze a calibration check standard.

9.6.3.1 If the check standard provides a response within 20% of the predicted value, then follow procedures itemized in Sect. 9.6.2 for each sample failing the IS response criterion.

9.6.3.2 If the check standard provides a response which deviates more than 20% of the predicted value, then the analyst must recalibrate, as specified in Sect. 10.

9.7 ASSESSING LABORATORY PERFORMANCE - LABORATORY FORTIFIED BLANK

9.7.1 The laboratory must analyze at least one laboratory fortified blank (LFB) sample with every 20 samples or one per sample set (all samples extracted within a 24-hr period) whichever is greater. The concentration of each analyte in the LFB should be 10 times EDL or a concentration which represents a mid-point in the calibration. Calculate accuracy as percent recovery (X_i). If the recovery of any analyte falls outside the control limits (see Sect. 9.7.2), that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

9.7.2 Until sufficient data become available from within their own laboratory, usually a minimum of results from 20 to 30 analyses, the laboratory should assess laboratory performance against the control limits in Sect. 9.3.2 that are derived from the data in Table 2. When sufficient internal performance data becomes available, develop control limits from the mean percent recovery ($\bar{X}$) and standard deviation (S) of the percent recovery. These data are used to establish upper and lower control limits as follows:

$$\text{UPPER CONTROL LIMIT} = \bar{X} + 3S$$
$$\text{LOWER CONTROL LIMIT} = \bar{X} - 3S$$

After each five to ten new recovery measurements, new control limits should be calculated using only the most recent 20-30 data points. These calculated control limits should not exceed those established in Section 9.3.2.

9.7.3 It is recommended that the laboratory periodically determine and document its detection limit capabilities for the analytes of interest.

9.7.4 At least quarterly, analyze a QC sample from an outside source.

9.8 ASSESSING ANALYTE RECOVERY - LABORATORY FORTIFIED SAMPLE MATRIX

9.8.1 The laboratory must add a known concentration to a minimum of 10% of the routine samples or one sample per set, whichever is greater. The concentration should not be less then the background concentration of the sample selected for fortification. Ideally, the concentration should be the same as that used for the laboratory fortified blank (Sect. 9.7). Over time, samples from all routine sample sources should be fortified.

9.8.2 Calculate the percent recovery, P, of the concentration for each analyte, after correcting the analytical result, X, from the fortified sample for the background concentration, b, measured in the unfortified sample, i.e.,:

$$P = 100 (X - b) / \text{fortifying concentration},$$

and compare these values to control limits appropriate for reagent water data collected in the same fashion. The value for P must fall between 65%-135% of the fortified concentration.

9.8.3 If the recovery of any such analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control (Sect. 9.7), the recovery problem encountered with the fortified sample is judged to be matrix related, not system related. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

9.9 ASSESSING INSTRUMENT SYSTEM - LABORATORY PERFORMANCE CHECK SAMPLE - Instrument performance should be monitored on a daily basis by analysis of the LPC sample. The LPC sample contains compounds designed to monitor instrument sensitivity, column performance (primary column) and chromatographic performance. LPC sample components and performance criteria are listed in Table 4. Inability to demonstrate acceptable instrument performance indicates the need for reevaluation of the instrument system. The sensitivity requirements are set based on the EDLs published in this method. If laboratory EDLs differ from those listed in this method,

concentrations of the LPC compounds must be adjusted to be compatible with the laboratory EDLs.

9.10 The laboratory may adopt additional quality control 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. For example, field or laboratory duplicates may be analyzed to assess the precision of the environmental measurements or field reagent blanks may be used to assess contamination of samples under site conditions, transportation and storage.

10. CALIBRATION AND STANDARDIZATION

10.1 Establish GC operating parameters equivalent to those indicated in Sect. 6.10. The GC system may be calibrated using either the internal standard technique (Sect. 10.2) or the external standard technique (Sect. 10.3). NOTE: Calibration standard solutions must be prepared such that no unresolved analytes are mixed together.

10.2 INTERNAL STANDARD CALIBRATION PROCEDURE -- To use this approach, the analyst must select one or more internal standards compatible 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. DBOB has been identified as a suitable internal standard.

10.2.1 Prepare calibration standards at a minimum of three (recommend five) concentration levels for each analyte of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more of the internal standards and 250 µL methanol, and dilute to volume with MTBE. Esterify acids with diazomethane as described in Sect. 11.4 or 11.5.

Guidance on the number of standards is as follows: A minimum of three calibration standards are required to calibrate a range of a factor of 20 in concentration. For a factor of 50 use at least four standards, and for a factor of 100 at least five standards. One calibration standard should contain each analyte of concern at a concentration 2 to 10 times greater than the method detection limit for that compound. The other calibration standards should contain each analyte of concern at concentrations that define the range of the sample analyte concentrations or should define the working range of the detector.

10.2.2 Analyze each calibration standard according to the procedure (Sect. 11.9). Tabulate response (peak height or area) against concentration for each compound and internal standard. Calculate the response factor (RF) for each analyte and surrogate using Equation 1.

$$RF = \frac{(A_s)\ (C_{is})}{(A_{is})\ (C_s)} \qquad \text{Equation 1}$$

where:

A_s = Response for the analyte to be measured.
A_{is} = Response for the internal standard.
C_{is} = Concentration of the internal standard (µg/L).
C_s = Concentration of the analyte to be measured (µg/L).

10.2.3 If the RF value over the working range is constant (20% RSD or less) the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios (A_s/A_{is}) vs. C_s.

10.2.4 The working calibration curve or RF must be verified on each working day by the measurement of a minimum of two calibration check standards, one at the beginning and one at the end of the analysis day. These check standards should be at two different concentration levels to verify the calibration curve. For extended periods of analysis (greater than 8 hr), it is strongly recommended that check standards be interspersed with samples at regular intervals during the course of the analyses. If the response for any analyte varies from the predicted response by more than ± 20%, the test must be repeated using a fresh calibration standard. If the results still do not agree, generate a new calibration curve. For those analytes that failed the calibration verification, results from field samples analyzed since the last passing calibration should be considered suspect. Reanalyze sample extracts for these analytes after acceptable calibration is restored.

10.3 EXTERNAL STANDARD CALIBRATION PROCEDURE

10.3.1 Prepare calibration standards as described in Sect 10.2.1, omitting the use of an internal standard.

10.3.2 Starting with the standard of lowest concentration, analyze each calibration standard according to Sect. 11.9 and tabulate response (peak height or area) versus the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (20% RSD or less), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

10.3.3 The working calibration curve or calibration factor must be verified on each working day as described in Section 10.2.4.

10.4 Verify calibration standards periodically, recommend at least quarterly, by analyzing a standard prepared from reference material obtained from an independent source. Results from these analyses must be within the limits used to routinely check calibration.

11. PROCEDURE

11.1 MANUAL HYDROLYSIS, PREPARATION, AND EXTRACTION.

11.1.1 Add preservative(s) (Sect.8) to LRBs and LFBs. Mark the water meniscus on the side of the sample bottle for later determination of sample volume (Sect. 11.1.9). Pour the entire sample into a 2-L separatory funnel. Fortify sample with 50 μL of the surrogate standard solution.

11.1.2 Add 250 g NaCl to the sample, seal, and shake to dissolve salt.

11.1.3 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 hr, shaking the separatory funnel and contents periodically. Note: Since many of the analytes contained in this method are applied as a variety of esters and salts, it is vital to hydrolyze them to the parent acid prior to extraction. This step must be included in the analysis of all extracted field samples, LRBs, LFBs, LFMs, and QCS.

11.1.4 Add 60 mL 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 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 technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Discard the methylene chloride phase (Sect. 14,15).

11.1.5 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.

11.1.6 Add 17 mL of 12 N H_2SO_4 to the 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 12 N H_2SO_4.

11.1.7 Add 120 mL ethyl 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 technique 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 ethyl ether phase in a 500-mL round-bottom flask containing approximately 10 g of acidified anhydrous sodium sulfate. Periodically, vigorously shake the sample and drying agent. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hours.

11.1.8 Return the aqueous phase to the separatory funnel, add a 60-mL volume of ethyl 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 of ethyl ether in the same manner.

11.1.9 Determine the original sample volume by refilling the sample bottle to the mark and transferring the water to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11.2 AUTOMATED HYDROLYSIS, PREPARATION, AND EXTRACTION. -- Data presented in this method were generated using the automated extraction procedure with the mechanical separatory funnel shaker.

11.2.1 Add preservative (Sect. 8.2) to any samples not previously preserved, e.g., LRBs and LFBs. Mark the water meniscus on the side of the sample bottle for later determination of sample volume (Sect. 11.2.9). Fortify sample with 50 μL of the surrogate standard solution. If the mechanical separatory funnel shaker is used, pour the entire sample into a 2-L separatory funnel. If the mechanical tumbler is used, pour the entire sample into a tumbler bottle.

11.2.2 Add 250 g NaCl to the sample, seal, and shake to dissolve salt.

11.2.3 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. Shake sample for 1 hr using the appropriate mechanical mixing device. Note: Since many of the analytes contained in this method are applied as a variety of esters and salts, it is vital to hydrolyze them to the parent acid prior to extraction. This step must be included in the analysis of all extracted field samples, LRBs, LFBs, LFMs, and QCS.

11.2.4 Add 300 mL methylene chloride to the sample bottle to rinse the bottle, transfer the methylene chloride to the separatory funnel or tumbler bottle, seal, and shake for 10 s, venting periodically. Repeat shaking and venting until pressure release is not observed during venting. Reseal and place sample container in appropriate mechanical mixing device. Shake or tumble the sample for 1 hr. Complete and thorough mixing of the organic and aqueous phases should be observed at least 2 min after starting the mixing device.

11.2.5 Remove the sample container from the mixing device. If the tumbler is used, pour contents of tumbler bottle into a 2-L separatory funnel. 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 technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Drain and discard the organic phase. If the tumbler is used, return the aqueous phase to the tumbler bottle.

11.2.6 Add 17 mL of 12 N H_2SO_4 to the 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 12 N H_2SO_4.

11.2.7 Add 300 mL ethyl ether to the sample, seal, and shake for 10 s, venting periodically. Repeat shaking and venting until pressure release is not observed during venting. Reseal and place sample container in appropriate mechanical mixing device. Shake or tumble sample for 1 hr. Complete and thorough mixing of the organic and aqueous phases should be observed at least 2 min after starting the mixing device.

11.2.8 Remove the sample container from the mixing device. If the tumbler is used, pour contents of tumbler bottle into a 2-L separatory funnel. 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 technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Drain and discard the aqueous phase. Collect the extract in a 500-mL round-bottom flask containing about 10 g of acidified anhydrous sodium sulfate. Periodically vigorously shake the sample and drying agent. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hr.

11.2.9 Determine the original sample volume by refilling the sample bottle to the mark and transferring the water to a 1000-mL

graduated cylinder. Record the sample volume to the nearest 5 mL.

11.3 EXTRACT CONCENTRATION

11.3.1 Assemble a K-D concentrator by attaching a concentrator tube to a 500-mL evaporative flask.

11.3.2 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 ethyl ether to complete the quantitative transfer.

11.3.3 Add 1 to 2 clean boiling stones to the evaporative flask and attach a macro Snyder column. Prewet the Snyder column by adding about 1 mL ethyl ether to the top. Place the K-D apparatus on a hot water bath, 60 to 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 with hot vapor. 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 min.

11.3.4 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of ethyl ether. Add 2 mL of MTBE and a fresh boiling stone. Attach a micro-Snyder column to the concentrator tube and prewet the column by adding about 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 to 10 min. When the apparent volume of liquid reaches 0.5 mL, remove the micro K-D from the bath and allow it to drain and cool. Remove the micro Snyder column and add 250 µL of methanol. If the gaseous diazomethane procedure (Sect. 11.4) or trimethylsilyldiazomethane procedure (11.6) is used for esterification of pesticides, rinse the walls of the concentrator tube while adjusting the volume to 5.0 mL with MTBE. If the pesticides will be esterified using the diazomethane solution (Sect. 11.5), rinse the walls of the concentrator tube while adjusting the volume to 4.5 mL with MTBE.

11.4 ESTERIFICATION OF ACIDS USING GASEOUS DIAZOMETHANE -- Results presented in this method were generated using the gaseous diazomethane derivatization procedure. See Section 11.5 and 11.6 for alternative procedures.

11.4.1 Assemble the diazomethane generator (Figure 1) in a hood.

11.4.2 Add 5 mL of ethyl ether to Tube 1. Add 1 mL of ethyl ether, 1 mL of carbitol, 1.5 mL of 37% aqueous KOH, and 0.2 grams Diazald to Tube 2. 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 1 min. Remove first sample. Rinse the tip of the diazomethane generator with ethyl ether after methylation of each sample. Bubble diazomethane through the second sample extract for 1 min. Diazomethane reaction mixture should be used to esterify only two samples; prepare new reaction mixture in Tube 2 to esterify each two additional samples. Samples should turn yellow after addition of diazomethane and remain yellow for at least 2 min. Repeat methylation procedure if necessary.

11.4.3 Seal concentrator tubes with stoppers. Store at room temperature in a hood for 30 min.

11.4.4 Destroy any unreacted diazomethane by adding 0.1 to 0.2 grams silicic acid to the concentrator tubes. Allow to stand until the evolution of nitrogen gas has stopped (approximately 20 min). Adjust the sample volume to 5.0 mL with MTBE.

11.5 ESTERIFICATION OF ACIDS USING DIAZOMETHANE SOLUTION -- Alternative procedure.

11.5.1 Assemble the diazomethane generator (Figure 2) in a hood. The collection vessel is a 10- or 15-mL vial, equipped with a Teflon-lined screw cap and maintained at 0-5C.

11.5.2 Add a sufficient amount of ethyl ether to tube 1 to cover the first impinger. Add 5 mL of MTBE to the collection vial. Set the nitrogen flow at 5-10 mL/min. Add 2 mL Diazald solution (Sect. 7.10) and 1.5 mL of 37% KOH solution to the second impinger. Connect the tubing as shown and allow the nitrogen flow to purge the diazomethane from the reaction vessel into the collection vial for 30 min. Cap the vial when collection is complete and maintain at 0-5°C. When stored at 0-5°C this diazomethane solution may be used over a period of 48 hr.

11.5.3 To each concentrator tube containing sample or standard, add 0.5 mL diazomethane solution. Samples should turn yellow after addition of the diazomethane solution and remain yellow for at least 2 min. Repeat methylation procedure if necessary.

11.5.4 Seal concentrator tubes with stoppers. Store at room temperature in a hood for 30 min.

11.5.5 Destroy any unreacted diazomethane by adding 0.1 to 0.2 grams silicic acid to the concentrator tubes. Allow to stand until the evolution of nitrogen gas has stopped (approximately 20 min). Adjust the sample volume to 5.0 mL with MTBE.

11.6 ESTERIFICATION OF ACIDS USING TRIMETHYLSILYLDIAZOMETHANE (TMSD) -- Alternative procedure. It should be noted that the gas chromatographic background is increased when TMSD is used as the derivatizing reagent instead of the generated diazomethane. Although no method analyte is affected by this increased background, the recommended surrogate, 2,4-dichloro-phenylacetic acid, is masked by an interfering peak. This renders the surrogate useless at 1 µg/L or lower. Any compound found suitable when TMSD is used is acceptable as a surrogate.

11.6.1 Carry out the hydrolysis, clean-up, and extraction of the method analytes as described up to Sect. 11.4.

11.6.2 Add 50 µL of the 2 M TMSD solution to each 5 mL sample extract.

11.6.3 Place the tube containing the extract into a heating block at 50°C and heat the extract for 1 hour.

11.6.4 Allow the extract to cool to room temperature, then add 100 µL of 2 M acetic acid in methanol to react any excess TMSD.

11.6.5 Proceed with the identification and measurement of the analytes using GC/ECD according to the procedures described in the method.

11.7 FLORISIL SEPARATION (optional)

11.7.1 Place a small plug of glass wool into a 5-mL disposable glass pipet. Tare the pipet, and measure 1 g of activated Florisil into the pipet.

11.7.2 Apply 5 mL of 5 percent methanol in MTBE to the Florisil. Allow the liquid to just reach the top of the Florisil. In this and subsequent steps, allow the liquid level to just reach the top of the Florisil before applying the next rinse, however, do not allow the Florisil to go dry. Discard eluate.

11.7.3 Apply 5 mL methylated sample to the Florisil leaving silicic acid in the tube. Collect eluate in K-D tube.

11.7.4 Add 1 mL of 5 percent methanol in MTBE to the sample container, rinsing walls. Transfer the rinse to the Florisil column leaving silicic acid in the tube. Collect eluate in a K-D tube. Repeat with 1-mL and 3-mL aliquots of 5 percent methanol in MTBE, collecting eluates in K-D tube.

11.7.5 If necessary, dilute eluate to 10 mL with 5 percent methanol in MTBE.

11.7.6 Seal the vial and store in a refrigerator if further processing will not be performed immediately. Analyze by GC-ECD.

11.8 GAS CHROMATOGRAPHY

11.8.1 Sect. 6.10 summarizes the recommended operating conditions for the GC. Included in Table 1 are retention times observed using this method. Other GC columns or chromatographic conditions may be used if the requirements of Sect. 9.3 are met.

11.8.2 Calibrate or verify the calibration of the system daily as described in Sect. 10. The standards and extracts must be in MTBE.

11.8.3 If the internal standard calibration procedure is used, fortify the extract with 25 µL of internal standard solution. Thoroughly mix sample and place aliquot in a GC vial for subsequent analysis.

11.8.4 Inject 2 µL of the sample extract. Record the resulting peak size in area units.

11.8.5 If the response for the peak exceeds the working range of the system, dilute the extract and reanalyze. If internal standard calibration is used, add an additional amount of the IS, so that the amount in the diluted extract will match the calibration standards.

11.9 IDENTIFICATION OF ANALYTES

11.9.1 Identify a sample component by comparison of its retention time to the retention time of a reference chromatogram. If the retention time of an unknown compound corresponds, within limits, to the retention time of a standard compound, then identification is considered positive.

11.9.2 The width of the retention time window used to make identifications should be based upon 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.

11.9.3 Identification requires expert judgement when sample components are not resolved chromatographically. When GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima, or any time doubt exists over the identification of a peak on a chromatogram, appropriate alternative techniques, to help confirm peak identification, need to be employed. For example, more positive identification may be made by the use of an alternative detector which operates on a chemical/physical principle different from that originally used, e.g., mass spectrom-

etry, or the use of a second chromatography column. A suggested alternative column in described in Sect. 6.10.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Calculate analyte concentrations in the sample from the response for the analyte using the calibration procedure described in Sect. 10. Use the multi-point calibration to make all calculations. Do not use the daily calibration verification data to quantitate analytes in samples.

12.2 If the internal standard calibration procedure is used, calculate the concentration (C) in the sample using the response factor (RF) determined in Sect. 10.2 and Equation 2, or determine sample concentration from the calibration curve.

$$C\ (\mu g/L) = \frac{(A_s)(I_s)}{(A_{is})(RF)(V_o)} \qquad \text{Equation 2.}$$

where:

A_s = Response for the parameter to be measured.
A_{is} = Response for the internal standard.
I_s = Amount of internal standard added to each extract (μg).
V_o = Volume of water extracted (L).

12.3 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor determined in Sect. 10.3. The concentration (C) in the sample can be calculated from Equation 3.

$$C\ (\mu g/L) = \frac{(A)(V_t)}{(V_i)(V_s)} \qquad \text{Equation 3.}$$

where:

A = Amount of material injected (ng).
V_i = Volume of extract injected (μL).
V_t = Volume of total extract (μL).
V_s = Volume of water extracted (mL).

13. METHOD PERFORMANCE

13.1 In a single laboratory, analyte recoveries from reagent water were used to determine analyte MDLs, EDLs (Table 3) and demonstrate method range. Analyte recoveries and standard deviation about the percent recoveries at one concentration are given in Table 3. All data in Tables 1-3 were obtained using diazomethane for esterification.

13.2 In a single laboratory, analyte recoveries from one standard synthetic ground waters were determined at one concentration level. Results were used to demonstrate applicability of the method to different ground water matrices. Analyte recoveries from the one synthetic matrix are given in Table 2.

13.3 The performance of dalapon using this method has been variable. Different users have had varying success in the accuracy and precision of dalapon measurements. Because the dalapon methyl ester is much more volatile than the rest of the method analytes, it is suspected that extract concentration technique may be involved with poor recoveries of this analyte. Therefore it is recommended that the analyst use caution to avoid losses due to volatization.

14. POLLUTION PREVENTION

14.1 This method uses significant volumes of organic solvents. It is highly recommended that laboratories use solvent recovery systems to recover used solvent as sample extracts are being concentrated. Recovered solvents should be recycled or properly disposed of.

14.2 For information about pollution prevention that may be applicable to laboratory operations, consult "Less is Better: Laboratory Chemical Management for Waste Reduction" available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

15. WASTE MANAGEMENT

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions. The laboratory using this method has the responsibility to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations. For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel," also available from the American Chemical Society at the address in Sect. 14.2.

16. REFERENCES

1. ASTM Annual Book of Standards, Part 11, Volume 11.02, D3694-82, "Standard Practice for Preparation of Sample Containers and for Preservation," American Society for Testing and Materials, Philadelphia, PA, p. 86, 1986.

2. "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, Aug. 1977.

3. "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

4. "*Safety in Academic Chemistry Laboratories,*" *American Chemical* Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

5. ASTM Annual Book of Standards, Part 11, Volume 11.01, D3370-82, "Standard Practice for Sampling Water," American Society for Testing and Materials, Philadelphia, PA, p. 130, 1986.

TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. RETENTION TIMES FOR METHOD ANALYTES

Analyte	Retention Time[a] (minutes) Primary	Confirmation
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
Dichlorprop	25.0	25.6
2,4-D	25.5	27.0
DBOB (int. std.)	27.5	27.6
Pentachlorophenol (PCP)	28.3	27.0
Chloramben	29.7	32.8
2,4,5-TP	29.7	29.5
5-Hydroxydicamba	30.0	30.7
2,4,5-T	30.5	30.9
2,4-DB	32.2	32.2
Dinoseb	32.4	34.1
Bentazon	33.3	34.6
Picloram	34.4	37.5
DCPA acid metabolites	35.8	37.8
Acifluorfen	41.5	42.8

[a] Columns and analytical conditions are described in Sect. 6.10.1 and 6.10.2.

TABLE 2. SINGLE LABORATORY ACCURACY AND PRECISION FOR ANALYTES FROM REAGENT WATER AND SYNTHETIC GROUNDWATERS[a]

Analyte	Conc. µg/L	Reagent Water R[b]	Reagent Water S_R[c]	Synthetic Water 1[d] R	Synthetic Water 1[d] S_R
Acifluorfen	0.2	121	15.7	103	20.6
Bentazon	1	120	16.8	82	37.7
Chloramben	0.4	111	14.4	112	10.1
2,4-D	1	131	27.5	110	5.5
Dalapon	10	100	20.0	128	30.7
2,4-DB	4	87	13.1	0	0
DCPA acid metabolites	0.2	74	9.7	81	21.9
Dicamba	0.4	135	32.4	92	17.5
3,5-Dichlorobenzoic acid	0.6	102	16.3	82	7.4
Dichlorprop	2	107	20.3	106	5.3
Dinoseb	0.4	42	14.3	89	13.4
5-Hydroxydicamba	0.2	103	16.5	88	5.3
4-Nitrophenol	1	131	23.6	127	34.3
Pentachlorophenol (PCP)	0.04	130	31.2	84	9.2
Picloram	0.6	91	15.5	97	23.3
2,4,5-T	0.4	117	16.4	96	3.8
2,4,5-TP	0.2	134	30.8	105	6.3

[a] Data corrected for amount detected in blank and represent the mean of 7-8 samples.

[b] R = average percent recovery.

[c] S_R = standard deviation of the percent recovery

[d] Corrected for amount found in blank; Absopure Nature Artesian Spring Water Obtained from the Absopure Water Company in Plymouth, Michigan.

TABLE 3. SINGLE LABORATORY ACCURACY, PRECISION, METHOD DETECTION LIMITS (MDLs) AND ESTIMATED DETECTION LIMITS (EDLs) FOR ANALYTES FROM REAGENT WATER

Analyte	Fortified Conc. µg/L	N[a]	Recovery %	RSD %	MDL[b] µg/L	EDL[c] µg/L
Acifluorfen	0.040	7	88	23	0.026	0.04
Bentazon	0.20	7	92	19	0.11	0.20
Chloramben	0.080	7	118	33	0.097	0.097
2,4-D	0.20	7	90	14	0.078	0.20
Dalapon	1.0	6	90	45	1.3	1.3
2,4-DB	4.0	6	87	15	1.7	4.0
DCPA acid metabolites	0.20	6	74	13	0.067	0.20
Dicamba	0.080	7	155	22	0.085	0.085
3,5-Dichlorobenzoic acid	0.060	6	69	38	0.065	0.065
Dichlorprop	0.40	7	110	16	0.22	0.40
Dinoseb	0.40	6	42	34	0.33	0.40
5-Hydroxydicamba	0.040	7	49	28	0.017	0.040
4-Nitrophenol	0.20	7	148	15	0.14	0.20
Pentachlorophenol (PCP)	0.10	6	82	9	0.032	0.10
Picloram	0.12	7	166	24	0.15	0.15
2,4,5-T	0.080	7	87	21	0.045	0.80
2,4,5-TP	0.20	6	134	23	0.21	0.21

[a] N = Number of replicates

[b] $MDL = S\ t_{(n-1,1-alpha = 0.99)}$

where:

$t_{(n-1,1-alpha = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom
n = number of replicates
S = standard deviation of replicate analyses.

EDL = estimated detection limit; defined as either MDL (Appendix B to 40 CFR Part 136 - Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11) or a level of compound in a sample yielding a peak in the final extract with signal-to-noise ratio of approximately 5, whichever value is higher.

TABLE 4. LABORATORY PERFORMANCE CHECK SOLUTION

Test	Analyte	Conc, µg/mL	Requirements
Sensitivity	Dinoseb	0.004	Detection of analyte; S/N > 3
Chromatographic performance	4-Nitrophenol	1.6	0.70 <PGF<1.05[b]
Column performance	3,5-Dichlorobenzoic acid 4-Nitrophenol	0.6 1.6	Resolution >0.40[b]

[a] PGF = peak Gaussian factor. Calculated using the equation:

$$PGF = \frac{1.83 \times W(1/2)}{W(1/10)}$$

where W(1/2) is the peak width at half height and W(1/10) is the peak width at tenth height.

[b] Resolution between the two peaks as defined by the equation:

$$R = \frac{t}{W}$$

where t is the difference in elution times in secs. between the two peaks and W is the average peak width in secs., at the baseline, of the two peaks.

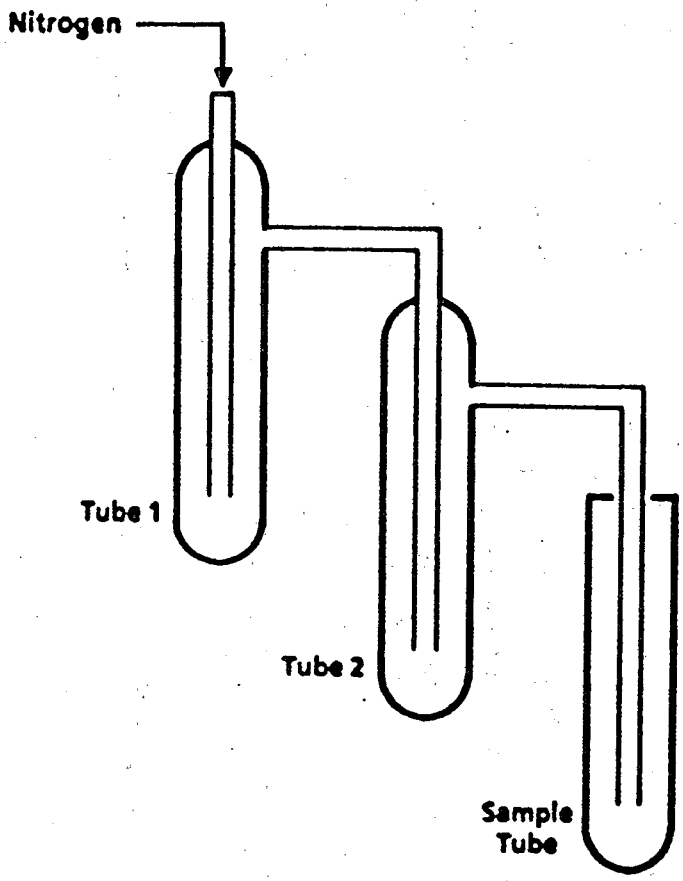

FIGURE 1. GASEOUS DIAZOMETHANE GENERATOR

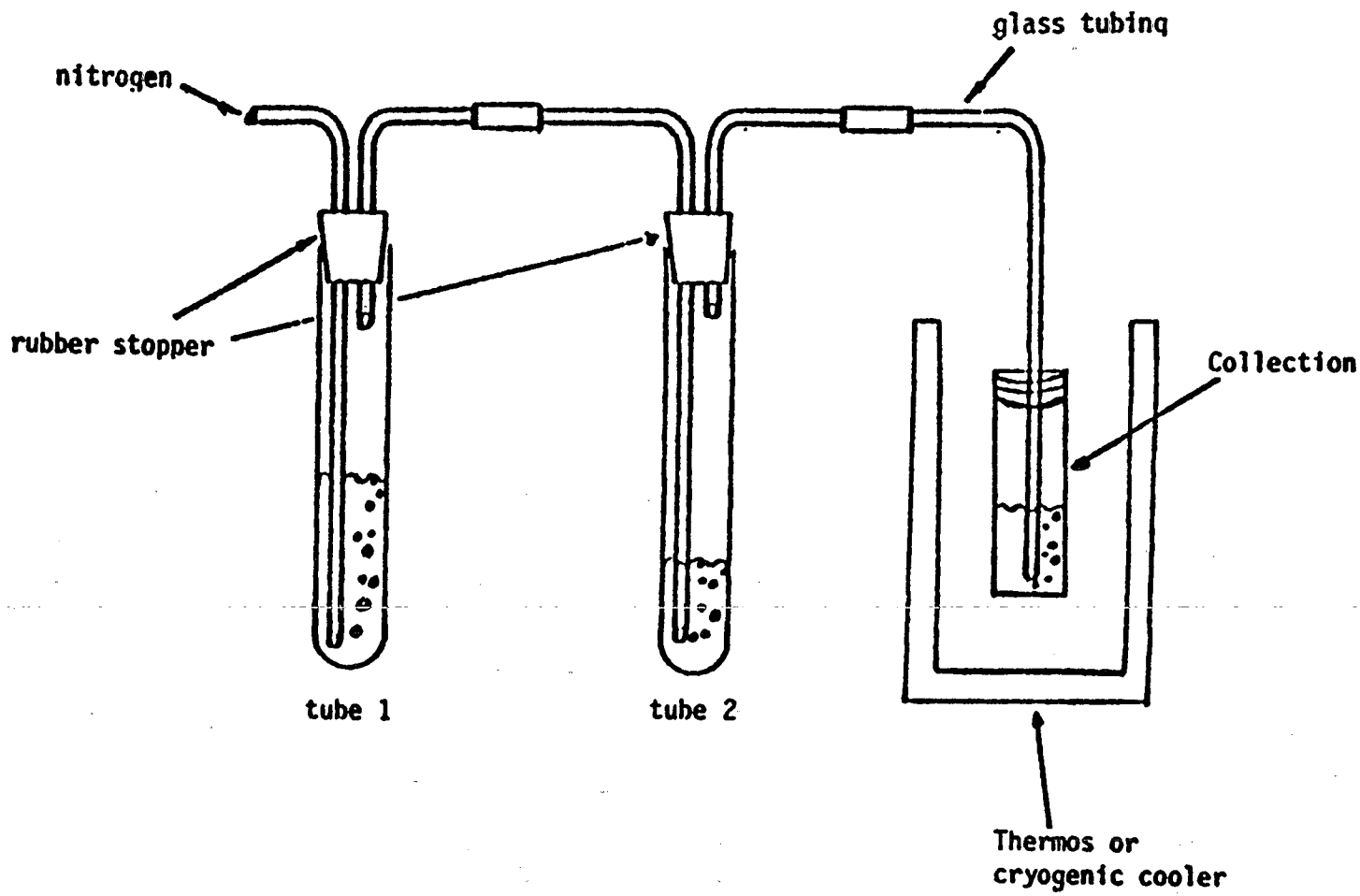

FIGURE 2. DIAZOMETHANE SOLUTION GENERATOR

METHOD 515.2. DETERMINATION OF CHLORINATED ACIDS IN WATER USING LIQUID-SOLID EXTRACTION AND GAS CHROMATOGRAPHY WITH AN ELECTRON CAPTURE DETECTOR

Revision 1.1

Edited by J.W. Munch (1995)

R.C. Dressman and J.J. Lichtenberg - EPA 600/4-81-053, Revision 1.0 (1981)

J.W. Hodgeson - Method 515, Revision 2.0 (1986)

T. Engel (Battelle Columbus Laboratories) - National Pesticide Survey Method 3, Revision 3.0 (1987)

R.L. Graves - Method 515.1, Revision 4.0 (1989)

J.W. Hodgeson - Method 515.2, Revision 1.0 (1992)

NATIONAL EXPOSURE RESEARCH LABORATORY
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METHOD 515.2

DETERMINATION OF CHLORINATED ACIDS IN WATER USING LIQUID-SOLID EXTRACTION AND GAS CHROMATOGRAPHY WITH AN ELECTRON CAPTURE DETECTOR

1. SCOPE AND APPLICATION

1.1 This is a gas chromatographic (GC) method applicable to the determination of certain chlorinated acids in ground water and finished drinking water. The following compounds can be determined by this method:

Analyte	Chemical Abstract Services Registry Number
Acifluorfen	50594-66-6
Bentazon	25057-89-0
2,4-D	94-75-7
2,4-DB	94-82-6
Dacthal acid metabolites [a]	
Dicamba	1918-00-9
3,5-Dichlorobenzoic acid	51-36-5
Dichlorprop	120-36-5
Dinoseb	88-85-7
5-Hydroxydicamba	7600-50-2
Pentachlorophenol (PCP)	87-86-5
Picloram	1918-02-1
2,4,5-T	93-76-5
2,4,5-TP(Silvex)	93-72-1

[a] Dacthal monoacid and diacid metabolites included in method scope; Dacthal diacid metabolite used for validation studies.

1.2 This method is applicable to the determination of salts and esters of analyte acids. The form of each acid is not distinguished by this method. Results are calculated and reported for each listed analyte as the total free acid.

1.3 Single laboratory accuracy and precision data and method detection limits (MDLs) have been determined for the analytes above (Sect. 13). Observed detection limits may vary among water matrices, depending upon the nature of interferences in the sample matrix and the specific instrumentation used.

1.4 This method is restricted to use by or under the supervision of analysts experienced in the use of GC 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 Sect. 9.3.

1.5 Analytes that are not separated chromatographically, (i.e., have very similar retention times) cannot be individually identified and measured in the same calibration mixture or water sample unless an alternative technique for identification and quantitation exists (Sect. 11.7).

1.6 When this method is used to analyze unfamiliar samples for any or all of the analytes above, analyte identifications should be confirmed by analysis on a second gas chromatographic column or by gas chromatography/mass spectrometry (GC/MS).

2. SUMMARY OF METHOD

2.1 A 250-mL measured volume of sample is adjusted to pH 12 with 6 N sodium hydroxide for 1 hr to hydrolyze derivatives. (Note: Since many of the analytes contained in this method are applied as a variety of esters and salts, it is vital to hydrolyze them to the parent acid prior to extraction.) Extraneous organic material is removed by a solvent wash. The sample is acidified, and the chlorinated acids are extracted with a 47 mm resin based extraction disk. The acids are converted to their methyl esters using diazomethane or alternatively, trimethylsilyldiazomethane (TMSD). Excess derivatizing reagent is removed, and the esters are determined by capillary column GC using an electron capture detector (ECD). Analytes are quantitated using procedural standard calibration (Sect. 3.14).

3. DEFINITIONS

3.1 INTERNAL STANDARD (IS) -- A pure analyte(s) added to a sample, extract, or standard solution in known amount(s), and used to measure the relative responses of other method analytes and surrogates that are components of the same sample or solution. The IS must be an analyte that is not a sample component.

3.2 SURROGATE ANALYTE (SA) -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction or other processing, and is measured with the same procedures used to measure other sample components. The purpose of the SA is to monitor method performance with each sample.

3.3 LABORATORY DUPLICATES (LD1 AND LD2) -- Two aliquots of the same sample taken in the analytical laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.4 FIELD DUPLICATES (FD1 AND FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated

with sample collection, preservation and storage, as well as with laboratory procedures.

3.5 LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.6 FIELD REAGENT BLANK (FRB) -- An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.7 INSTRUMENT PERFORMANCE CHECK SOLUTION (IPC) -- A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.8 LABORATORY FORTIFIED BLANK (LFB) -- An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.9 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot, and the measured values in the LFM corrected for background concentrations.

3.10 STOCK STANDARD SOLUTION (SSS) -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

3.11 PRIMARY DILUTION STANDARD SOLUTION (PDS) -- A solution of several analytes prepared in the laboratory from stock standard solutions, and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.12 CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution or stock standard solutions and the

internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.13 QUALITY CONTROL SAMPLE (QCS) -- A solution of method analytes of known concentrations which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.14 PROCEDURAL STANDARD CALIBRATION -- A calibration method where aqueous calibration standards are prepared and processed (e.g. purged,extracted, and/or derivatized) in exactly the same manner as a sample. All steps in the process from addition of sampling preservatives through instrumental analyses are included in the calibration. Using procedural standard calibration compensates for any inefficiencies in the processing procedure.

4. INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or elevated baselines in gas chromatograms. All reagents and apparatus must be routinely demonstrated to be free from interferences under analytical conditions by analyzing laboratory reagent blanks as described in Sect. 9.2.

4.1.1 Glassware must be scrupulously cleaned. (1) Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot water and detergent and thorough rinsing with dilute acid, tap and reagent water. Drain dry, and heat in an oven or muffle furnace at 400°C for 1 hr. Do not heat volumetric glassware. Thermally stable materials such as PCBs might not be eliminated by this treatment. Thorough rinsing with acetone may be substituted for the heating. After glassware is dry and cool, store it in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

4.1.2 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. WARNING: When a solvent is purified, stabilizers and preservatives added by the manufacturer are removed, thus potentially making the solvent hazardous and reducing the shelf life.

4.2 The acid forms of the analytes are strong organic acids which react readily with alkaline substances and can be lost during sample preparation. Glassware and glass wool must be acid-rinsed with 1 N

hydrochloric acid and the sodium sulfate must be acidified with sulfuric acid prior to use to avoid analyte losses due to adsorption.

4.3 Organic acids and phenols, especially chlorinated compounds, cause the most direct interference with the determination. Alkaline hydrolysis and subsequent extraction of the basic sample removes many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis.

4.4 Interferences by phthalate esters can pose a major problem in pesticide analysis when using the ECD. Phthalates generally appear in the chromatogram as large peaks. Common flexible plastics contain varying amounts of phthalates, that are easily extracted or leached 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 phthalates can best be minimized by avoiding the use of plastics in the laboratory. Exhaustive purification of reagents and glassware may be required to eliminate background phthalate contamination. (2,3)

4.5 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. Between-sample rinsing of the sample syringe and associated equipment with methyl-tert-butyl-ether (MTBE) can minimize sample cross-contamination. After analysis of a sample containing high concentrations of analytes, one or more injections of MTBE should be made to ensure that accurate values are obtained for the next sample.

4.6 Matrix interferences may be caused by contaminants that are coextracted from the sample. Also, note that all analytes listed in the Scope and Application Section are not resolved from each other on any one column, i.e., one analyte of interest may interfere with another analyte of interest. The extent of matrix interferences will vary considerably from source to source, depending upon the water sampled. The procedures in Sect. 11 can be used to overcome many of these interferences. Analyte identifications should be confirmed (Sect. 11.7).

4.7 Gas chromatographic background is significantly increased when TMSD is used as the derivatizing reagent instead of the generated diazomethane. Although no method analyte is affected by this increased background, the recommended surrogate, 2,4-dichloro-phenylacetic acid, is masked by an interfering peak. This renders the surrogate useless at 1 µg/L or lower. Any compound found suitable when TMSD is used is acceptable as a surrogate.

4.8 It is important that samples and working standards be contained in the same solvent. The solvent for working standards must be the same as the final solvent used in sample preparation. If this is

not the case, chromatographic comparability of standards to sample extracts may be affected.

5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound must be treated as a potential health hazard. Accordingly, exposure to these chemicals must be reduced to the lowest possible level. 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 also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified (5-7) for the information of the analyst.

5.2 DIAZOMETHANE -- A toxic carcinogen which can explode under certain conditions. The following precautions must be followed:

5.2.1 Use the diazomethane generator behind a safety shield in a well ventilated fume hood. Under no circumstances can the generator be heated above 90°C, and all grinding surfaces such as ground glass joints, sleeve bearings, and glass stirrers must be avoided. Diazomethane solutions must not be stored. Only generate enough for the immediate needs. The diazomethane generator apparatus used in the esterification procedure (Sect. 11.4) produces micromolar amounts of diazomethane in solution to minimize safety hazards. If the procedure is followed exactly, no possibility for explosion exists.

5.3 METHYL-TERT-BUTYL ETHER -- Nanograde, redistilled in glass, if necessary. Must be free of peroxides as indicated by EM Quant test strips (available from Scientific Products Co., Cat. No. P1126-8, and other suppliers).

5.4 WARNING: When a solvent is purified, stabilizers added by the manufacturer are removed, thus potentially making the solvent hazardous.

6. EQUIPMENT AND SUPPLIES (All specifications are suggested. Catalog numbers are included for illustration only.)

6.1 KONTES FILTER FUNNELS -- Fisher Cat. No. 953755-0000 or equivalent.

6.2 VACUUM FLASKS -- 1000 mL with glass side arm

6.3 VACUUM MANIFOLD -- The manifold should be capable of holding 6-8 filter flasks in series with house vacuum. Commercial manifolds are available from a number of suppliers, e.g., Baker, Fisher, and Varian.

6.4 CULTURE TUBES (25 x 200 mm) WITH TEFLON-LINED SCREW CAPS -- Fisher Cat. No. 14-933-1C, or equivalent.

6.5 PASTEUR PIPETS -- Glass disposable (5 mL)

6.6 LARGE VOLUME PIPETS -- Disposable, Fisher Cat. No. 13-678-8 or equivalent.

6.7 BALANCE -- Analytical, capable of weighing to .0001 g.

6.8 pH METER -- Wide range capable of accurate measurements in the pH = 1-12 range.

6.9 DIAZOMETHANE GENERATOR -- See Figure 1 for a diagram of an all glass system custom made for these validation studies. A micromolar generator is also available from Aldrich Chemical.

6.10 ANALYTICAL CONCENTRATOR -- Six or twelve positions, Organomation N-EVAP Model No. 111-6917 or equivalent.

6.11 GAS CHROMATOGRAPHY -- Analytical system complete with gas chromatograph equipped with ECD, split/splitless capillary injector, temperature programming, differential flow control and all required accessories. A data system is recommended for measuring peak areas. An autoinjector is recommended to improve precision of analysis.

6.12 GC COLUMNS AND RECOMMENDED OPERATING CONDITIONS

6.12.1 Primary -- DB-5 or equivalent, 30 m x .32 mm ID, 0.25 µm film thickness. Injector Temp. = 200°C, Detector Temp. = 280°C, Helium linear velocity is 30 cm/sec at 200°C and 10 psi, 2 µL splitless injection with purge on 3 min. Program: Hold at 60°C 1 min., increase to 260°C at 5°C/min. and hold 5 min.

6.12.2 Confirmation -- DB-1701 or equivalent, 30 m x .32 mm ID, 0.25 µm film thickness. Injector Temp. = 200 °C, Detector Temp. = 280°C, Helium linear velocity is 30 cm/sec at 200°C and 10 psi, 2 µL splitless injection with purge on 3 min. Program: Hold at 60°C 1 min., increase to 260°C at 5°C/min. and hold 5 min.

6.13 GLASS WOOL -- Acid washed with 1N HCl and heated at 450°C for 4 hr.

6.14 SHORT RANGE pH PAPER (pH=0-3).

6.15 VOLUMETRIC FLASKS -- 50 mL, 100 mL, and 250 mL

6.16 MICROSYRINGES -- 25 µL, 50 µL, 100 µL, 250 µL, 500 µL

6.17 AMBER BOTTLES -- 15 mL, with Teflon-lined screw caps

6.18 GRADUATED CYLINDER -- 250 mL

6.19 SEPARATORY FUNNEL -- 500 mL

6.20 GRADUATED CENTRIFUGE TUBES -- 15 mL or 10 mL Kuderna Danish Concentrator tubes

7. REAGENTS AND STANDARDS

7.1 EXTRACTION DISKS, 47 mm -- Resin based polystyrenedivinylbenzene

7.2 REAGENT WATER -- Reagent water is defined as a water in which an interference is not observed at the MDL of each analyte of interest.

7.2.1 A Millipore Super-Q water system or its equivalent may be used to generate deionized reagent water. Distilled water that has been passed through granular charcoal may also be suitable.

7.2.2 Test reagent water each day it is used by analyzing according to Sect. 11.

7.3 METHANOL -- Pesticide quality or equivalent.

7.4 METHYL-TERT-BUTYL ETHER (MTBE) -- Nanograde, redistilled in glass if necessary. Ether must be demonstrated to be free of peroxides. One test kit (EM Quant Test Strips), is available from EM Science, Gibbstown, NJ. Procedures for removing peroxides from the ether are provided with the test strips. Ethers must be periodically tested (at least monthly) for peroxide formation during use. Any reliable test kit may be used.

7.5 SODIUM SULFATE -- (ACS) GRANULAR, ANHYDROUS -- Heat in a shallow tray at 400°C for a minimum of 4 hr to remove phthalates and other interfering organic substances. Alternatively, extract with methylene chloride in a Soxhlet apparatus for 48 hr. After cleaning, store in a glass (not plastic) bottle.

7.5.1 Sodium sulfate drying tubes -- Plug the bottom of a large volume disposable pipet with a minimum amount of acidified glass wool (Supelco Cat. No. 20383 or equivalent). Fill the pipet halfway (3 g) with acidified sodium sulfate (See Sect. 7.9).

7.6 SULFURIC ACID -- Reagent grade.

7.6.1 Sulfuric acid, 12 N -- Slowly add 335 mL concentrated sulfuric acid to 665 mL of reagent water.

7.7 SODIUM HYDROXIDE -- ACS reagent grade or equivalent.

7.7.1 Sodium hydroxide 1N -- Dissolve 4.0 g reagent grade sodium hydroxide in reagent water and dilute to 100 mL in volumetric flasks.

7.7.2 Sodium hydroxide 6N

7.8 ETHYL ETHER, UNPRESERVED -- Nanograde, redistilled in glass if necessary. Must be free of peroxides as indicated by EM Quant test strips (available from Scientific Products Co., Cat. No. PI126-8, and other suppliers). Procedures recommended for removal of peroxides are provided with the test strips.

7.9 ACIDIFIED SODIUM SULFATE -- Cover 500 g sodium sulfate (Sect. 7.5) with ethyl ether (Sect. 7.8). While agitating vigorously, add dropwise approximately 0.7 mL concentrated sulfuric acid. Remove the ethyl ether overnight under vacuum and store the sodium sulfate in a 100°C oven.

7.10 CARBITOL, ACS GRADE -- Available from Aldrich Chemical.

7.11 DIAZALD, ACS GRADE -- Available from Aldrich Chemical.

7.12 DIAZALD SOLUTION -- Prepare a solution containing 10 g Diazald in 100 mL of a 50:50 by volume mixture of ethyl ether and carbitol. This solution is stable for 1-month or longer when stored at 4°C in an amber bottle with a Teflon-lined screw cap.

7.13 TRIMETHYLSILYLDIAZOMETHANE (TMSD) -- Available from Aldrich Chemical Co. as a 2 molar solution in hexane. TMSD is stable during storage in this solution.

7.14 4,4'-DIBROMOOCTAFLUOROBIPHENYL (DBOB) -- 99% purity, for use as internal standard.

7.15 2,4-DICHLOROPHENYLACETIC ACID (DCAA) -- 99% purity, for use as surrogate standard.

7.16 POTASSIUM HYDROXIDE -- ACS reagent grade or equivalent.

7.16.1 Potassium hydroxide solution, 37% -- Using extreme caution, dissolve 37 g reagent grade potassium hydroxide in reagent water and dilute to 100 mL.

7.17 STOCK STANDARD SOLUTIONS (1.00-2.00 $\mu g/\mu L$) -- Stock standard solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedure:

7.17.1 Prepare stock standard solutions by accurately weighing approximately 0.0100-0.0200 g of pure material. Dissolve the material in methanol and dilute to volume in a 10-mL volumetric flask. 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. Commercially prepared stock standards may be used at any concentration if

they are certified by the manufacturer or by an independent source.

7.17.2 Transfer the stock standard solutions into 15-mL TFE-fluorocarbon-sealed screw cap amber vials. Store at 4°C or less when not in use.

7.17.3 Stock standard solutions should be replaced after 2 months or sooner if comparison with laboratory fortified blanks, or QC samples indicate a problem.

7.17.4 Primary Dilution Standards -- Prepare two sets of standards according to the sets labeled A and B in Table 1. For each set, add approximately 25 mL of methanol to a 50 mL volumetric flask. Add aliquots of each stock standard in the range of approximately 20 to 400 µL and dilute to volume with methanol. Individual analyte concentrations will then be in the range of 0.4 to 8 µg/mL (for a 1.0 mg/mL stock). The minimum concentration would be appropriate for an analyte with strong electron capture detector (ECD) response, e.g. pentachlorophenol. The maximum concentration is for an analyte with weak response, e.g., 2,4-DB. The concentrations given in Table 2 reflect the relative volumes of stock standards used for the primary dilution standards used in generating the method validation data. Use these relative values to determine the aliquot volumes of individual stock standards above.

7.18 INTERNAL STANDARD SOLUTION -- Prepare a stock internal standard solution by accurately weighing approximately 0.050 g of pure DBOB. Dissolve the DBOB in methanol and dilute to volume in a 10-mL volumetric flask. Transfer the DBOB solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Prepare a primary dilution standard at approximately 1.00 µg/mL by the addition of 20 µL of the stock standard to 100 mL of methanol. Addition of 100 µL of the primary dilution standard solution to the final 5 mL of sample extract (Sect. 11) results in a final internal standard concentration of 0.020 µg/mL. Solution should be replaced when ongoing QC (Sect. 9) indicates a problem. Note that DBOB has been shown to be an effective internal standard for the method analytes, but other compounds may be used if the QC requirements in Sect. 9 are met.

7.19 SURROGATE ANALYTE SOLUTION -- Prepare a surrogate analyte stock standard solution by accurately weighing approximately 0.050 g of pure DCAA. Dissolve the DCAA in methanol and dilute to volume in a 10-mL volumetric flask. Transfer the surrogate analyte solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Prepare a primary dilution standard at approximately 2.0 µg/mL by addition of 40 µL at the stock standard to 100 mL of methanol. Addition of 250 µL of the surrogate analyte solution to a 250-mL sample prior to extraction results in a surrogate concentra-

tion in the sample of 2 µg/L and, assuming quantitative recovery of DCAA, a surrogate analyte concentration in the final 5 mL extract of 0.1 µg/mL. The surrogate standard solution should be replaced when ongoing QC (Sect. 9) indicates a problem. DCAA has been shown to be an effective surrogate standard for the method analytes, but other compounds may be used if the QC requirements in Sect. 9 are met.

7.20 INSTRUMENT PERFORMANCE CHECK SOLUTION -- Prepare a diluted dinoseb solution by adding 10 µL of the 1.0 µg/µL dinoseb stock solution to the MTBE and diluting to volume in a 10-mL volumetric flask. To prepare the check solution, add 40 µL of the diluted dinoseb solution, 16 µL of the 4-nitrophenol stock solution, 6 µL of the 3,5-dichlorobenzoic acid stock solution, 50 µL of the surrogate standard solution, 25 µL of the internal standard solution, and 250 µL of methanol to a 5-mL volumetric flask and dilute to volume with MTBE. Methylate sample as described in Sect. 11.4. Dilute the sample to 10 mL in MTBE. Transfer to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Solution should be replaced when ongoing QC (Sect. 9) indicates a problem.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Grab samples should be collected in 1-L amber glass containers. Conventional sampling practices (7) should be followed; however, the bottle must not be prerinsed with sample before collection.

8.2 SAMPLE PRESERVATION AND STORAGE

8.2.1 If residual chlorine is present, add 80 mg of sodium thiosulfate (or 50 mg of sodium sulfite) per liter of sample to the sample bottle prior to collecting the sample. Demonstration data in Section 17 of this method was obtained using sodium thiosulfate.

8.2.2 After the sample is collected in the bottle containing the dechlorinating agent, seal the bottle and mix to dissolve the thiosulfate.

8.2.3 Add hydrochloric acid (diluted 1:1 in reagent water) to the sample at the sampling site in amounts to produce a sample pH $\leq$ 2. Short range (0-3) pH paper (Sect. 6.14) may be used to monitor the pH. Note: Do not attempt to mix sodium thiosulfate and HCl in the sample bottle prior to sample collection.

8.2.4 The samples must be iced or refrigerated at 4°C away from light from the time of collection until extraction. Preservation study results indicate that the sample analytes (measured as total acid), except 5-hydroxy-dicamba, are stable in water for 14 days when stored under these conditions (Tables 8 and 9). The concentration of 5-hydroxydicamba is seriously degraded over 14 days in a biologically active matrix. However, analyte stability will very likely be affected by the

matrix; therefore, the analyst should verify that the preservation technique is applicable to the samples under study.

8.3 EXTRACT STORAGE

8.3.1 Extracts should be stored at 4°C or less away from light. Preservation study results indicate that most analytes are stable for 14 days (Tables 8 and 9); however, the analyst should verify appropriate extract holding times applicable to the samples under study.

9. QUALITY CONTROL

9.1 Minimum QC requirements are initial demonstration of laboratory capability, determination of surrogate compound recoveries in each sample and blank, monitoring internal standard peak area or height in each sample and blank, analysis of laboratory reagent blanks, laboratory fortified matrices, laboratory fortified blanks, and QC samples. A MDL for each analyte must also be determined.

9.2 LABORATORY REAGENT BLANKS (LRB) -- Before processing any samples, the analyst must demonstrate that all glassware and reagent interferences are under control. Each time a set of samples is extracted or reagents are changed, a LRB must be analyzed. If within the retention time window of any analyte the LRB produces a peak that would prevent the determination of that analyte, determine the source of contamination and eliminate the interference before processing samples.

9.3 INITIAL DEMONSTRATION OF CAPABILITY

9.3.1 Select a representative fortified concentration (about 10 to 20 times MDL, or a mid-point in the calibration range - see Table 4) for each analyte. Prepare a primary dilution standard containing each analyte at 1000 times selected concentration. With a syringe, add 250 µL of the concentrate to each of four to seven 250 mL aliquots of reagent water, and analyze each aliquot according to procedures beginning in Sect. 11.

9.3.2 For each analyte the recovery value for all of these samples must fall in the range of ± 40% of the fortified concentration. The RSD of the measurements must be 30% or less. For compounds failing this criteria, this procedure must be repeated using fresh samples until satisfactory performance has been demonstrated for all analytes.

9.3.3 For each analyte, determine the MDL. Prepare a minimum of 7 LFBs at a low concentration. Fortification concentration in Table 2 may be used as a guide, or use calibration data obtained in Section 10 to estimate a concentration for each analyte that will produce a peak with a 3-5 times signal to

noise response. Extract and analyze each replicate according to Sections 11 and 12. It is recommended that these LFBs be prepared and analyzed over a period of several days, so that day to day variations are reflected in the precision measurement. Calculate mean recovery and standard deviation for each analyte. Use the equation given in Section 13 to calculate the MDL.

9.3.4 The initial demonstration of capability is used primarily to preclude a laboratory from analyzing unknown samples via a new, unfamiliar method prior to obtaining some experience with it. As laboratory personnel gain experience with this method the quality of data should improve beyond those required here.

9.4 The analyst is permitted to modify GC columns, GC conditions, concentration techniques (i.e., evaporation techniques), internal standard or surrogate compounds. Each time such method modifications are made, the analyst must repeat the procedures in Sect. 9.3.

9.5 ASSESSING SURROGATE RECOVERY

9.5.1 When surrogate recovery from a sample or a blank is <60% or > 140%, check calculations to locate possible errors, fortifying solutions for degradation, contamination, and instrument performance. If those steps do not reveal the cause of the problem, reanalyze the extract.

9.5.2 If a blank extract reanalysis fails the 60-140% recovery criteria, the problem must be identified and corrected before continuing.

9.5.3 If sample extract reanalysis meets the surrogate recovery criteria, report only data for the reanalyzed extract. If sample extract continues to fail the recovery criteria, report all data for that sample as suspect.

9.6 ASSESSING THE INTERNAL STANDARD

9.6.1 When using the internal standard (IS) calibration procedure, the analyst must monitor the IS response (peak area or peak height) of all samples during each analysis day. The IS response for any sample chromatogram should not deviate from the daily calibration check standard IS response by more than 30%.

9.6.2 If >30% deviation occurs with an individual extract, optimize instrument performance and inject a second aliquot of that extract.

9.6.2.1 If the reinjected aliquot produces an acceptable internal standard response, report results for that aliquot.

9.6.2.2 If a deviation of greater than 30% is obtained for the reinjected extract, analysis of the samples should be repeated beginning with Sect. 11, provided the sample is still available. Otherwise, report results obtained from the reinjected extract, but annotate as suspect.

9.6.3 If consecutive samples fail the IS response acceptance criteria, immediately analyze a medium calibration standard.

9.6.3.1 If the standard provides a response within 20% of the predicted value, then follow procedures itemized in Sect. 9.6.2 for each sample failing the IS response criterion.

9.6.3.2 If the check standard provides a response which deviates more than 20% of the predicted value, then the analyst must recalibrate as specified in Sect. 10.

9.7 ASSESSING LABORATORY PERFORMANCE -- LABORATORY FORTIFIED BLANK

9.7.1 The laboratory must analyze at least one laboratory fortified blank (LFB) sample with every 20 samples or one per sample set (all samples extracted within a 24-hr period) whichever is greater. The concentration of each analyte in the LFB should be approximately the same as in Sect. 9.3.1. Calculate percent recovery (X_i). If the recovery of any analyte falls outside the control limits (See Sect. 9.7.2), that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

9.7.2 Until sufficient data become available, usually a minimum of results from 20 to 30 analyses, each laboratory should assess laboratory performance against the control limits in Sect. 9.3.2 that are derived from the data in Table 2. When sufficient internal performance data become available, develop control limits from the mean percent recovery (X) and standard deviation (S) of the percent recovery. These data are used to establish upper and lower control limits as follows:

$$\text{UPPER CONTROL LIMIT} = X + 3S$$
$$\text{LOWER CONTROL LIMIT} = X - 3S$$

After each five to ten new recovery measurements, new control limits should be calculated using only the most recent

20-30 data points. These calculated control limits should not exceed those established in Sect. 9.3.2.

9.7.3 At least quarterly, analyze a QCS (Sect. 3.13) from an outside source.

9.8 ASSESSING ANALYTE RECOVERY - LABORATORY FORTIFIED SAMPLE MATRIX

9.8.1 Each laboratory must analyze a LFM for 10% of the samples or one sample concentration per set, whichever is greater. The concentration should not be less then the background concentration of the sample selected for fortification. Ideally, the concentration should be the same as that used for the laboratory fortified blank (Sect. 9.7). Over time, samples from all routine sample sources should be fortified.

9.8.2 Calculate the percent recovery, P, of the concentration for each analyte, after correcting the measured concentration, X, from the fortified sample for the background concentration, b, measured in the unfortified sample.

$$P = 100\ (X - b)\ /\ \text{fortified concentration},$$

and compare these values to control limits appropriate for reagent water data collected in the same fashion. Acceptance criteria are the same as those in Section 9.7 for LFBs.

9.8.3 If the recovery of any such analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control (Sect. 9.7), the recovery problem encountered with the fortified sample is judged to be matrix related, not system related. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

9.9 ASSESSING INSTRUMENT SYSTEM/INSTRUMENT PERFORMANCE CHECK (IPC) SAMPLE -- Instrument performance should be monitored on a daily basis by analysis of the IPC sample. The IPC sample contains compounds designed to monitor instrument sensitivity, column performance (primary column) and chromatographic performance. IPC sample components and performance criteria are listed in Table 11. The sensitivity requirements are set based on the MDLs published in this method. If the laboratory MDLs differ from those demonstrated here, the amount of dinoseb in the IPC sample should be adjusted accordingly.

9.10 The laboratory may adopt additional QC 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. For example, field or laboratory duplicates may be analyzed to assess the precision of the environmental measurements or field

reagent blanks may be used to assess contamination of samples under site conditions, transportation, and storage.

10. CALIBRATION AND STANDARDIZATION

10.1 Establish GC operating parameters equivalent to those indicated in Sect. 6.12. This calibration procedure employs procedural calibration standards, i.e., fortified aqueous standards which are processed through the method (Sect. 11). The GC system is calibrated by means of the internal standard technique (Sect. 10.2). NOTE: Calibration standard solutions must be prepared such that no unresolved analytes are mixed together (See Table 1).

10.2 INTERNAL STANDARD CALIBRATION PROCEDURE -- To use this approach, the analyst must select one or more internal standards compatible 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. DBOB (Sect. 7.14) has been identified as a suitable internal standard.

10.2.1 Prepare aqueous calibration standards at a minimum of three (five are recommended) concentration levels for each method analyte as follows: for each concentration, fill a 250-mL volumetric flask with 240 mL of reagent water at pH 1 and containing 50 g of dissolved sodium sulfate. Add an appropriate aliquot of the primary dilution standard (Sect. 7.17-.4) and dilute to 250 mL with the same reagent water. Guidance on the number of standards is as follows: A minimum of three calibration standards are required to calibrate a range of a factor of 20 in concentration. For a factor of 50 use at least four standards, and for a factor of 100 at least five standards. The lowest standard should represent analyte concentrations near, but above, their respective MDLs. The remaining standards should bracket the analyte concentrations expected in the sample extracts, or should define the working range of the detector. Process each aqueous calibration sample through the analytical procedure beginning with Sect. 11.1.2. The internal standard is added to the final 5 mL extract as specified in Sect. 11.4.3 or 11.5.9.

10.2.2 Analyze each calibration standard according to the procedure beginning in Sect. 11.1.2. Tabulate response (peak height or area) against concentration for each compound and internal standard. Calculate the response factor (RF) for each analyte and surrogate using Equation 1.

$$RF = \frac{(A_s)\ (C_{is})}{(A_{is})\ (C_s)} \qquad \text{Equation 1}$$

where:

A_s = Response for the analyte to be measured.
A_{is} = Response for the internal standard.
C_{is} = Concentration of the internal standard (µg/L).
C_s = Concentration of the analyte to be measured (µg/L).

10.2.3 If the RF value over the working range is constant (30% RSD or less) the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios (A_s/A_{is}) vs. C_s. A data station may be used to collect the chromatographic data, calculate response factors and generate linear or second order regression curves.

10.2.4 The working calibration curve or RF must be verified on each working shift (not to exceed 12 hours) by the measurement of one or more calibration standards. It is highly recommended that a calibration verification be performed at the beginning and at the end of every extended period of instrument operation so that field sample extracts are bracketed by calibration standards. It is also recommended that more that one standard concentration be analyzed so that the calibration is verified at more than one point. New calibration standards need not be derivatized each day. The same standard extract can be used up to 14 days. If the response for any analyte varies from the predicted response by more than ±30%, the test must be repeated using a fresh calibration standard. If the repetition also fails, a new calibration curve must be generated for that analyte using freshly prepared standards. For those analytes that failed the calibration verification, results from field samples analyzed since the last passing calibration should be considered suspect. Reanalyze sample extracts for these analytes after acceptable calibration is restored.

10.2.5 Verify calibration standards periodically, at least quarterly is recommended, by analyzing a standard prepared from reference material obtained from an independent source. Results from these analyses must be within the limits used to routinely check calibration.

11. PROCEDURE

11.1 MANUAL HYDROLYSIS AND SEPARATION OF INTERFERENCES

11.1.1 Remove the sample bottles from cold storage and allow them to equilibrate to room temperature. Acidify and add sodium thiosulfate to LFBs, LRBs and QCSs as specified in Sect. 8.

11.1.2 Measure a 250-mL aliquot of each sample with a 250-mL graduated cylinder and pour into a 500-mL separatory funnel. Add 250 µL of the surrogate primary dilution standard (Sect.

7.19) to each 250-mL sample. The surrogate will be at a concentration of 2 μg/L. Dissolve 50 g sodium sulfate in the sample.

11.1.3 Add 4 mL of 6 N NaOH to each sample, seal, and shake. Check the pH of the sample with pH paper or a pH meter; 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 hr, shaking the separatory funnel and contents periodically. Note: Since many of the herbicides contained in this method are applied as a variety of esters and salts, it is vital to hydrolyze them to the parent acid prior to extraction. This step must be included in the analysis of all extracted field samples, LRBs, LFBs, LFMs, and QCS.

11.1.4 Add 15 mL methylene chloride to the graduated cylinder to rinse the walls, transfer the methylene chloride to the separatory funnel 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 technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Discard the methylene chloride phase (Sect.14,15).

11.1.5 Add a second 15-mL volume of methylene chloride to the separatory funnel and repeat the extraction procedure a second time, discarding the methylene chloride layer. Perform a third extraction in the same manner.

11.1.6 Drain the contents of the separatory funnel into a 500-mL beaker. Adjust the pH to 1.0 ± 0.1 by the dropwise addition of concentrated sulfuric acid with constant stirring. Monitor the pH with a pH meter (Sect. 6.8) or short range (0-3) pH paper (Sect. 6.14).

11.2 SAMPLE EXTRACTION

11.2.1 Vacuum Manifold -- Assemble a manifold (Sect. 6.3) consisting of 6-8 vacuum flasks with filter funnels (Sect. 6.1,6.2). Individual vacuum control, on-off and vacuum release valves and vacuum gauges are desirable. Place the 47 mm extraction disks (Sect. 7.1) on the filter frits.

11.2.2 Add 20 mL of 10% by volume of methanol in MTBE to the top of each disk without vacuum and allow the solvent to remain for 2 min. Turn on full vacuum and draw the solvent through the disks, followed by room air for 5 min.

11.2.3 Adjust the vacuum to approximately 5 in. (mercury) and add the following in series to the filter funnel (a) 20 mL methanol (b) 20 mL reagent water (c) sample. Do not allow the disk to dry between steps and maintain the vacuum at 5 in.

11.2.4 After all the sample has passed through the disk, apply maximum vacuum and draw room air through the disks for 20 min.

11.2.5 Place the culture tubes (Sect. 6.4) in the vacuum tubes to collect the eluates. Elute the disks with two each 2-mL aliquots of 10% methanol in MTBE. Allow each aliquot to remain on the disk for one min before applying vacuum.

11.2.6 Rinse each 500-mL beaker (Sect.11.1.6) with 4 mL of pure MTBE and elute the disk with this solvent as in Sect. 11.2.5.

11.2.7 Remove the culture tubes and cap.

11.3 EXTRACT PREPARATION

11.3.1 Pre-rinse the drying tubes (Sect. 7.5.1) with 2 mL of MTBE.

11.3.2 Remove the entire extract with a 5-mL pipet and drain the lower aqueous layer back into the culture tube. Add the organic layer to the sodium sulfate drying tube (Sect. 7.5.1). Maintain liquid in the drying tube between this and subsequent steps. Collect the dried extract in a 15-mL graduated centrifuge tube or a 10-mL Kuderna-Danish tube.

11.3.3 Rinse the culture tube with an additional 1 mL of MTBE and repeat Sect. 11.3.2.

11.3.4 Repeat step Sect. 11.3.3 and finally add a 1-mL aliquot of MTBE to the drying tube before it empties. The final volume should be 6-9 mL. In this form the extract is esterified as described below.

11.4 EXTRACT ESTERIFICATION WITH DIAZOMETHANE -- See Section 11.5 for alternative procedure.

11.4.1 Assemble the diazomethane generator (Figure 1) in a hood.

11.4.2 Add 5 mL of ethyl ether to Tube 1. Add 4 mL of Diazald solution (Sect. 7.12) and 3 mL of 37% KOH solution (Sect. 7.16.1) to the reaction tube 2. Immediately place the exit tube into the collection tube containing the sample extract. Apply nitrogen flow (10 mL/min) to bubble diazo-methane through the extract. Each charge of the generator should be sufficient to esterify four samples. The appearance of a persistent yellow color is an indication that esterification is complete. The first sample should require 30 sec to 1 min

and each subsequent sample somewhat longer. The final sample may require 2-3 min.

11.4.3 Cap each collection tube and allow to remain stored at room temperature in a hood for 30 min. No significant fading of the yellow color should occur during this period. Fortify each sample with 100 µL of the internal standard primary dilution solution (Sect. 7.18) and reduce the volume to 5.0 mL with the analytical concentrator (Sect. 6.10), a stream of dry nitrogen, or an equivalent concentration technique. NOTE: The excess diazomethane is volatilized from the extract during the concentration procedure.

11.4.4 Cap the tubes and store in a refrigerator if further processing will not be performed immediately. Analyze by GC-ECD.

11.5 EXTRACT ESTERIFICATION WITH TRIMETHYLSILYLDIAZOMETHANE (TMSD) -- Alternative procedure. It should be noted that the gas chromatographic background is significantly increased when TMSD is used as the derivatizing reagent instead of the generated diazomethane. Although no method analyte is affected by this increased background, the recommended surrogate, 2,4-dichlorophenylacetic acid, is masked by an interfering peak. This renders the surrogate useless at 1 µg/L or lower. Any compound found suitable when TMSD is used is acceptable as a surrogate.

11.5.1 Carry out the hydrolysis, clean-up, and extraction of the method analytes as described up to Sect. 11.2.4.

11.5.2 Elute the herbicides from the disk by passing two 2 mL aliquots of methyl tertiary butyl ether (MTBE) through the disk into the collection tube. Rinse the sample container with 4 mL of MTBE and pass it through the disk into the tube.

11.5.3 Transfer the MTBE extract from the collection tube into an anhydrous sodium sulfate drying tube which has been prewetted with 1 mL MTBE. Be sure to discard any water layer.

11.5.4 Before the extract passes completely through the sodium sulfate, add an additional 2 mL of MTBE as a rinse.

11.5.5 Concentrate the dried extract to approximately 4 mL. Add methanol (approx. 1 mL) to the extract to yield a 20% (v/v) methanol in MTBE solution. Adjust the volume to 5 mL with MTBE. (TMSD produces the most efficient methylation of the herbicides in a 20% methanol, 80% MTBE solution.)

11.5.6 Add 50 µL of the 2 M TMSD solution to each 5 mL sample extract.

11.5.7 Place the tube containing the extract into a heating block at 50°C and heat the extract for 1 hour.

11.5.8 Allow the extract to cool to room temperature, then add 100 µL of 2 M acetic acid in methanol to react with any excess TMSD.

11.5.9 Fortify the extract with 100 µL of the internal standard solution (See Sect. 7.18) to yield a concentration of 0.020 µg/mL.

11.5.10 Proceed with the identification and measurement of the analytes using GC/ECD according to the procedures described in Sect 11.6.

11.6 GAS CHROMATOGRAPHY

11.6.1 Sect. 6.12 summarizes the recommended GC operating conditions. Included in Table 1 are retention times observed using this method. Figures 2A and 2B illustrate the chromatographic performance of the primary column (Sect. 6.12.1) for groups A and B of the method analytes. Other GC columns or chromatographic conditions, may be used if the requirements of Sect. 9.3 are met.

11.6.2 Calibrate or verify the existing calibration daily as described in Sect. 10.

11.6.3 Inject 2 µL of the sample extract. Record the resulting peak size in area units.

11.6.4 If the response for any sample peak exceeds the working range of the detector, dilute the extract and reanalyze. Add additional IS, so that the IS amount in the extract will be the same as in the calibration standards.

11.7 IDENTIFICATION OF ANALYTES

11.7.1 Identify a sample component by comparison of its retention time to the retention time of a reference chromatogram. If the retention time of an unknown compound corresponds, within limits, to the retention time of a standard compound, then an analyte is considered to be identified.

11.7.2 The width of the retention time window used to make identifications should be based upon 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 interpretation of chromatograms.

11.7.3 Identification requires expert judgment when sample components are not resolved chromatographically. When GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more

maxima, or any time doubt exists over the identification of a peak in a chromatogram, appropriate alternative techniques to help confirm peak identification need to be employed. For example, more positive identification may be made by the use of an alternative detector which operates on a chemical/physical principle different from that originally used, e.g., mass spectrometry, or the use of a second chromatography column. A suggested alternative column is described in Sect. 6.12.2.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Calculate analyte concentrations in the sample from the response for the analyte using the calibration procedure described in Sect. 10. Use the multi-point calibration for each analyte to make all calculations. Do not use the daily calibration verification data to quantitate analytes in samples.

12.2 Calculate the concentration (C) in the sample using the response factor (RF) determined in Sect. 10.2.2 and Equation 2, or determine sample concentration from the calibration curve (Sect. 10.2.3).

$$C\ (\mu g/L) = \frac{(A_s)(I_s)}{(A_{is})(RF)(V_o)} \qquad \text{Equation 2.}$$

where:

A_s = Response for the analyte to be measured.
A_{is} = Response for the internal standard.
I_s = Amount of internal standard added to each extract (μg).
V_o = Volume of water extracted (L).

13. METHOD PERFORMANCE

13.1 All data shown in Section 17 of this method were obtained with the diazomethane esterification option.

13.2 In a single laboratory, analyte recoveries from reagent water were determined at three concentration levels, Tables 2-4. Results were used to determine the analyte MDLs (8) listed in Table 2. The calculation for determining MDL is:

$$MDL = S\ t_{(n-1,1-alpha\ =\ 0.99)}$$

where:

$t_{(n-1,1-alpha\ =\ 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom

n = number of replicates

S = standard deviation of replicate analyses.

13.3 In a single laboratory, analyte recoveries from dechlorinated tap water were determined at two concentrations, Tables 5 and 6. In addition, analyte recoveries were determined at two concentrations from an ozonated surface (river) water, Tables 7 and 8, and at one level from a high humectant surface (reservoir) water, Table 10. Finally, a holding study was conducted on the preserved, ozonated surface water and recovery data are presented for day 1 and day 14 of this study, Tables 8 and 9. The ozonated surface water was chosen as the matrix in which to study analyte stability during a 14-day holding time because it was very biologically active.

14. POLLUTION PREVENTION

14.1 This method utilizes liquid-solid extraction technology which requires the use of very small quantities of organic solvents. This feature eliminates the hazards involved with the use of large volumes of potentially harmful organic solvents needed for conventional liquid-liquid extractions. Also, mercuric chloride, a highly toxic and environmentally hazardous chemical, has been replaced with hydrochloric acid as the sample preservative. These features make this method much safer and a great deal less harmful to the environment.

14.2 For information about pollution prevention that may be applicable to laboratory operations, consult "Less is Better: Laboratory Chemical Management for Waste Reduction" available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

15. WASTE MANAGEMENT

15.1 Due to the nature of this method, there is little need for waste management. No large volumes of solvents or hazardous chemicals are used. The matrices of concern are finished drinking water or source water. However, the Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations, and that laboratories protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel," also available from the American Chemical Society at the address in Sect. 14.2.

16. REFERENCES

1. ASTM Annual Book of Standards, Part 11, Volume 11.02, D3694-82, "Standard Practice for Preparation of Sample Containers and for Preservation," American Society for Testing and Materials, Philadelphia, PA, p. 86, 1986.

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17. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

TABLE 1. RETENTION DATA

Analyte	Group[a]	Retention Time, min.[b] Primary	Confirmation
3,5-Dichlorobenzoic acid	A	16.72	18.98
2,4-Dichlorophenylacetic acid (SA)	A,B	19.78	22.83
Dicamba	B	20.18	23.42
Dichlorprop	A	22.53	25.90
2,4-D	B	23.13	27.01
4,4'-Dibromooctafluorobiphenyl (IS)	A,B	24.26	26.57
Pentachlorophenol	A	25.03	27.23
Silvex	B	25.82	29.08
5-Hydroxydicamba	B	26.28	30.18
2,4,5-T	A	26.57	30.33
2,4-DB	B	27.95	31.47
Dinoseb	A	28.03	33.02
Bentazon	B	28.70	33.58
Picloram	B	29.93	35.90
Dacthal diacid metabolite	A	31.02	34.32
Acifluorfen	B	35.62	40.58

a Analytes were divided into two groups during method development to avoid chromatographic overlap.

b Columns and chromatographic conditions are described in Sect. 6.12.

TABLE 2. SINGLE LABORATORY RECOVERY, PRECISION DATA AND METHOD DETECTION LIMIT WITH FORTIFIED REAGENT WATER - LEVEL 1

Analyte	Fortified Conc. µg/L	Mean[a] Recovery %	Relative Std. Dev. %	MDL µg/L
Acifluorfen	0.50	78	21	0.25
Bentazon	2.50	70	11	0.63
2,4-D	0.25	96	38	0.28
2,4-DB	2.50	79	12	0.72
Dacthal diacid metabolite	0.25	96	16	0.13
Dicamba	0.75	109	11	0.28
3,5-Dichlorobenzoic acid	1.25	126	24	1.23
Dichlorprop	0.25	106	15	0.13
Dinoseb	0.50	87	22	0.28
5-Hydroxydicamba	0.75	90	12	0.25
Pentachlorophenol	0.25	103	18	0.16
Picloram	0.75	95	15	0.35
2,4,5-T	0.25	116	18	0.16
2,4,5-TP	0.25	98	9	0.06

a Based on the analyses of seven replicates.

TABLE 3. SINGLE LABORATORY RECOVERY AND PRECISION DATA FOR FORTIFIED REAGENT WATER - LEVEL 2

Analyte	Fortified Conc. µg/L	Mean[a] Recovery %	Relative Std. Dev. %
Acifluorfen	0.80	61	27
Bentazon	4.0	81	8
2,4-D	0.40	96	38
2,4-DB	4.0	90	13
Dacthal diacid metabolite	0.40	96	16
Dicamba	1.20	109	11
3,5-Dichlorobenzoic acid	2.00	126	24
Dichlorprop	0.40	76	21
Dinoseb	0.80	87	22
5-Hydroxydicamba	1.20	90	12
Pentachlorophenol	0.40	66	26
Picloram	1.20	68	21
2,4,5-T	0.40	116	18
2,4,5-TP	0.40	105	7

a Based on the analyses of six-seven replicates.

TABLE 4. SINGLE LABORATORY RECOVERY AND PRECISION DATA FOR FORTIFIED REAGENT WATER - LEVEL 3

Analyte	Fortified Conc. µg/L	Mean[a] Recovery %	Relative Std. Dev. %
Acifluorfen	2.0	59	13
Bentazon	10.0	68	8
2,4-D	1.0	90	20
2,4-DB	10.0	74	6
Dacthal diacid metabolite	1.0	60	10
Dicamba	3.0	75	9
3,5-Dichlorobenzoic acid	5.0	62	18
Dichlorprop	1.0	97	17
Dinoseb	2.0	63	10
5-Hydroxydicamba	3.0	77	8
Pentachlorophenol	1.0	69	11
Picloram	3.0	66	9
2,4,5-T	1.0	64	15
2,4,5-TP	1.0	68	8

a Based on the analyses of six-seven replicates.

TABLE 5. SINGLE LABORATORY RECOVERY AND PRECISION DATA FOR FORTIFIED, DECHLORINATED TAP WATER - LEVEL 1

Analyte	Fortified Conc. µg/L	Mean[a] Recovery %	Relative Std. Dev. %
Acifluorfen	0.50	117	21
Bentazon	2.50	96	12
2,4-D	0.25	59[b]	55
2,4-DB	2.50	112	15
Dacthal diacid metabolite	0.25	101	10
Dicamba	0.75	91	14
3,5-Dichlorobenzoic acid	1.25	103	15
Dichlorprop	0.25	218[c]	37
Dinoseb	0.50	134	10
5-Hydroxydicamba	0.75	90	14
Pentachlorophenol	0.25	91	8
Picloram	0.75	76	28
2,4,5-T	0.25	118	16
2,4,5-TP	0.25	99	10

a Based on the analyses of six-seven replicates.

b 2,4-D background value was 0.29 µg/L.

c Probable interference.

TABLE 6. SINGLE LABORATORY RECOVERY AND PRECISION DATA FOR FORTIFIED, DECHLORINATED TAP WATER - LEVEL 2

Analyte	Fortified Conc. µg/L	Mean[a] Recovery %	Relative Std. Dev. %
Acifluorfen	2.0	150	7
Bentazon	10.0	112	9
2,4-D	1.0	90	16
2,4-DB	10.0	111	10
Dacthal diacid metabolite	1.0	118	8
Dicamba	3.0	86	10
3,5-Dichlorobenzoic acid	5.0	111	5
Dichlorprop	1.0	88	30
Dinoseb	2.0	121	6
5-Hydroxydicamba	3.0	96	6
Pentachlorophenol	1.0	96	6
Picloram	3.0	132	12
2,4,5-T	1.0	108	10
2,4,5-TP	1.0	115	7
2,4-Dichlorophenylacetic acid[b]	1.0	120	19

a Based on the analyses of six-seven replicates.

b Surrogate analyte.

TABLE 7. SINGLE LABORATORY RECOVERY AND PRECISION DATA FOR FORTIFIED, OZONATED SURFACE WATER - LEVEL 1

Analyte	Fortified Conc. µg/L	Mean[a] Recovery %	Relative Std. Dev. %
Acifluorfen	0.50	172	14
Bentazon	2.50	92	22
2,4-D	0.25	127	13
2,4-DB	2.50	154	19
Dacthal diacid metabolite	0.25	113	17
Dicamba	0.75	107	13
3,5-Dichlorobenzoic acid	1.25	100	17
Dichlorprop	0.25	115	20
Dinoseb	0.50	134	28
5-Hydroxydicamba	0.75	89	13
Pentachlorophenol	0.25	110	22
Picloram	0.75	109	27
2,4,5-T	0.25	102	19
2,4,5-TP	0.25	127	8
2,4-Dichlorophenylacetic acid[b]	0.25	72	31

a Based on the analyses of six-seven replicates.

b Surrogate analyte.

TABLE 8. SINGLE LABORATORY RECOVERY AND PRECISION DATA FOR FORTIFIED, OZONATED SURFACE WATER - LEVEL 2, STABILITY STUDY DAY 1[b]

Analyte	Fortified Conc. µg/L	Mean[a] Recovery %	Relative Std. Dev. %
Acifluorfen	2.0	173	11
Bentazon	10.0	122	7
2,4-D	1.0	126	10
2,4-DB	10.0	130	7
Dacthal diacid metabolite	1.0	116	11
Dicamba	3.0	109	9
3,5-Dichlorobenzoic acid	5.0	115	11
Dichlorprop	1.0	116	11
Dinoseb	2.0	116	9
5-Hydroxydicamba	3.0	121	9
Pentachlorophenol	1.0	118	10
Picloram	3.0	182	14
2,4,5-T	1.0	112	9
2,4,5-TP	1.0	122	10
2,4-Dichlorophenylacetic acid[c]	1.0	110	26

a Based on the analyses of six-seven replicates.

b Samples preserved at pH = 2.0.

c Surrogate analyte.

TABLE 9. SINGLE LABORATORY RECOVERY AND PRECISION DATA FOR FORTIFIED, OZONATED SURFACE WATER - LEVEL 2, STABILITY STUDY DAY 14[b]

Analyte	Fortified Conc. µg/L	Mean[a] Recovery %	Relative Std. Dev. %
Acifluorfen	2.0	151	18
Bentazon	10.0	97	9
2,4-D	1.0	84	11
2,4-DB	10.0	128	10
Dacthal diacid metabolite	1.0	116	7
Dicamba	3.0	103	9
3,5-Dichlorobenzoic acid	5.0	81	12
Dichlorprop	1.0	107	11
Dinoseb	2.0	118	7
5-Hydroxydicamba	3.0	20	14
Pentachlorophenol	1.0	94	7
Picloram	3.0	110	32
2,4,5-T	1.0	113	8
2,4,5-TP	1.0	113	11
2,4-Dichlorophenylacetic acid[c]	1.0	87	6

a Based on the analyses of six-seven replicates.

b Samples preserved at pH = 2.0.

c Surrogate analyte.

TABLE 10. SINGLE LABORATORY RECOVERY AND PRECISION DATA FOR FORTIFIED, HIGH HUMIC CONTENT SURFACE WATER

Analyte	Fortified Conc. µg/L	Mean[a] Recovery %	Relative Std. Dev. %
Acifluorfen	2.0	120	13
Bentazon	10.0	87	11
2,4-D	1.0	59	7
2,4-DB	10.0	80	14
Dacthal diacid metabolite	1.0	100	6
Dicamba	3.0	76	9
3,5-Dichlorobenzoic acid	5.0	87	4
Dichlorprop	1.0	110	22
Dinoseb	2.0	97	6
5-Hydroxydicamba	3.0	82	9
Pentachlorophenol	1.0	70	5
Picloram	3.0	124	9
2,4,5-T	1.0	101	4
2,4,5-TP	1.0	80	6

a Based on the analyses of six-seven replicates.

TABLE 11. LABORATORY PERFORMANCE CHECK SOLUTION

Test	Analyte	Conc, µg/mL	Requirements
Sensitivity	Dinoseb	0.004	Detection of analyte; S/N > 3
Chromatographic performance	4-Nitrophenol	1.6	0.70 <PGF<1.05[b]
Column performance	3,5-Dichlorobenzoic acid 4-Nitrophenol	0.6 1.6	Resolution >0.40[b]

[a] PGF = peak Gaussian factor. Calculated using the equation:

$$PGF = \frac{1.83 \times W(1/2)}{W(1/10)}$$

where W(1/2) is the peak width at half height in secs. and W(1/10) is the peak width in secs. at one tenth height.

[b] Resolution between the two peaks as defined by the equation:

$$R = \frac{t}{W}$$

where t is the difference in elution times in secs. between the two peaks and W is the average peak width in secs., at the baseline of the two peaks.

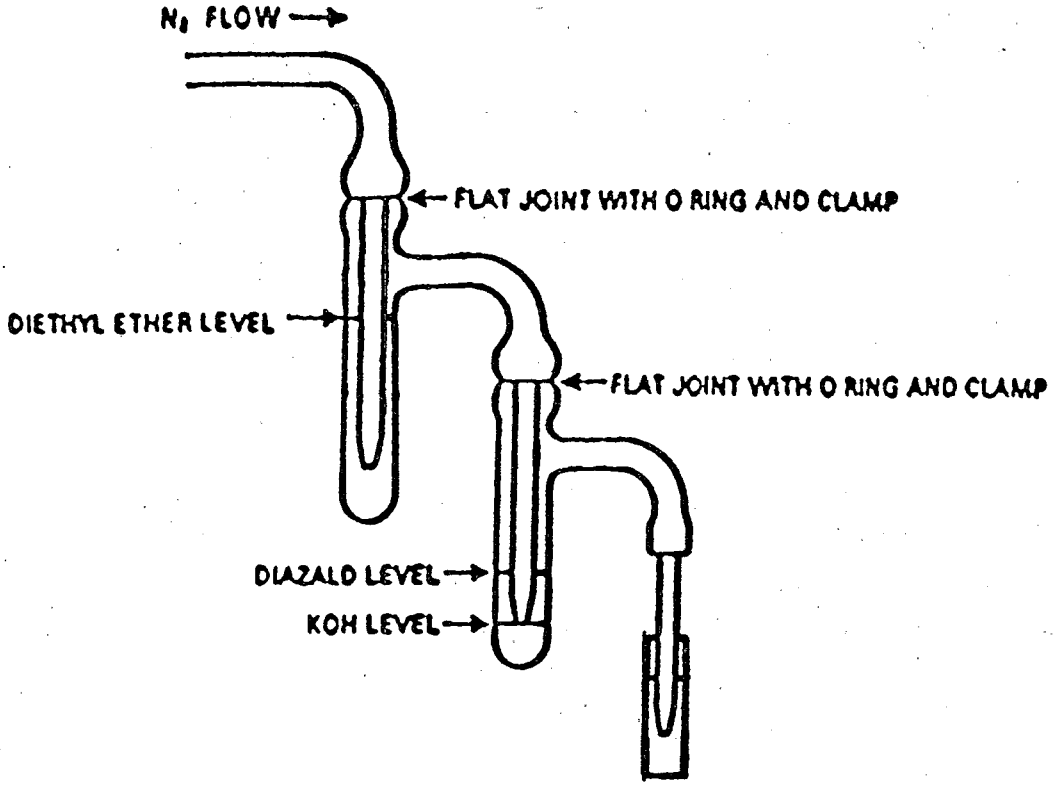

FIGURE 1. DIAZOMETHANE GENERATOR

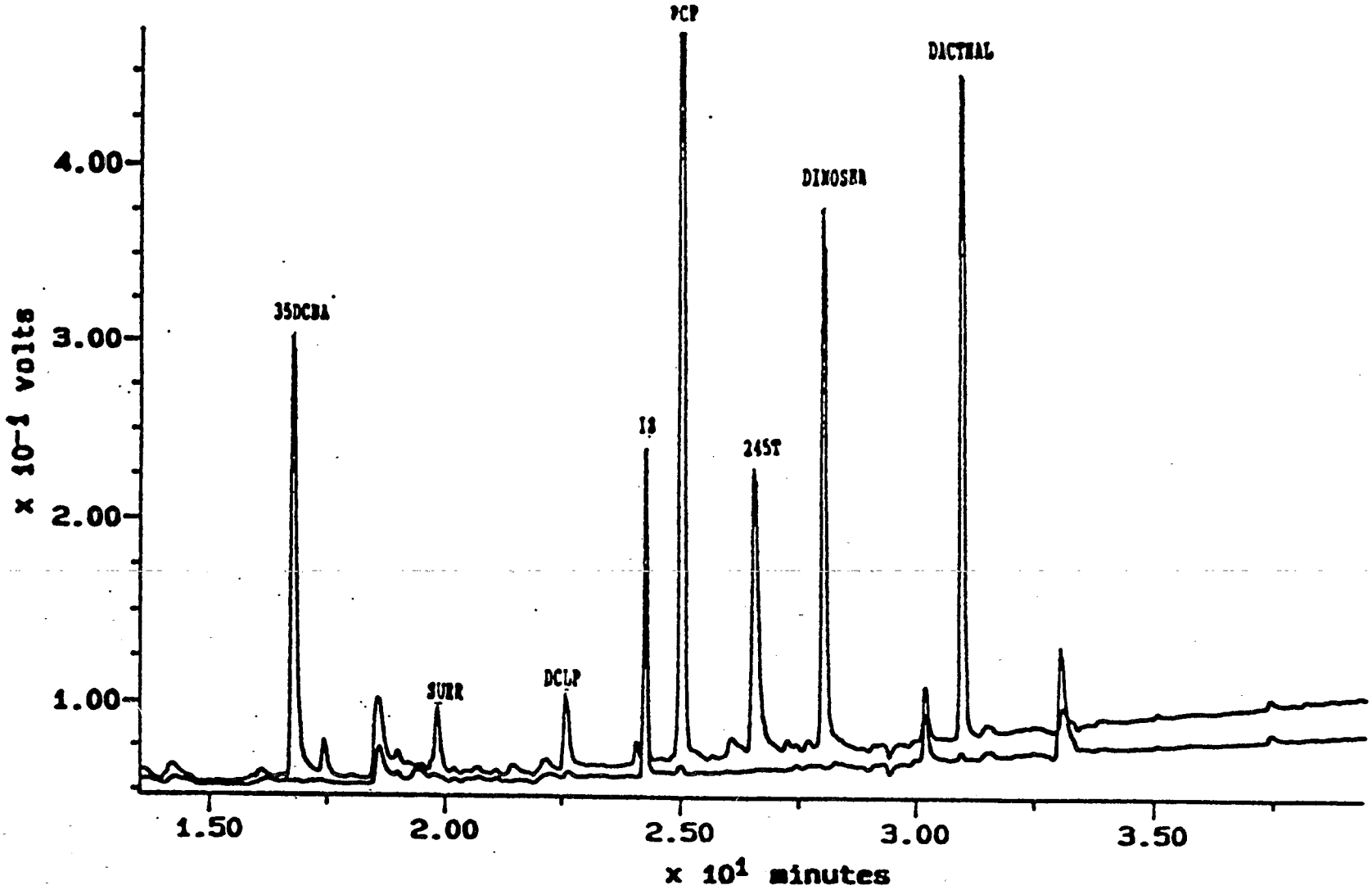

Figure 2A. Chromatogram of Group A Analytes Extracted From Ozonated Surface Water (bottom chromatogram is the laboratory reagent blank)

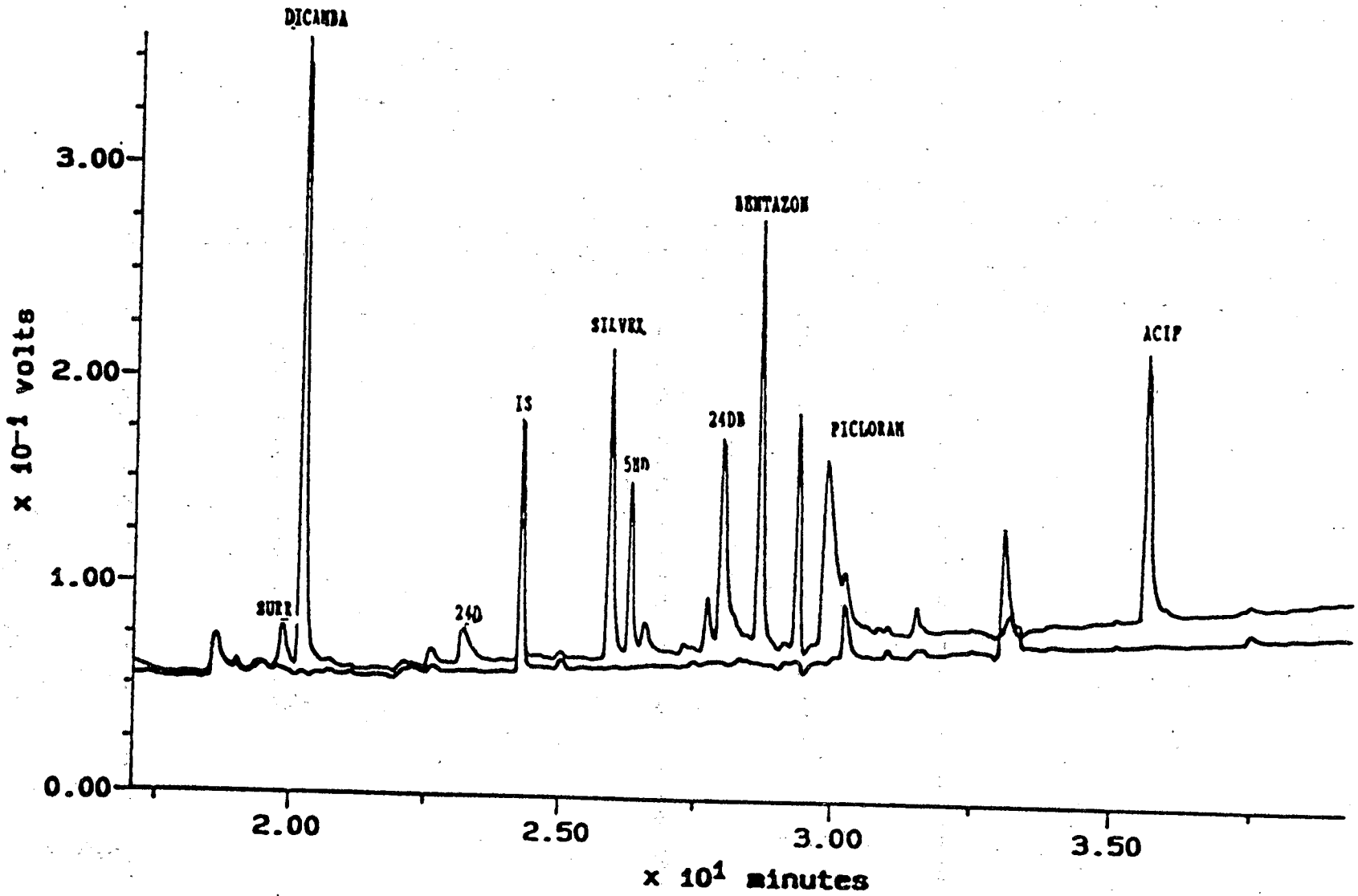

Figure 2B. Chromatogram of Group B Analytes Extracted From Ozonated Surface Water (bottom chromatogram is the laboratory reagent blank)

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METHOD 524.2. MEASUREMENT OF PURGEABLE ORGANIC COMPOUNDS IN WATER BY CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Revision 4.1

Edited by J.W. Munch (1995)

A. Alford-Stevens, J.W. Eichelberger, W.L. Budde - Method 524, Rev. 1.0 (1983)

R.W. Slater, Jr. - Revision 2.0 (1986)

J.W. Eichelberger, and W.L. Budde - Revision 3.0 (1989)

J.W. Eichelberger, J.W. Munch, and T.A. Bellar - Revision 4.0 (1992)

NATIONAL EXPOSURE RESEARCH LABORATORY
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METHOD 524.2

MEASUREMENT OF PURGEABLE ORGANIC COMPOUNDS IN WATER BY CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

1. SCOPE AND APPLICATION

1.1 This is a general purpose method for the identification and simultaneous measurement of purgeable volatile organic compounds in surface water, ground water, and drinking water in any stage of treatment (1,2). The method is applicable to a wide range of organic compounds, including the four trihalomethane disinfection by-products, that have sufficiently high volatility and low water solubility to be removed from water samples with purge and trap procedures. The following compounds can be determined by this method.

Analyte	Chemical Abstract Service Registry Number
Acetone*	67-64-1
Acrylonitrile*	107-13-1
Allyl chloride*	107-05-1
Benzene	71-43-2
Bromobenzene	108-86-1
Bromochloromethane	74-97-5
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Bromomethane	74-83-9
2-Butanone*	78-93-3
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
Carbon disulfide*	75-15-0
Carbon tetrachloride	56-23-5
Chloroacetonitrile*	107-14-2
Chlorobenzene	108-90-7
1-Chlorobutane*	109-69-3
Chloroethane	75-00-3
Chloroform	67-66-3
Chloromethane	74-87-3
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
Dibromochloromethane	124-48-1
1,2-Dibromo-3-chloropropane	96-12-8
1,2-Dibromoethane	106-93-4
Dibromomethane	74-95-3
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
trans-1,4-Dichloro-2-butene*	110-57-6
Dichlorodifluoromethane	75-71-8

1,1-Dichloroethane	75-34-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-4
cis-1,2-Dichloroethene	156-59-2
trans-1,2-Dichloroethene	156-60-5
1,2-Dichloropropane	78-87-5
1,3-Dichloropropane	142-28-9
2,2-Dichloropropane	590-20-7
1,1-Dichloropropene	563-58-6
1,1-Dichloropropanone*	513-88-2
cis-1,3-Dichloropropene	10061-01-5
trans-1,3-Dichloropropene	10061-02-6
Diethyl ether*	60-29-7
Ethylbenzene	100-41-4
Ethyl methacrylate*	97-63-2
Hexachlorobutadiene	87-68-3
Hexachloroethane*	67-72-1
2-Hexanone*	591-78-6
Isopropylbenzene	98-82-8
4-Isopropyltoluene	99-87-6
Methacrylonitrile*	126-98-7
Methylacrylate*	96-33-3
Methylene chloride	75-09-2
Methyl iodide*	74-88-4
Methylmethacrylate*	80-62-6
4-Methyl-2-pentanone*	108-10-1
Methyl-t-butyl ether*	1634-04-4
Naphthalene	91-20-3
Nitrobenzene*	98-95-3
2-Nitropropane*	79-46-9
Pentachloroethane*	76-01-7
Propionitrile*	107-12-0
n-Propylbenzene	103-65-1
Styrene	100-42-5
1,1,1,2-Tetrachloroethane	630-20-6
1,1,2,2-Tetrachloroethane	79-34-5
Tetrachloroethene	127-18-4
Tetrahydrofuran*	109-99-9
Toluene	108-88-3
1,2,3-Trichlorobenzene	87-61-6
1,2,4-Trichlorobenzene	120-82-1
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethene	79-01-6
Trichlorofluoromethane	75-69-4
1,2,3-Trichloropropane	96-18-4
1,2,4-Trimethylbenzene	95-63-6
1,3,5-Trimethylbenzene	108-67-8
Vinyl chloride	75-01-4
o-Xylene	95-47-6
m-Xylene	108-38-3
p-Xylene	106-42-3

* New Compound in Revision 4.0

1.2 Method detection limits (MDLs) (3) are compound, instrument and especially matrix dependent and vary from approximately 0.02 to 1.6 µg/L. The applicable concentration range of this method is primarily column and matrix dependent, and is approximately 0.02 to 200 µg/L when a wide-bore thick-film capillary column is used. Narrow--bore thin-film columns may have a capacity which limits the range to about 0.02 to 20 µg/L. Volatile water soluble, polar compounds which have relatively low purging efficiencies can be determined using this method. Such compounds may be more susceptible to matrix effects, and the quality of the data may be adversely influenced.

1.3 Analytes that are not separated chromatographically, but which have different mass spectra and noninterfering quantitation ions (Table 1), can be identified and measured in the same calibration mixture or water sample as long as their concentrations are somewhat similar (Sect. 11.6.2). Analytes that have very similar mass spectra cannot be individually identified and measured in the same calibration mixture or water sample unless they have different retention times (Sect. 11.6.3). Coeluting compounds with very similar mass spectra, typically many structural isomers, must be reported as an isomeric group or pair. Two of the three isomeric xylenes and two of the three dichlorobenzenes are examples of structural isomers that may not be resolved on the capillary column, and if not, must be reported as isomeric pairs. The more water soluble compounds (> 2% solubility) and compounds with boiling points above 200°C are purged from the water matrix with lower efficiencies. These analytes may be more susceptible to matrix effects.

2. SUMMARY OF METHOD

2.1 Volatile organic compounds and surrogates with low water solubility are extracted (purged) from the sample matrix by bubbling an inert gas through the aqueous sample. 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 the trapped sample components into a capillary gas chromatography (GC) column interfaced to a mass spectrometer (MS). The column is temperature programmed to facilitate the separation of the method analytes which are then detected with the MS. Compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a data base. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for samples. Analytes are quantitated using procedural standard calibration (Sect. 3.14). The concentration of each identified component is measured by relating the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by a compound that is used as an internal standard. Surrogate analytes, whose concentrations are known in every sample, are measured with the same internal standard calibration procedure.

3. DEFINITIONS

3.1 INTERNAL STANDARD (IS) -- A pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component.

3.2 SURROGATE ANALYTE (SA) -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction or other processing and is measured with the same procedures used to measure other sample components. The purpose of the SA is to monitor method performance with each sample.

3.3 LABORATORY DUPLICATES (LD1 and LD2) -- Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.4 FIELD DUPLICATES (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.5 LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.6 FIELD REAGENT BLANK (FRB) -- An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.7 LABORATORY PERFORMANCE CHECK SOLUTION (LPC) -- A solution of one or more compounds (analytes, surrogates, internal standard, or other test compounds) used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.8 LABORATORY FORTIFIED BLANK (LFB) -- An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is

in control, and whether the laboratory is capable of making accurate and precise measurements.

3.9 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.10 STOCK STANDARD SOLUTION (SSS) -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

3.11 PRIMARY DILUTION STANDARD SOLUTION (PDS) -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.12 CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.13 QUALITY CONTROL SAMPLE (QCS) -- A solution of method analytes of known concentrations which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.14 PROCEDURAL STANDARD CALIBRATION -- A calibration method where aqueous calibration standards are prepared and processed (e.g. purged,extracted, and/or derivatized) in exactly the same manner as a sample. All steps in the process from addition of sampling preservatives through instrumental analyses are included in the calibration. Using procedural standard calibration compensates for any inefficiencies in the processing procedure.

4. INTERFERENCES

4.1 During analysis, major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of Teflon tubing, Teflon thread sealants, or flow controllers with rubber components in the purging device should be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of laboratory reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in laboratory reagent blanks, the analyst should change the purge gas source

and regenerate the molecular sieve purge gas filter. Subtracting blank values from sample results is not permitted.

4.2 Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing relatively high concentrations of volatile organic compounds. A preventive technique is between-sample rinsing of the purging apparatus and sample syringes with two portions of reagent water. After analysis of a sample containing high concentrations of volatile organic compounds, one or more laboratory reagent blanks should be analyzed to check for cross-contamination.

4.3 Special precautions must be taken to determine 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 Teflon tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory worker's clothing should be cleaned frequently since clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination.

4.4 Traces of ketones, methylene chloride, and some other organic solvents can be present even in the highest purity methanol. This is another potential source of contamination, and should be assessed before standards are prepared in the methanol.

5. SAFETY

5.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available (4-6) for the information of the analyst.

5.2 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichlorethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane,tetrachloroethene, trichloroethene, and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6. EQUIPMENT AND SUPPLIES (All specifications are suggested. Catalog numbers are included for illustration only.)

6.1 SAMPLE CONTAINERS -- 40-mL to 120-mL screw cap vials each equipped with a Teflon faced silicone septum. Prior to use, wash vials and septa with detergent and rinse with tap and distilled water. Allow

the vials and septa to air dry at room temperature, place in a 105°C oven for 1 hr, then remove and allow to cool in an area known to be free of organics.

6.2 PURGE AND TRAP SYSTEM -- The purge and trap system consists of three separate pieces of equipment: purging device, trap, and desorber. Systems are commercially available from several sources that meet all of the following specifications.

6.2.1 The all glass purging device (Figure 1) should be designed to accept 25-mL samples with a water column at least 5 cm deep. A smaller (5-mL) purging device is recommended if the GC/MS system has adequate sensitivity to obtain the method detection limits required. Gaseous volumes above the sample must be kept to a minimum (< 15 mL) to eliminate dead volume effects. A glass frit should be installed at the base of the sample chamber so the purge gas passes through the water column as finely divided bubbles with a diameter of < 3 mm at the origin. Needle spargers may be used, however, the purge gas must be introduced at a point about 5 mm from the base of the water column. The use of a moisture control device is recommended to prohibit much of the trapped water vapor from entering the GC/MS and eventually causing instrumental problems.

6.2.2 The trap (Figure 2) must be at least 25 cm long and have an inside diameter of at least 0.105 in. Starting from the inlet, the trap should contain 1.0 cm of methyl silicone coated packing and the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. If it is not necessary to determine dichlorodifluoromethane, the charcoal can be eliminated and the polymer increased to fill 2/3 of the 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 min 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. The use of alternative sorbents is acceptable provided the data acquired meets all quality control criteria described in Section 9, and <u>provided the purge and desorption procedures specified in Section 11 of the method are not changed</u>. Specifically, the purging time, the purge gas flow rate, and the desorption time may not be changed. Since many of the potential alternate sorbents may be thermally stable above 180°C, alternate traps may be desorbed and baked out at higher temperatures than those described in Section 11. If higher temperatures are used, the analyst should monitor the data for possible analyte and/or trap decomposition.

6.2.3 The use of the methyl silicone coated packing is recommended, but not mandatory. The packing serves a dual purpose of protecting the Tenax adsorbant from aerosols, and also of insuring that the Tenax is fully enclosed within the heated zone of the trap thus eliminating potential cold spots. Alternatively, silanized glass wool may be used as a spacer at the trap inlet.

6.2.4 The desorber (Figure 2) must be capable of rapidly heating the trap to 180°C either prior to or at the beginning of the flow of desorption gas. The polymer section of the trap should not be heated higher than 200°C or the life expectancy of the trap will decrease. Trap failure is characterized by a pressure drop in excess of 3 lb/in^2 across the trap during purging or by poor bromoform sensitivities. The desorber design illustrated in Fig. 2 meets these criteria.

6.3 GAS CHROMATOGRAPHY/MASS SPECTROMETER/DATA SYSTEM (GC/MS/DS)

6.3.1 The GC must be capable of temperature programming and should be equipped with variable-constant differential flow controllers so that the column flow rate will remain constant throughout desorption and temperature program operation. If the column oven is to be cooled to 10°C or lower, a subambient oven controller will likely be required. If syringe injections of 4-bromofluorobenzene (BFB) will be used, a split/splitless injection port is required.

6.3.2 Capillary GC Columns. Any gas chromatography column that meets the performance specifications of this method may be used (Sect. 10.2.4.1). Separations of the calibration mixture must be equivalent or better than those described in this method. Four useful columns have been evaluated, and observed compound retention times for these columns are listed in Table 2.

6.3.2.1 Column 1 -- 60 m x 0.75 mm ID VOCOL (Supelco, Inc.) glass wide-bore capillary with a 1.5 μm film thickness.

Column 2 -- 30 m x 0.53 mm ID DB-624 (J&W Scientific, Inc.) fused silica capillary with a 3 μm film thickness.

Column 3 -- 30 m x 0.32 mm ID DB-5 (J&W Scientific, Inc.) fused silica capillary with a 1 μm film thickness.

Column 4 -- 75 m x 0.53 mm id DB-624 (J&W Scientific, Inc.) fused silica capillary with a 3 μm film thickness.

6.3.3 Interfaces between the GC and MS. The interface used depends on the column selected and the gas flow rate.

6.3.3.1 The wide-bore columns 1, 2, and 4 have the capacity to accept the standard gas flows from the trap during thermal desorption, and chromatography can begin with the onset of thermal desorption. Depending on the pumping capacity of the MS, an additional interface between the end of the column and the MS may be required. An open split interface (7) or an all-glass jet separator is an acceptable interface. Any interface can be used if the performance specifications described in this method (Sect. 9 and 10) can be achieved. The end of the transfer line after the interface, or the end of the analytical column if no interface is used, should be placed within a few mm of the MS ion source.

6.3.3.2 When narrow bore column 3 is used, a cryogenic interface placed just in front of the column inlet is suggested. This interface condenses the desorbed sample components in a narrow band on an uncoated fused silica precolumn using liquid nitrogen cooling. When all analytes have been desorbed from the trap, the interface is rapidly heated to transfer them to the analytical column. The end of the analytical column should be placed within a few mm of the MS ion source. A potential problem with this interface is blockage of the interface by frozen water from the trap. This condition will result in a major loss in sensitivity and chromatographic resolution.

6.3.4 The mass spectrometer must be capable of electron ionization at a nominal electron energy of 70 eV. The spectrometer must be capable of scanning from 35 to 260 amu with a complete scan cycle time (including scan overhead) of 2 sec or less. (Scan cycle time = Total MS data acquisition time in seconds divided by number of scans in the chromatogram.) The spectrometer must produce a mass spectrum that meets all criteria in Table 3 when 25 ng or less of 4-bromofluorobenzene (BFB) is introduced into the GC. An average spectrum across the BFB GC peak may be used to test instrument performance.

6.3.5 An interfaced data system is required to acquire, store, reduce, and output mass spectral data. The computer software should have the capability of processing stored GC/MS data by recognizing a GC peak within any given retention time window, comparing the mass spectra from the GC peak with spectral data in a user-created data base, and generating a list of tentatively identified compounds with their retention times and scan numbers. The software must allow integration of the ion abundance of any specific ion between specified time or scan number limits. The software should also allow calculation of response factors as defined in Sect. 10.2.6 (or construction of a linear or second order regression calibration curve), calculation of response factor statistics (mean and standard deviation), and calculation of concentrations of

analytes using either the calibration curve or the equation in Sect. 12.

6.4 SYRINGE AND SYRINGE VALVES

6.4.1 Two 5-mL or 25-mL glass hypodermic syringes with Luer-Lok tip (depending on sample volume used).

6.4.2 Three 2-way syringe valves with Luer ends.

6.4.3 Micro syringes - 10, 100 μL.

6.4.4 Syringes - 0.5, 1.0, and 5-mL, gas tight with shut-off valve.

6.5 MISCELLANEOUS

6.5.1 Standard solution storage containers -- 15-mL bottles with Teflon lined screw caps.

7. REAGENTS AND STANDARDS

7.1 TRAP PACKING MATERIALS

7.1.1 2,6-Diphenylene oxide polymer, 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

7.1.2 Methyl silicone packing (optional) -- OV-1 (3%) on Chromosorb W, 60/80 mesh, or equivalent.

7.1.3 Silica gel -- 35/60 mesh, Davison, grade 15 or equivalent.

7.1.4 Coconut charcoal -- Prepare from Barnebey Cheney, CA-580-26 lot #M-2649 (or equivalent) by crushing through 26 mesh screen.

7.2 REAGENTS

7.2.1 Methanol -- Demonstrated to be free of analytes.

7.2.2 Reagent water -- Prepare reagent water by passing tap water through a filter bed containing about 0.5 kg of activated carbon, by using a water purification system, or by boiling distilled water for 15 min followed by a 1-h purge with inert gas while the water temperature is held at 90°C. Store in clean, narrow-mouth bottles with Teflon lined septa and screw caps.

7.2.3 Hydrochloric acid (1+1) -- Carefully add measured volume of conc. HCl to equal volume of reagent water.

7.2.4 Vinyl chloride -- Certified mixtures of vinyl chloride in nitrogen and pure vinyl chloride are available from several sources (for example, Matheson, Ideal Gas Products, and Scott Gases).

7.2.5 Ascorbic acid -- ACS reagent grade, granular.

7.2.6 Sodium thiosulfate -- ACS reagent grade, granular.

7.3 STOCK STANDARD SOLUTIONS -- These solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedures. One of these solutions is required for every analyte of concern, every surrogate, and the internal standard. A useful working concentration is about 1-5 mg/mL.

7.3.1 Place about 9.8 mL of methanol into a 10-mL ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried and weigh to the nearest 0.1 mg.

7.3.2 If the analyte is a liquid at room temperature, use a 100-μL syringe and immediately add two or more drops of reference standard to the flask. Be sure that the reference standard falls directly into the alcohol without contacting the neck of the flask. If the analyte is a gas at room temperature, fill a 5-mL valved gas-tight syringe with the standard to the 5.0-mL mark, lower the needle to 5 mm above the methanol meniscus, and slowly inject the standard into the neck area of the flask. The gas will rapidly dissolve in the methanol.

7.3.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in μg/μL from the net gain in weight. When compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard.

7.3.4 Store stock standard solutions in 15-mL bottles equipped with Teflon lined screw caps. Methanol solutions of acrylonitrile, methyl iodide, and methyl acrylate are stable for only one week at 4°C. Methanol solutions prepared from other liquid analytes are stable for at least 4 weeks when stored at 4°C. Methanol solutions prepared from gaseous analytes are not stable for more than 1 week when stored at < 0°C; at room temperature, they must be discarded after 1 day.

7.4 PRIMARY DILUTION STANDARDS -- Use stock standard solutions to prepare primary dilution standard solutions that contain all the analytes of concern in methanol or other suitable solvent. The primary dilution standards should be prepared at concentrations that can be easily diluted to prepare aqueous calibration solutions that will bracket the working concentration range. Store the primary dilution standard solutions with minimal headspace and check frequently for signs of deterioration or evaporation, especially just before preparing calibration solutions. Storage times described for stock standard solutions in Sect. 7.3.4 also apply to primary dilution standard solutions.

7.5 FORTIFICATION SOLUTIONS FOR INTERNAL STANDARD AND SURROGATES

7.5.1 A solution containing the internal standard and the surrogate compounds is required to prepare laboratory reagent blanks

(also used as a laboratory performance check solution), and to fortify each sample. Prepare a fortification solution containing fluorobenzene (internal standard), 1,2- dichlorobenzene-d_4 (surrogate), and BFB (surrogate) in methanol at concentrations of 5 µg/mL of each (any appropriate concentration is acceptable). A 5-µL aliquot of this solution added to a 25-mL water sample volume gives concentrations of 1 µg/L of each. A 5-µL aliquot of this solution added to a 5-mL water sample volume gives a concentration of 5 µg/L of each. Additional internal standards and surrogate analytes are optional. Additional surrogate compounds should be similar in physical and chemical characteristics to the analytes of concern.

7.6 PREPARATION OF LABORATORY REAGENT BLANK (LRB) -- Fill a 25-mL (or 5-mL) syringe with reagent water and adjust to the mark (no air bubbles). Inject an appropriate volume of the fortification solution containing the internal standard and surrogates through the Luer Lok valve into the reagent water. Transfer the LRB to the purging device. See Sect. 11.1.2.

7.7 PREPARATION OF LABORATORY FORTIFIED BLANK -- Prepare this exactly like a calibration standard (Sect. 7.8). This is a calibration standard that is treated as a sample.

7.8 PREPARATION OF CALIBRATION STANDARDS

7.8.1 The number of calibration solutions (CALs) needed depends on the calibration range desired. A minimum of three CAL solutions is required to calibrate a range of a factor of 20 in concentration. For a factor of 50, use at least four standards, and for a factor of 100 at least five standards. One calibration standard should contain each analyte of concern at a concentration of 2-10 times the method detection limit (Tables 4, 5, and 7) for that compound. The other CAL standards should contain each analyte of concern at concentrations that define the range of the method. Every CAL solution contains the internal standard and the surrogate compounds at the same concentration (5 µg/L suggested for a 5-mL sample; 1 µg/L for a 25-mL sample).

7.8.2 To prepare a calibration standard, add an appropriate volume of a primary dilution standard containing all analytes of concern to an aliquot of acidified (pH 2) reagent water in a volumetric flask. Also add an appropriate volume of internal standard and surrogate compound solution from Sect. 7.5.1. Use a microsyringe and rapidly inject the methanol solutions 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 in a volumetric flask and should be discarded after 1 hr unless transferred to a sample bottle and sealed immediately. Alternately, aqueous calibration

standards may be prepared in a gas tight, 5 mL or 25 mL syringe. **NOTE:** If unacidified samples are being analyzed for THMs only, calibration standards should be prepared without acid.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 SAMPLE COLLECTION AND DECHLORINATION

8.1.1 Collect all samples in duplicate. If samples, such as finished drinking water, are suspected to contain residual chlorine, add about 25 mg of ascorbic acid per 40 mL of sample to the sample bottle before filling. If analytes that are gases at room temperature (such as vinyl chloride), or analytes in Table 7 are not to be determined, sodium thiosulfate is recommended to reduce the residual chlorine. Three milligrams of sodium thiosulfate should be added for each 40 mL of water sample.
NOTE: If the residual chlorine is likely to be present > 5 mg/L, a determination of the amount of the chlorine may be necessary. Diethyl-p-phenylenediamine (DPD) test kits are commercially available to determine residual chlorine in the field. Add an additional 25 mg of ascorbic acid or 3 mg of sodium thiosulfate per each 5 mg/L of residual chlorine.

8.1.2 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 10 min). Adjust the flow to about 500 mL/min and collect duplicate samples containing the desired dechlorinating agent from the flowing stream.

8.1.3 When sampling from an open body of water, partially fill a 1-quart wide-mouth bottle or 1-L beaker with sample from a representative area. Fill duplicate sample bottles containing the desired dechlorinating agent with sample from the larger container.

8.1.4 Fill sample bottles to overflowing, but take care not to flush out the rapidly dissolving dechlorinating agent. No air bubbles should pass through the sample as the bottle is filled, or be trapped in the sample when the bottle is sealed.

8.2 SAMPLE PRESERVATION

8.2.1 Adjust the pH of all samples to < 2 <u>at the time of collection</u>, but after dechlorination, by carefully adding two drops of 1:1 HCl for each 40 mL of sample. Seal the sample bottles, Teflon face down, and mix for 1 min. Exceptions to the acidification requirement are detailed in Sections 8.2.2 and 8.2.3. **NOTE:** Do not mix the ascorbic acid or sodium thiosulfate with the HCl in the sample bottle prior to sampling.

8.2.2 **When sampling for THM analysis only**, acidification may be omitted if sodium thiosulfate is used to dechlorinate the sample. This exception to acidification does not apply if ascorbic acid is used for dechlorination.

8.2.3 If a sample foams vigorously when HCl is added, discard that sample. Collect a set of duplicate samples but do not acidify them. These samples must be flagged as "not acidified" and must be stored at 4°C or below. These samples must be analyzed within 24 hr of collection time if they are to be analyzed for any compounds other than THMs.

8.2.4 The samples must be chilled to about 4°C when collected and maintained at that temperature until analysis. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to ensure that they will arrive at the laboratory with a substantial amount of ice remaining in the cooler.

8.2 SAMPLE STORAGE

8.2.1 Store samples at ≤ 4°C until analysis. The sample storage area must be free of organic solvent vapors and direct or intense light.

8.2.2 Analyze all samples within 14 days of collection. Samples not analyzed within this period must be discarded and replaced.

8.3 FIELD REAGENT BLANKS (FRB)

8.3.1 Duplicate FRBs must be handled along with each sample set, which is composed of the samples collected from the same general sample site at approximately the same time. At the laboratory, fill field blank sample bottles with reagent water and sample preservatives, seal, and ship to the sampling site along with empty sample bottles and back to the laboratory with filled sample bottles. Wherever a set of samples is shipped and stored, it is accompanied by appropriate blanks. FRBs must remain hermetically sealed until analysis.

8.3.2 Use the same procedures used for samples to add ascorbic acid and HCl to blanks (Sect. 8.1.1). The same batch of ascorbic acid and HCl should be used for the field reagent blanks as for the field samples.

9. QUALITY CONTROL

9.1 Quality control (QC) requirements are the initial demonstration of laboratory capability followed by regular analyses of laboratory reagent blanks, field reagent blanks, and laboratory fortified blanks. A MDL for each analyte must also be determined. Each

laboratory must maintain records to document the quality of the data generated. Additional quality control practices are recommended.

9.2 Initial demonstration of low system background. Before any samples are analyzed, it must be demonstrated that a laboratory reagent blank (LRB) is reasonably free of contamination that would prevent the determination of any analyte of concern. Sources of background contamination are glassware, purge gas, sorbents, reagent water, and equipment. Background contamination must be reduced to an acceptable level before proceeding with the next section. In general, background from method analytes should be below the method detection limit.

9.3 Initial demonstration of laboratory accuracy and precision. Analyze four to seven replicates of a laboratory fortified blank containing each analyte of concern at a concentration in the range of 2-5 μg/L depending upon the calibration range of the instrumentation.

9.3.1 Prepare each replicate by adding an appropriate aliquot of a quality control sample to reagent water. It is recommended that a QCS from a source different than the calibration standards be used for this set of LFBs, since it will serve as a check to verify the accuracy of the standards used to generate the calibration curve. This is particularly useful if the laboratory is using the method for the first time, and has no historical data base for standards. Prepare each replicate by adding an appropriate aliquot of a quality control sample to reagent water. Also add the appropriate amounts of internal standard and surrogates. If it is expected that field samples will contain a dechlorinating agent and HCl, then add these to the LFBs in the same amounts proscribed in Sect. 8.1.1. If only THMs are to be determined and field samples do not contain HCl, then do not acidify LFBs. Analyze each replicate according to the procedures described in Section 11.

9.3.2 Calculate the measured concentration of each analyte in each replicate, the mean concentration of each analyte in all replicates, and mean accuracy (as mean percentage of true value) for each analyte, and the precision (as relative standard deviation, RSD) of the measurements for each analyte.

9.3.3 Some analytes, particularly early eluting gases and late eluting higher molecular weight compounds, will be measured with less accuracy and precision than other analytes. However, the accuracy and precision for all analytes must fall within the limits expressed below. If these criteria are not met for an analyte of interest, take remedial action and repeat the measurements for that analyte until satisfactory performance is achieved. For each analyte, the mean accuracy must be 80-120% (i.e. an accuracy of ± 20%). The precision

of the recovery (accuracy) for each analyte must be less than twenty percent (<20%). These criteria are different than the ± 30% response factor criteria specified in Sect. 10.3.5. The criteria differ, because the measurements in Sect. 9.3.3 as part of the initial demonstration of capability are meant to be more stringent than the continuing calibration measurements in Sect. 10.3.5.

9.3.4 To determine the MDL, analyze a minimum of 7 LFBs prepared at a low concentration. MDLs in Table 5 were calculated from samples fortified from 0.1-0.5 µg/L, which can be used as a guide, or use calibration data to estimate a concentration for each analyte that will yield a peak with a 3-5 signal to noise response. Analyze the 7 replicates as described in Sect.11, and on a schedule that results in the analyses being conducted over several days. Calculate the mean accuracy and standard deviation for each analyte. Calculate the MDL using the equation in Sect. 13.

9.3.5 Develop and maintain a system of control charts to plot the precision and accuracy of analyte and surrogate measurements as a function of time. Charting surrogate recoveries is an especially valuable activity because surrogates are present in every sample and the analytical results will form a significant record of data quality.

9.4 Monitor the integrated areas of the quantitation ions of the internal standards and surrogates (Table 1) in all samples, continuing calibration checks, and blanks. These should remain reasonably constant over time. An abrupt change may indicate a matrix effect or an instrument problem. If a cryogenic interface is utilized, it may indicate an inefficient transfer from the trap to the column. These samples must be reanalyzed or a laboratory fortified duplicate sample analyzed to test for matrix effect. A more gradual drift of more than 50% in any area is indicative of a loss in sensitivity, and the problem must be found and corrected.

9.5 LABORATORY REAGENT BLANKS (LRB) -- With each batch of samples processed as a group within a work shift, analyze a LRB to determine the background system contamination.

9.6 Assessing Laboratory Performance. Use the procedures and criteria in Sects. 10.3.4 and 10.3.5 to evaluate the accuracy of the measurement of the laboratory fortified blank (LFB), which must be analyzed with each batch of samples that is processed as a group within a work shift. If more than 20 samples are in a work shift batch, analyze one LFB per 20 samples. Prepare the LFB with the concentration of each analyte that was used in the Sect. 9.3.3 analysis. If the acceptable accuracy for this measurement (±30%) is not achieved, the problem must be solved before additional samples may be reliably analyzed. Acceptance criteria for the IS and surrogate given in Sect.10.3.4 also applies to this LFB.

Since the calibration check sample in Sect. 10.3.5 and the LFB are made the same way and since procedural standards are used, the sample analyzed here may also be used as a calibration check in Sect. 10.3.5. Add the results of the LFB analysis to the control charts to document data quality.

9.7 If a water sample is contaminated with an analyte, verify that it is not a sampling error by analyzing a field reagent blank. The results of these analyses will help define contamination resulting from field sampling, storage and transportation activities. If the field reagent blank shows unacceptable contamination, the analyst should identify and eliminate the contamination.

9.8 At least quarterly, replicate LFB data should be evaluated to determine the precision of the laboratory measurements. Add these results to the ongoing control charts to document data quality.

9.9 At least quarterly, analyze a quality control sample (QCS) from an external source. If measured analyte concentrations are not of acceptable accuracy, check the entire analytical procedure to locate and correct the problem source.

9.10 Sample matrix effects have not been observed when this method is used with distilled water, reagent water, drinking water, or ground water. Therefore, analysis of a laboratory fortified sample matrix (LFM) is not required unless the criteria in Section 9.4 are not met. If matrix effects are observed or suspected to be causing low recoveries, analyze a laboratory fortified matrix sample for that matrix. The sample results should be flagged and the LFM results should be reported with them.

9.11 Numerous other quality control measures are incorporated into other parts of this procedure, and serve to alert the analyst to potential problems.

10. CALIBRATION AND STANDARDIZATION

10.1 Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed. In addition, acceptable performance must be confirmed intermittently throughout analysis of samples by performing continuing calibration checks. These checks are required at the beginning of each work shift, but no less than every 12 hours. Additional periodic calibration checks are good laboratory practice. It is highly recommended that an additional calibration check be performed at the end of any cycle of continuous instrument operation, so that each set of field samples is bracketed by calibration check standards. **NOTE:** Since this method uses procedural standards, the analysis of the laboratory fortified blank, which is required in Sect. 9.6, may be used here as a calibration check sample.

10.2 INITIAL CALIBRATION

10.2.1 Calibrate the mass and abundance scales of the MS with calibration compounds and procedures prescribed by the manufacturer with any modifications necessary to meet the requirements in Sect. 10.2.2.

10.2.2 Introduce into the GC (either by purging a laboratory reagent blank or making a syringe injection) 25 ng or less of BFB and acquire mass spectra for m/z 35-260 at 70 eV (nominal). Use the purging procedure and/or GC conditions given in Sect. 11. If the spectrum does not meet all criteria in Table 3, the MS must be returned and adjusted to meet all criteria before proceeding with calibration. An average spectrum across the GC peak may be used to evaluate the performance of the system.

10.2.3 Purge a medium CAL solution, (e.g., 10-20 μg/L) using the procedure given in Sect. 11.

10.2.4 Performance criteria for calibration standards. Examine the stored GC/MS data with the data system software. Figures 3 and 4 shown acceptable total ion chromatograms.

10.2.4.1 GC performance. Good column performance will produce symmetrical peaks with minimum tailing for most compounds. If peaks are unusually broad, or if there is poor resolution between peaks, the wrong column has been selected or remedial action is probably necessary (Sect.10.3.6).

10.2.4.2 MS sensitivity. The GC/MS/DS peak identification software should be able to recognize a GC peak in the appropriate retention time window for each of the compounds in calibration solution, and make correct tentative identifications. If fewer than 99% of the compounds are recognized, system maintenance is required. See Sect. 10.3.6.

10.2.5 If all performance criteria are met, purge an aliquot of each of the other CAL solutions using the same GC/MS conditions.

10.2.6 Calculate a response factor (RF) for each analyte and isomer pair for each CAL solution using the internal standard fluorobenzene. Table 1 contains suggested quantitation ions for all compounds. This calculation is supported in acceptable GC/MS data system software (Sect. 6.3.5), and many other software programs. RF is a unitless number, but units used to express quantities of analyte and internal standard must be equivalent.

$$RF = \frac{(A_x)(Q_{is})}{(A_{is})(Q_x)}$$

where: A_x = integrated abundance of the quantitation ion of the analyte.

A_{is} = integrated abundance of the quantitation ion of the internal standard.

Q_x = quantity of analyte purged in nanograms or concentration units.

Q_{is} = quantity of internal standard purged in ng or concentration units.

10.2.6.1 For each analyte and surrogate, calculate the mean RF from analyses of CAL solutions. Calculate the standard deviation (SD) and the relative standard deviation (RSD) from each mean: RSD = 100 (SD/M). If the RSD of any analyte or surrogate mean RF exceeds 20%, either analyze additional aliquots of appropriate CAL solutions to obtain an acceptable RSD of RFs over the entire concentration range, or take action to improve GC/MS performance Sect. 10.3.6). Surrogate compounds are present at the same concentration on every sample, calibration standard, and all types of blanks.

10.2.7 As an alternative to calculating mean response factors and applying the RSD test, use the GC/MS data system software or other available software to generate a linear or second order regression calibration curve, by plotting A/A_{is} vs. Q_x.

10.3 CONTINUING CALIBRATION CHECK -- Verify the MS tune and initial calibration at the beginning of each 12-hr work shift during which analyses are performed using the following procedure. Additional periodic calibration checks are good laboratory practice. It is highly recommended that an additional calibration check be performed at the end of any cycle of continuous instrument operation, so that each set of field samples is bracketed by calibration check standards.

10.3.1 Introduce into the GC (either by purging a laboratory reagent blank or making a syringe injection) 25 ng or less of BFB and acquire a mass spectrum that includes data for m/z 35-260. If the spectrum does not meet all criteria (Table 3), the MS must be returned and adjusted to meet all criteria before proceeding with the continuing calibration check.

10.3.2 Purge a CAL solution and analyze with the same conditions used during the initial calibration. Selection of the concentration level of the calibration check standard should be varied so that the calibration is verified at more than one point over the course of several days.

10.3.3 Demonstrate acceptable performance for the criteria shown in Sect. 10.2.4.

10.3.4 Determine that the absolute areas of the quantitation ions of the internal standard and surrogates have not decreased by more than 30% from the areas measured in the most recent continuing calibration check, or by more than 50% from the areas measured during initial calibration. If these areas have decreased by more than these amounts, adjustments must be made to restore system sensitivity. These adjustments may require cleaning of the MS ion source, or other maintenance as indicated in Sect. 10.3.6, and recalibration. Control charts are useful aids in documenting system sensitivity changes.

10.3.5 Calculate the RF for each analyte of concern and surrogate compound from the data measured in the continuing calibration check. The RF for each analyte and surrogate must be within 30% of the mean value measured in the initial calibration. Alternatively, if a linear or second order regression is used, the concentration measured using the calibration curve must be within 30% of the true value of the concentration in the calibration solution. If these conditions do not exist, remedial action must be taken which may require recalibration. All data from field samples obtained after the last successful calibration check standard, should be considered suspect. After remedial action has been taken, duplicate samples should be analyzed if they are available.

10.3.6 Some possible remedial actions. Major maintenance such as cleaning an ion source, cleaning quadrupole rods, etc. require returning to the initial calibration step.

10.3.6.1 Check and adjust GC and/or MS operating conditions; check the MS resolution, and calibrate the mass scale.

10.3.6.2 Clean or replace the splitless injection liner; silanize a new injection liner. This applies only if the injection liner is an integral part of the system.

10.3.6.3 Flush the GC column with solvent according to manufacturer's instructions.

10.3.6.4 Break off a short portion (about 1 meter) of the column from the end near the injector; or replace GC column. This action will cause a slight change in retention times. Analyst may need to redefine retention windows.

10.3.6.5 Prepare fresh CAL solutions, and repeat the initial calibration step.

10.3.6.6 Clean the MS ion source and rods (if a quadrupole).

10.3.6.7 Replace any components that allow analytes to come into contact with hot metal surfaces.

10.3.6.8 Replace the MS electron multiplier, or any other faulty components.

10.3.6.9 Replace the trap, especially when only a few compounds fail the criteria in Sect. 10.3.5 while the majority are determined successfully. Also check for gas leaks in the purge and trap unit as well as the rest of the analytical system.

10.4 Optional calibration for vinyl chloride using a certified gaseous mixture of vinyl chloride in nitrogen can be accomplished by the following steps.

10.4.1 Fill the purging device with 25.0 mL (or 5-mL) of reagent water or aqueous calibration standard.

10.4.2 Start to purge the aqueous mixture. Inject a known volume (between 100 and 2000 µL) of the calibration gas (at room temperature) directly into the purging device with a gas tight syringe. Slowly inject the gaseous sample through a septum seal at the top of the purging device at 2000 µL/min. If the injection of the standard is made through the aqueous sample inlet port, flush the dead volume with several mL of room air or carrier gas. Inject the gaseous standard before 5 min of the 11-min purge time have elapsed.

10.4.3 Determine the aqueous equivalent concentration of vinyl chloride standard, in µg/L, injected with the equation:

$$S = 0.102\ (C)(V)$$

where S = Aqueous equivalent concentration of vinyl chloride standard in µg/L;
C = Concentration of gaseous standard in mg/L (v/v);
V = Volume of standard injected in mL.

11. PROCEDURE

11.1 SAMPLE INTRODUCTION AND PURGING

11.1.1 This method is designed for a 25-mL or 5-mL sample volume, but a smaller (5 mL) sample volume is recommended if the GC/MS system has adequate sensitivity to achieve the required method detection limits. Adjust the helium purge gas flow rate to 40 mL/min. Attach the trap inlet to the purging device and open the syringe valve on the purging device.

11.1.2 Remove the plungers from two 25-mL (or 5-mL depending on sample size) syringes and attach a closed syringe valve to each. Warm the sample to room temperature, open the sample

bottle, and carefully pour the sample into one of the syringe barrels to just short of overflowing. Replace the syringe plunger, invert the syringe, and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 25.0-mL (or 5-mL). To all samples, blanks, and calibration standards, add 5-μL (or an appropriate volume) of the fortification solution containing the internal standard and the surrogates to the sample through the syringe valve. Close the valve. Fill the second syringe in an identical manner from the same sample bottle. Reserve this second syringe for a reanalysis if necessary.

11.1.3 Attach the sample syringe valve to the syringe valve on the purging device. Be sure that the trap is cooler than 25°C, then open the sample syringe valve and inject the sample into the purging chamber. Close both valves and initiate purging. Purge the sample for 11.0 min at ambient temperature.

11.1.4 Standards and samples must be analyzed in exactly the same manner. Room temperature must be reasonably constant, and changes in excess of 10°F will adversely affect the accuracy and precision of the method.

11.2 SAMPLE DESORPTION

11.2.1 Non-cryogenic interface -- After the 11-min purge, place the purge and trap system in the desorb mode and preheat the trap to 180°C without a flow of desorption gas. Then simultaneously start the flow of desorption gas at a flow rate suitable for the column being used (optimum desorb flow rate is 15 mL/min) for about 4 min, begin the GC temperature program, and start data acquisition.

11.2.2 Cryogenic interface -- After the 11-min purge, place the purge and trap system in the desorb mode, make sure the cryogenic interface is a -150°C or lower, and rapidly heat the trap to 180°C while backflushing with an inert gas at 4 mL/min for about 5 min. At the end of the 5 min desorption cycle, rapidly heat the cryogenic trap to 250°C, and simultaneously begin the temperature program of the gas chromatograph, and start data acquisition.

11.2.3 While the trapped components are being introduced into the gas chromatograph (or cryogenic interface), empty the purging device using the sample syringe and wash the chamber with two 25-mL flushes of reagent water. After the purging device has been emptied, leave syringe valve open to allow the purge gas to vent through the sample introduction needle.

11.3 GAS CHROMATOGRAPHY/MASS SPECTROMETRY -- Acquire and store data over the nominal mass range 35-260 with a total cycle time (including scan overhead time) of 2 sec or less. If water, methanol, or carbon dioxide cause a background problem, start at 47 or 48 m/z. If

ketones are to be determined, data must be acquired starting at m/z 43. Cycle time must be adjusted to measure five or more spectra during the elution of each GC peak. Suggested temperature programs are provided below. Alternative temperature programs can be used.

11.3.1 Single ramp linear temperature program for wide bore column 1 and 2 with a jet separator. Adjust the helium carrier gas flow rate to within the capacity of the separator, or about 15 mL/min. The column temperature is reduced 10°C and held for 5 min from the beginning of desorption, then programmed to 160°C at 6°C/min, and held until all components have eluted.

11.3.2 Multi-ramp temperature program for wide bore column 2 with the open split interface. Adjust the helium carrier gas flow rate to about 4.6 mL/min. The column temperature is reduced to 10°C and held for 6 min from the beginning of desorption, then heated to 70°C at 10°/min, heated to 120°C at 5°/min, heated to 180° at 8°/min, and held at 180° until all compounds have eluted.

11.3.3 Single ramp linear temperature program for narrow bore column 3 with a cryogenic interface. Adjust the helium carrier gas flow rate to about 4 mL/min. The column temperature is reduced to 10°C and held for 5 min from the beginning of vaporization from the cryogenic trap, programmed at 6°/min for 10 min, then 15°/min for 5 min to 145°C, and held until all components have eluted.

11.3.4 Multi-ramp temperature program for wide bore column 4 with the open split interface. Adjust the helium carrier gas flow rate to about 7.0 mL/min. The column temperature is - 10°C and held for 6 min. from beginning of desorption, then heated to 100°C at 10°C/min, heated to 200°C at 5°C/min and held at 200°C for 8 min or until all compounds of interest had eluted.

11.4 TRAP RECONDITIONING -- After desorbing the sample for 4 min, recondition the trap by returning the purge and trap system to the purge mode. Wait 15 sec, then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. Maintain the moisture control module, if utilized, at 90°C to remove residual water. After approximately 7 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

11.5 TERMINATION OF DATA ACQUISITION -- When all the sample components have eluted from the GC, terminate MS data acquisition. Use appropriate data output software to display full range mass spectra and appropriate plots of ion abundance as a function of time. If any ion abundance exceeds the system working range, dilute the sample

aliquot in the second syringe with reagent water and analyze the diluted aliquot.

11.6 IDENTIFICATION OF ANALYTES -- Identify a sample component by comparison of its mass spectrum (after background subtraction) to a reference spectrum in the user-created data base. The GC retention time of the sample component should be within three standard deviations of the mean retention time of the compound in the calibration mixture.

11.6.1 In general, all ions that are present above 10% relative abundance in the mass spectrum of the standard should be present in the mass spectrum of the sample component and should agree within absolute 20%. For example, if an ion has a relative abundance of 30% in the standard spectrum, its abundance in the sample spectrum should be in the range of 10 to 50%. Some ions, particularly the molecular ion, are of special importance, and should be evaluated even if they are below 10% relative abundance.

11.6.2 Identification requires expert judgment when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), appropriate analyte spectra and background spectra can be selected by examining plots of characteristic ions for tentatively identified components. When analytes coelute (i.e., only one GC peak is apparent), the identification criteria can be met but each analyte spectrum will contain extraneous ions contributed by the coeluting compound. Because purgeable organic compounds are relatively small molecules and produce comparatively simple mass spectra, this is not a significant problem for most method analytes.

11.6.3 Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different GC retention times. Acceptable resolution is achieved if the height of the valley between two peaks is less than 25% of the average height of the two peaks. Otherwise, structural isomers are identified as isomeric pairs. Two of the three isomeric xylenes and two of the three dichlorobenzenes are examples of structural isomers that may not be resolved on the capillary columns. If unresolved, these groups of isomers must be reported as isomeric pairs.

11.6.4 Methylene chloride, acetone, carbon disulfide, and other background components appear in variable quantities in laboratory and field reagent blanks, and generally cannot be accurately measured. Subtraction of the concentration in the blank from the concentration in the sample is not acceptable

because the concentration of the background in the blank is highly variable.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Complete chromatographic resolution is not necessary for accurate and precise measurements of analyte concentrations if unique ions with adequate intensities are available for quantitation. If the response for any analyte exceeds the linear range of the calibration established in Section 10, obtain and dilute a duplicate a duplicate sample. Do not extrapolate beyond the calibration range.

12.1.1 Calculate analyte and surrogate concentrations, using the multi-point calibration established in Section 10. Do not use the daily calibration verification data to quantitate analytes in samples.

$$C_x = \frac{(A_x)(Q_{is})\ 1000}{(A_{is})\ RF\ V}$$

where: C_x = concentration of analyte or surrogate in µg/L in the water sample.
A_x = integrated abundance of the quantitation ion of the analyte in the sample.
A_{is} = integrated abundance of the quantitation ion of the internal standard in the sample.
Q_{is} = total quantity (in micrograms) of internal standard added to the water sample.
V = original water sample volume in mL.
RF = mean response factor of analyte from the initial calibration.

12.1.2 Alternatively, use the GC/MS system software or other available proven software to compute the concentrations of the analytes and surrogates from the linear or second order regression curve established in Section 10. Do not use the daily calibration verification data to quantitate analytes in samples.

12.1.3 Calculations should utilize all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty). Experience indicates that three significant figures may be used for concentrations above 99 µg/L, two significant figures for concentrations between 1- 99 µg/L, and one significant figure for lower concentrations.

12.1.4 Calculate the total trihalomethane concentration by summing the four individual trihalomethane concentrations.

13. METHOD PERFORMANCE

13.1 Single laboratory accuracy and precision data were obtained for the method analytes using laboratory fortified blanks with analytes at

concentrations between 0.1 and 5 µg/L. Results were obtained using the four columns specified (Sect. 6.3.2.1) and the open split or jet separator (Sect. 6.3.3.1), or the cryogenic interface (Sect. 6.3.3.2). These data are shown in Tables 4-8.

13.2 With these data, method detection limits were calculated using the formula (3):

$$MDL = S\ t_{(n-1,1-alpha = 0.99)}$$

where:

$t_{(n-1,1-alpha = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom,

n = number of replicates

S = the standard deviation of the replicate analyses.

14. POLLUTION PREVENTION

14.1 No solvents are utilized in this method except the extremely small volumes of methanol needed to make calibration standards. The only other chemicals used in this method are the neat materials in preparing standards and sample preservatives. All are used in extremely small amounts and pose no threat to the environment.

15. WASTE MANAGEMENT

15.1 There are no waste management issues involved with this method. Due to the nature of this method, the discarded samples are chemically less contaminated than when they were collected.

16. REFERENCES

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17. TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. MOLECULAR WEIGHTS AND QUANTITATION IONS FOR METHOD ANALYTES

Compound	MW[a]	Primary Quantitation Ion	Secondary Quantitation Ions
Internal standard			
Fluorobenzene	96	96	77
Surrogates			
4-Bromofluorobenzene	174	95	174,176
1,2-Dichlorobenzene-d4	150	152	115,150
Target Analytes			
Acetone	58	43	58
Acrylonitrile	53	52	53
Allyl chloride	76	76	49
Benzene	78	78	77
Bromobenzene	156	156	77,158
Bromochloromethane	128	128	49,130
Bromodichloromethane	162	83	85,127
Bromoform	250	173	175,252
Bromomethane	94	94	96
2-Butanone	72	43	57,72
n-Butylbenzene	134	91	134
sec-Butylbenzene	134	105	134
tert-Butylbenzene	134	119	91
Carbon disulfide	76	76	--
Carbon tetrachloride	152	117	119
Chloroacetonitrile	75	48	75
Chlorobenzene	112	112	77,114
1-Chlorobutane	92	56	49
Chloroethane	64	64	66
Chloroform	118	83	85
Chloromethane	50	50	52
2-Chlorotoluene	126	91	126
4-Chlorotoluene	126	91	126
Dibromochloromethane	206	129	127
1,2-Dibromo-3-Chloropropane	234	75	155,157
1,2-Dibromoethane	186	107	109,188
Dibromomethane	172	93	95,174
1,2-Dichlorobenzene	146	146	111,148
1,3-Dichlorobenzene	146	146	111,148
1,4-Dichlorobenzene	146	146	111,148

TABLE 1. (continued)

Compound	MW[a]	Primary Quantitation Ion	Secondary Quantitation Ions
trans-1,4-Dichloro-2-butene	124	53	88,75
Dichlorodifluoromethane	120	85	87
1,1-Dichloroethane	98	63	65,83
1,2-Dichloroethane	98	62	98
1,1-Dichloroethene	96	96	61,63
cis-1,2-Dichloroethene	96	96	61,98
trans-1,2-Dichloroethene	96	96	61,98
1,2-Dichloropropane	112	63	112
1,3-Dichloropropane	112	76	78
2,2-Dichloropropane	112	77	97
1,1-Dichloropropene	110	75	110,77
1,1-Dichloropropanone	126	43	83
cis-1,3-dichloropropene	110	75	110
trans-1,3-dichloropropene	110	75	110
Diethyl ether	74	59	45,73
Ethylbenzene	106	91	106
Ethyl methacrylate	114	69	99
Hexachlorobutadiene	258	225	260
Hexachloroethane	234	117	119,201
2-Hexanone	100	43	58
Isopropylbenzene	120	105	120
4-Isopropyltoluene	134	119	134,91
Methacrylonitrile	67	67	52
Methyl acrylate	86	55	85
Methylene chloride	84	84	86,49
Methyl iodide	142	142	127
Methylmethacrylate	100	69	99
4-Methyl-2-pentanone	100	43	58,85
Methyl-t-butyl ether	88	73	57
Naphthalene	128	128	--
Nitrobenzene	123	51	77
2-Nitropropane	89	46	--
Pentachloroethane	200	117	119,167
Propionitrile	55	54	--
n-Propylbenzene	120	91	120
Styrene	104	104	78
1,1,1,2-Tetrachloroethane	166	131	133,119
1,1,2,2-Tetrachloroethane	166	83	131,85
Tetrachloroethene	164	166	168,129
Tetrahydrofuran	72	71	72,42
Toluene	92	92	91
1,2,3-Trichlorobenzene	180	180	182
1,2,4-Trichlorobenzene	180	180	182
1,1,1-Trichloroethane	132	97	99,61
1,1,2-Trichloroethane	132	83	97,85

TABLE 1. (continued)

Compound	MW[a]	Primary Quantitation Ion	Secondary Quantitation Ions
Trichloroethene	130	95	130,132
Trichlorofluoromethane	136	101	103
1,2,3-Trichloropropane	146	75	77
1,2,4-Trimethylbenzene	120	105	120
1,3,5-Trimethylbenzene	120	105	120
Vinyl Chloride	62	62	64
o-Xylene	106	106	91
m-Xylene	106	106	91
p-Xylene	106	106	91

[a]Monoisotopic molecular weight calculated from the atomic masses of the isotopes with the smallest masses.

TABLE 2. CHROMATOGRAPHIC RETENTION TIMES FOR METHOD ANALYTES ON THREE COLUMNS WITH FOUR SETS OF CONDITIONS[a]

Compound	Retention Time (min:sec) Col. 1[b]	Col. 2[b]	Col. 2[c]	Col. 3[d]	Col. 4[e]
Internal standard					
Fluorobenzene	8:49	6:27	14:06	8:03	22:00
Surrogates					
4-Bromofluorobenzene	18:38	15:43	23:38		31:21
1,2-Dichlorobenzene-d4	22:16	19:08	27:25		35:51
Target Analytes					
Acetone					16:14
Acrylonitrile					17:49
Allyl chloride					16:58
Benzene	8:14	5:40	13:30	7:25	21:32
Bromobenzene	18:57	15:52	24:00	16:25	31:52
Bromochloromethane	6:44	4:23	12:22	5:38	20:20
Bromodichloromethane	10:35	8:29	15:48	9:20	23:36
Bromoform	17:56	14:53	22:46	15:42	30:32
Bromomethane	2:01	0:58	4:48	1:17	12:26
2-Butanone					19:41
n-Butylbenzene	22:13	19:29	27:32	17:57	35:41
sec-Butylbenzene	20:47	18:05	26:08	17:28	34:04
tert-Butylbenzene	20:17	17:34	25:36	17:19	33:26
Carbon Disulfide					16:30
Carbon Tetrachloride	7:37	5:16	13:10	7:25	21:11
Chloroacetonitrile					23:51
Chlorobenzene	15:46	13:01	20:40	14:20	28:26
1-Chlorobutane					21:00
Chloroethane	2:05	1:01		1:27	
Chloroform	6:24	4:48	12:36	5:33	20:27
Chloromethane	1:38	0:44	3:24	0:58	9:11
2-Chlorotoluene	19:20	16:25	24:32	16:44	32:21
4-Chlorotoluene	19:30	16:43	24:46	16:49	32:38
Cyanogen chloride (8)				1:03	
Dibromochloromethane	14:23	11:51	19:12	12:48	26:57
1,2-Dibromo-3-Chloropropane	24:32	21:05		18:02	38:20
1,2-Dibromoethane	14:44	11:50	19:24	13:36	27:19
Dibromomethane	10:39	7:56	15:26	9:05	23:22
1,2-Dichlorobenzene	22:31	19:10	27:26	17:47	35:55
1,3-Dichlorobenzene	21:13	18:08	26:22	17:28	34:31
1,4-Dichlorobenzene	21:33	18:23	26:36	17:38	34:45
t-1,4-Dichloro-2-butene					31:44
Dichlorodifluoromethane	1:33	0:42	3:08	0:53	7:16
1,1-Dichloroethane	4:51	2:56	10:48	4:02	18:46

TABLE 2. (continued)

Compound	Retention Time (min:sec) Col. 1[b]	Col. 2[b]	Col. 2[c]	Col. 3[d]	Col. 4[e]
1,2-Dichloroethane	8:24	5:50	13:38	7:00	21:31
1,1-Dichloroethene	2:53	1:34	7:50	2:20	16:01
cis-1,2-Dichloroethene	6:11	3:54	11:56	5:04	19:53
trans-1,2-Dichloroethene	3:59	2:22	9:54	3:32	17:54
1,2-Dichloropropane	10:05	7:40	15:12	8:56	23:08
1,3-Dichloropropane	14:02	11:19	18:42	12:29	26:23
2,2-Dichloropropane	6:01	3:48	11:52	5:19	19:54
1,1-Dichloropropanone					24:52
1,1-Dichloropropene	7:49	5:17	13:06	7:10	21:08
cis-1,3-dichloropropene	11.58		16:42		24:24
trans-1,3-dichloropropene	13.46		17:54		25:33
Diethyl ether					15:31
Ethylbenzene	15:59	13:23	21:00	14:44	28:37
Ethyl Methacrylate					25:35
Hexachlorobutadiene	26:59	23:41	32:04	19:14	42:03
Hexachloroethane					36:45
Hexanone					26:23
Isopropylbenzene	18:04	15:28	23:18	16:25	30:52
4-Isopropyltoluene	21:12	18:31	26:30	17:38	34:27
Methacrylonitrile					20:15
Methylacrylate					20:02
Methylene Chloride	3:36	2:04	9:16	2:40	17:18
Methyl Iodide					16:21
Methylmethacrylate					23:08
4-Methyl-2-pentanone					24:38
Methyl-t-butyl ether					17:56
Naphthalene	27:10	23:31	32:12	19:04	42:29
Nitrobenzene					39:02
2-Nitropropane					23:58
Pentachloroethane					33:33
Propionitrile					19:58
n-Propylbenzene	19:04	16:25	24:20	16:49	32:00
Styrene	17:19	14:36	22:24	15:47	29:57
1,1,1,2-Tetrachloroethane	15:56	13:20	20:52	14:44	28:35
1,1,2,2-Tetrachloroethane	18:43	16:21	24:04	15:47	31:35
Tetrachloroethene	13:44	11:09	18:36	13:12	26:27
Tetrahydrofuran					20:26
Toluene	12:26	10:00	17:24	11:31	25:13
1,2,3-Trichlorobenzene	27:47	24:11	32:58	19:14	43:31
1,2,4-Trichlorobenzene	26:33	23:05	31:30	18:50	41:26
1,1,1-Trichloroethane	7:16	4:50	12:50	6:46	20:51
1,1,2-Trichloroethane	13:25	11:03	18:18	11:59	25:59
Trichloroethene	9:35	7:16	14:48	9:01	22:42
Trichlorofluoromethane	2:16	1:11	6:12	1:46	14:18
1,2,3-Trichloropropane	19:01	16:14	24:08	16:16	31:47
1,2,4-Trimethylbenzene	20:20	17:42	31:30	17:19	33:33

TABLE 2. (continued)

Compound	Retention Time (min:sec) Col. 1[b]	Col. 2[b]	Col. 2[c]	Col. 3[d]	Col. 4[e]
1,3,5-Trimethylbenzene	19:28	16:54	24:50	16:59	32:26
Vinyl chloride	1:43	0:47	3:56	1:02	10:22
o-Xylene	17:07	14:31	22:16	15:47	29:56
m-Xylene	16:10	13:41	21:22	15:18	28:53
p-Xylene	16:07	13:41	21:18	15:18	28:53

[a]Columns 1-4 are those given in Sect. 6.3.2.1; retention times were measured from the beginning of thermal desorption from the trap (columns 1-2, and 4) or from the beginning of thermal release from the cryogenic interface (column 3).

[b]GC conditions given in Sect. 11.3.1.

[c]GC conditions given in Sect. 11.3.2.

[d]GC conditions given in Sect. 11.3.3.

[e]GC conditions given in Sect. 11.3.4.

TABLE 3. ION ABUNDANCE CRITERIA FOR 4-BROMOFLUOROBENZENE (BFB)

Mass (M/z)	Relative Abundance Criteria
50	15 to 40% of mass 95
75	30 to 80% of mass 95
95	Base Peak, 100% Relative Abundance
96	5 to 9% of mass 95
173	< 2% of mass 174
174	> 50% of mass 95
175	5 to 9% of mass 174
176	> 95% but < 101% of mass 174
177	5 to 9% of mass 176

TABLE 4. ACCURACY AND PRECISION DATA FROM 16-31 DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING WIDE BORE CAPILLARY COLUMN 1[a]

Compound	True Conc. Range (µg/L)	Mean Accuracy (% of True Value)	Rel. Std. Dev. (%)	Method Det. Limit[b] (µg/L)
Benzene	0.1-10	97	5.7	0.04
Bromobenzene	0.1-10	100	5.5	0.03
Bromochloromethane	0.5-10	90	6.4	0.04
Bromodichloromethane	0.1-10	95	6.1	0.08
Bromoform	0.5-10	101	6.3	0.12
Bromomethane	0.5-10	95	8.2	0.11
n-Butylbenzene	0.5-10	100	7.6	0.11
sec-Butylbenzene	0.5-10	100	7.6	0.13
tert-Butylbenzene	0.5-10	102	7.3	0.14
Carbon tetrachloride	0.5-10	84	8.8	0.21
Chlorobenzene	0.1-10	98	5.9	0.04
Chloroethane	0.5-10	89	9.0	0.10
Chloroform	0.5-10	90	6.1	0.03
Chloromethane	0.5-10	93	8.9	0.13
2-Chlorotoluene	0.1-10	90	6.2	0.04
4-Chlorotoluene	0.1-10	99	8.3	0.06
Dibromochloromethane	0.1-10	92	7.0	0.05
1,2-Dibromo-3-chloropropane	0.5-10	83	19.9	0.26
1,2-Dibromoethane	0.5-10	102	3.9	0.06
Dibromomethane	0.5-10	100	5.6	0.24
1,2-Dichlorobenzene	0.1-10	93	6.2	0.03
1,3-Dichlorobenzene	0.5-10	99	6.9	0.12
1,4-Dichlorobenzene	0.2-20	103	6.4	0.03
Dichlorodifluoromethane	0.5-10	90	7.7	0.10
1,1-Dichloroethane	0.5-10	96	5.3	0.04
1,2-Dichloroethane	0.1-10	95	5.4	0.06
1,1-Dichloroethene	0.1-10	94	6.7	0.12
cis-1,2 Dichloroethene	0.5-10	101	6.7	0.12
trans-1,2-Dichloroethene	0.1-10	93	5.6	0.06
1,2-Dichloropropane	0.1-10	97	6.1	0.04
1,3-Dichloropropane	0.1-10	96	6.0	0.04
2,2-Dichloropropane	0.5-10	86	16.9	0.35
1,1-Dichloropropene	0.5-10	98	8.9	0.10
cis-1,2-Dichloropropene				
trans-1,2-Dichloropropene				
Ethylbenzene	0.1-10	99	8.6	0.06
Hexachlorobutadiene	0.5-10	100	6.8	0.11
Isopropylbenzene	0.5-10	101	7.6	0.15
4-Isopropyltoluene	0.1-10	99	6.7	0.12
Methylene chloride	0.1-10	95	5.3	0.03
Naphthalene	0.1-100	104	8.2	0.04
n-Propylbenzene	0.1-10	100	5.8	0.04
Styrene	0.1-100	102	7.2	0.04

TABLE 4. (Continued)

Compound	True Conc. Range (µg/L)	Mean Accuracy (% of True Value)	Rel. Std. Dev. (%)	Method Det. Limit[b] (µg/L)
1,1,1,2-Tetrachloroethane	0.5-10	90	6.8	0.05
1,1,2,2-Tetrachloroethane	0.1-10	91	6.3	0.04
Tetrachloroethene	0.5-10	89	6.8	0.14
Toluene	0.5-10	102	8.0	0.11
1,2,3-Trichlorobenzene	0.5-10	109	8.6	0.03
1,2,4-Trichlorobenzene	0.5-10	108	8.3	0.04
1,1,1-Trichloroethane	0.5-10	98	8.1	0.08
1,1,2-Trichloroethane	0.5-10	104	7.3	0.10
Trichloroethene	0.5-10	90	7.3	0.19
Trichlorofluoromethane	0.5-10	89	8.1	0.08
1,2,3-Trichloropropane	0.5-10	108	14.4	0.32
1,2,4-Trimethylbenzene	0.5-10	99	8.1	0.13
1,3,5-Trimethylbenzene	0.5-10	92	7.4	0.05
Vinyl chloride	0.5-10	98	6.7	0.17
o-Xylene	0.1-31	103	7.2	0.11
m-Xylene	0.1-10	97	6.5	0.05
p-Xylene	0.5-10	104	7.7	0.13

[a]Data obtained by using column 1 with a jet separator interface and a quadrupole mass spectrometer (Sect. 11.3.1) with analytes divided among three solutions.

[b]Replicate samples at the lowest concentration listed in column 2 of this table were analyzed. These results were used to calculate MDLs.

TABLE 6. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING WIDE BORE CAPILLARY COLUMN 2[a]

Compound	No.[b]	Mean Accuracy (% of True Value, 2 µg/L Conc.)	RSD (%)	Mean Accuracy (% of True Value, 0.2 µg/L Conc.)	RSD (%)
Internal Standard					
Fluorobenzene	1	-	-	-	-
Surrogates					
4-Bromofluorobenzene	2	98	1.8	96	1.3
1,2-Dichlorobenzene-d_4	3	97	3.2	95	1.7
Target Analytes					
Benzene	37	97	4.4	113	1.8
Bromobenzene	38	102	3.0	101	1.9
Bromochloromethane	4	99	5.2	102	2.9
Bromodichloromethane	5	96	1.8	100	1.8
Bromoform	6	89	2.4	90	2.2
Bromomethane	7	55	27.	52	6.7
n-Butylbenzene	39	89	4.8	87	2.3
sec-Butylbenzene	40	102	3.5	100	2.8
tert-Butylbenzene	41	101	4.5	100	2.9
Carbon tetrachloride	8	84	3.2	92	2.6
Chlorobenzene	42	104	3.1	103	1.6
Chloroethane[c]					
Chloroform	9	97	2.0	95	2.1
Chloromethane	10	110	5.0	d	
2-Chlorotoluene	43	91	2.4	108	3.1
4-Chlorotoluene	44	89	2.0	108	4.4
Dibromochloromethane	11	95	2.7	100	3.0
1,2-Dibromo-3-chloropropane[c]					
1,2-Dibromoethane[c]					
Dibromomethane	13	99	2.1	95	2.2
1,2-Dichlorobenzene	45	93	2.7	94	5.1
1,3-Dichlorobenzene	46	100	4.0	87	2.3
1,4-Dichlorobenzene	47	98	4.1	94	2.8
Dichlorodifluoromethane	14	38	25.	d	
1,1-Dichloroethane	15	97	2.3	85	3.6
1,2-Dichloroethane	16	102	3.8	100	2.1
1,1-Dichloroethene	17	90	2.2	87	3.8
cis-1,2-Dichloroethene	18	100	3.4	89	2.9
trans-1,2-Dichloroethene	19	92	2.1	85	2.3

TABLE 6. (Continued)

Compound	No.[b]	Mean Accuracy (% of True Value, 2 µg/L Conc.)	RSD (%)	Mean Accuracy (% of True Value, 0.2 µg/L Conc.)	RSD (%)
1,2-Dichloropropane	20	102	2.2	103	2.9
1,3-Dichloropropane	21	92	3.7	93	3.2
2,2-Dichloropropane[c]					
1,1-Dichloropropene[c]					
cis-1,3-Dichloropropene[c]					
trans-1,3-Dichloropropene	25	96	1.7	99	2.1
Ethylbenzene	48	96	9.1	100	4.0
Hexachlorobutadiene	26	91	5.3	88	2.4
Isopropylbenzene	49	103	3.2	101	2.1
4-Isopropyltoluene	50	95	3.6	95	3.1
Methylene chloride	27	e		e	
Naphthalene	51	93	7.6	78	8.3
n-Propylbenzene	52	102	4.9	97	2.1
Styrene	53	95	4.4	104	3.1
1,1,1,2-Tetrachloroethane	28	99	2.7	95	3.8
1,1,2,2-Tetrachloroethane	29	101	4.6	84	3.6
Tetrachloroethene	30	97	4.5	92	3.3
Toluene	54	105	2.8	126	1.7
1,2,3-Trichlorobenzene	55	90	5.7	78	2.9
1,2,4-Trichlorobenzene	56	92	5.2	83	5.9
1,1,1-Trichloroethane	31	94	3.9	94	2.5
1,1,2-Trichloroethane	32	107	3.4	109	2.8
Trichloroethene	33	99	2.9	106	2.5
Trichlorofluoromethane	34	81	4.6	48	13.
1,2,3-Trichloropropane	35	97	3.9	91	2.8
1,2,4-Trimethylbenzene	57	93	3.1	106	2.2
1,3,5-Trimethylbenzene	58	88	2.4	97	3.2
Vinyl chloride	36	104	3.5	115	14.
o-Xylene	59	97	1.8	98	1.7
m-Xylene	60	f		f	
p-Xylene	61	98	2.3	103	1.4

[a]Data obtained using column 2 with the open split interface and an ion trap mass spectrometer (Sect. 11.3.2) with all method analytes in the same reagent water solution.
[b]Designation in Figures 1 and 2.
[c]Not measured; authentic standards were not available.
[d]Not found at 0.2 µg/L.
[e]Not measured; methylene chloride was in the laboratory reagent blank.
[f]m-xylene coelutes with and cannot be distinguished from its isomer p-xylene, No 61.

TABLE 7. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF METHOD ANALYTES IN REAGENT WATER USING WIDE BORE CAPILLARY COLUMN NUMBER 4[a]

Compound	True Conc. (µg/L)	Mean Conc. Detected (ug/L)	Rel. Std. Dev. (%)	Method Detect. Limit (µg/L)
Acetone	1.0	1.6	5.7	0.28
Acrylonitrile	1.0	0.81	8.7	0.22
Allyl chloride	1.0	0.90	4.7	0.13
2-Butanone	2.0	2.7	5.6	0.48
Carbon disulfide	0.20	0.19	15	0.093
Chloroacetonitrile	1.0	0.83	4.7	0.12
1-Chlorobutane	1.0	0.87	6.6	0.18
t-Dichloro-2-butene	1.0	1.3	8.7	0.36
1,1-Dichloropropanone	5.0	4.2	7.7	1.0
c-1,3-Dichloropropene	0.20	0.20	3.1	0.020
t-1,3-Dichloropropene	0.10	0.11	14	0.048
Diethyl ether	1.0	0.92	9.5	0.28
Ethyl methacrylate	0.20	0.23	3.9	0.028
Hexachloroethane	0.20	0.18	10	0.057
2-Hexanone	1.0	1.1	12	0.39
Methacrylonitrile	1.0	0.92	4.2	0.12
Methylacrylate	1.0	1.2	12	0.45
Methyl iodide	0.20	0.19	3.1	0.019
Methylmethacrylate	1.0	1.0	13	0.43
4-Methyl-2-pentanone	0.40	0.56	9.7	0.17
Methyl-tert-butylether	0.40	0.52	5.6	0.090
Nitrobenzene	2.0	2.1	18	1.2
2-Nitropropane	1.0	0.83	6.2	0.16
Pentachloroethane	0.20	0.23	20	0.14
Propionitrile	1.0	0.87	5.3	0.14
Tetrahydrofuran	5.0	3.9	13	1.6

[a] Data obtained using column 4 with the open split interface and an ion trap mass spectrometer.

TABLE 8. ACCURACY AND PRECISION FROM FOUR DETERMINATIONS OF METHOD ANALYTES IN THREE WATER MATRICES FORTIFIED AT 20 μG/L[a]

Compound	REAGENT WATER			RAW WATER			TAP WATER		
	Mean (μg/L)	Dev. (%)	(% of True Value)	Mean (μg/L)	Dev. (%)	(% of True Value)	Mean (μg/L)	Dev. (%)	(% of True Value)
Acetone	19	12%	95%	21	3.7%	105%	22	8.2%	110%
Acrylonitrile	20	4.7%	100%	22	3.4%	110%	21	1.3%	105%
Allyl chloride	20	5.1%	100%	20	2.8%	100%	19	3.5%	95%
2-Butanone	17	11%	85%	19	7.3%	95%	17	5.6%	85%
Carbon disulfide	19	6.4%	95%	18	2.5%	90%	18	3.0%	90%
Chloroacetonitrile	20	4.1%	100%	23	4.7%	115%	23	1.3%	115%
1-Chlorobutane	18	6.4%	90%	19	2.2%	95%	17	2.2%	85%
t-1,2-Dichloro-2-butene	19	4.1%	95%	22	2.9%	110%	21	0.90%	105%
1,1-Dichloropropanone	20	5.6%	100%	22	6.4%	110%	21	7.7%	105%
Diethyl ether	18	6.7%	90%	22	3.4%	110%	22	2.6%	110%
Ethyl methacrylate	20	3.7%	100%	23	2.6%	115%	22	1.8%	110%
Hexachloroethane	20	6.1%	100%	21	2.5%	105%	21	2.0%	105%
2-Hexanone	19	6.3%	95%	21	3.8%	105%	21	4.0%	105%
Methacrylonitrile	20	3.4%	100%	23	2.9%	115%	22	2.0%	110%
Methylacrylate	20	3.7%	100%	22	3.1%	110%	21	2.1%	105%

TABLE 8 (Continued)

Compound	REAGENT WATER			RAW WATER			TAP WATER		
	Mean (µg/L)	Dev. (%)	(% of True Value)	Mean (µg/L)	Dev. (%)	(% of True Value)	Mean (µg/L)	Dev. (%)	(% of True Value)
Methyl iodide	20	4.4%	100%	19	3.8%	95%	19	3.0%	95%
Methylmethacrylate	20	3.7%	100%	23	3.3%	115%	23	2.7%	115%
4-Methyl-2-pentanone	19	8.7%	95%	21	5.5%	105%	22	7.2%	110%
Methyl-tert-butylether	19	3.5%	95%	22	2.5%	110%	22	3.6%	110%
Nitrobenzene	20	5.4%	100%	22	4.8%	110%	21	2.4%	105%
2-Nitropropane	20	6.1%	100%	23	5.1%	115%	22	3.2%	110%
Pentachloroethane	19	5.2%	95%	21	2.6%	105%	22	1.7%	110%
Propionitrile	20	4.5%	100%	23	3.9%	115%	23	2.4%	115%
Tetrahydrofuran	20	2.8%	100%	24	3.2%	120%	21	2.9%	105%

[a] Data obtained using column 4 with the open split interface and an ion trap mass spectrometer with all Table 8 analytes in the same reagent water solution (1).

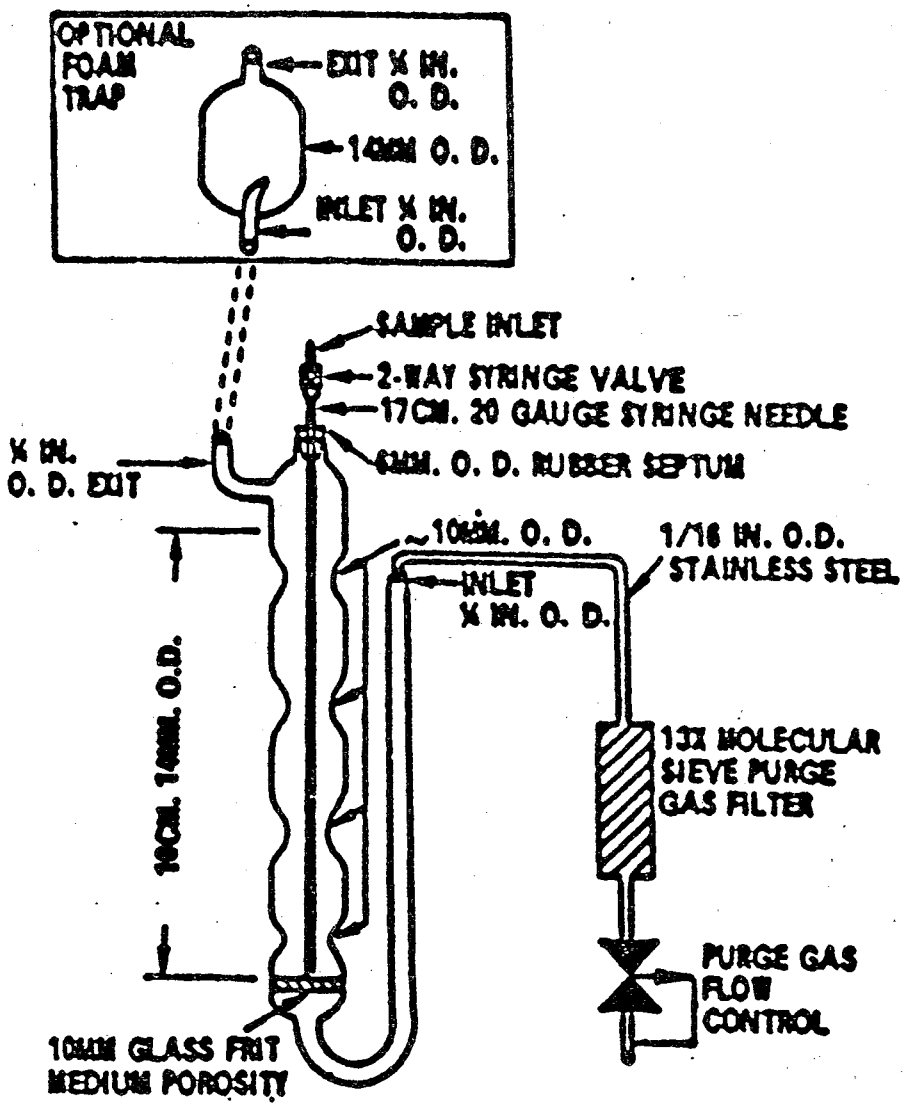


FIGURE 1. PURGING DEVICE

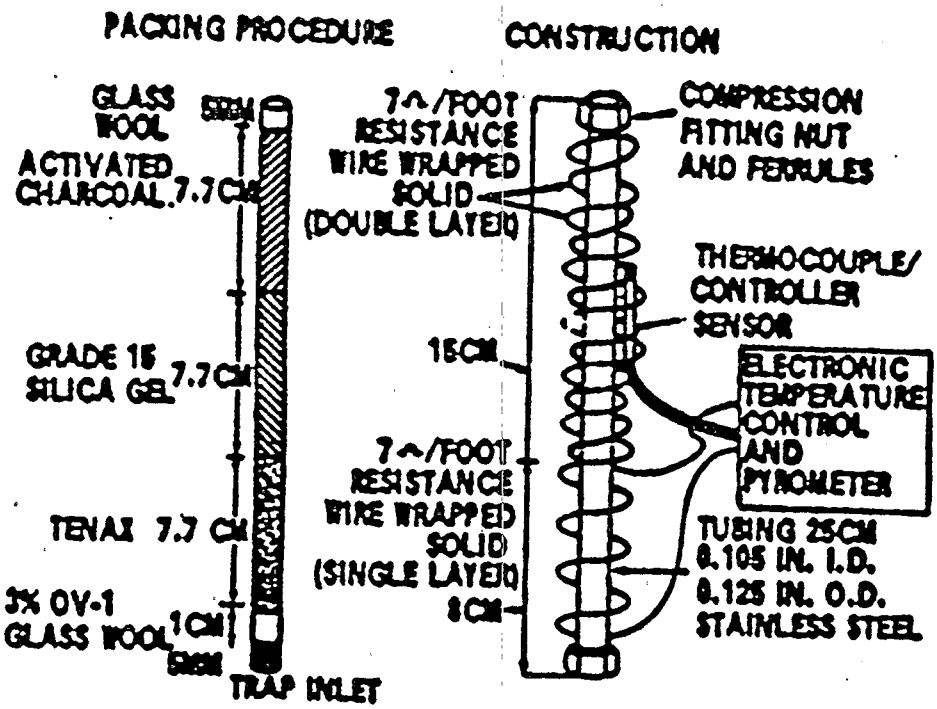


FIGURE 2. TRAP PACKINGS AND CONSTRUCTION TO INCLUDE DESORB CAPABILITY

FIGURE 3. NORMALIZED TOTAL ION CURRENT CHROMATOGRAM FROM A VOLATILE COMPOUND CALIBRATION MIXTURE CONTAINING 25 ng (5 µg/L) OF MOST COMPOUNDS. THE COMPOUND IDENTIFICATION NUMBERS ARE GIVEN IN TABLE 6.

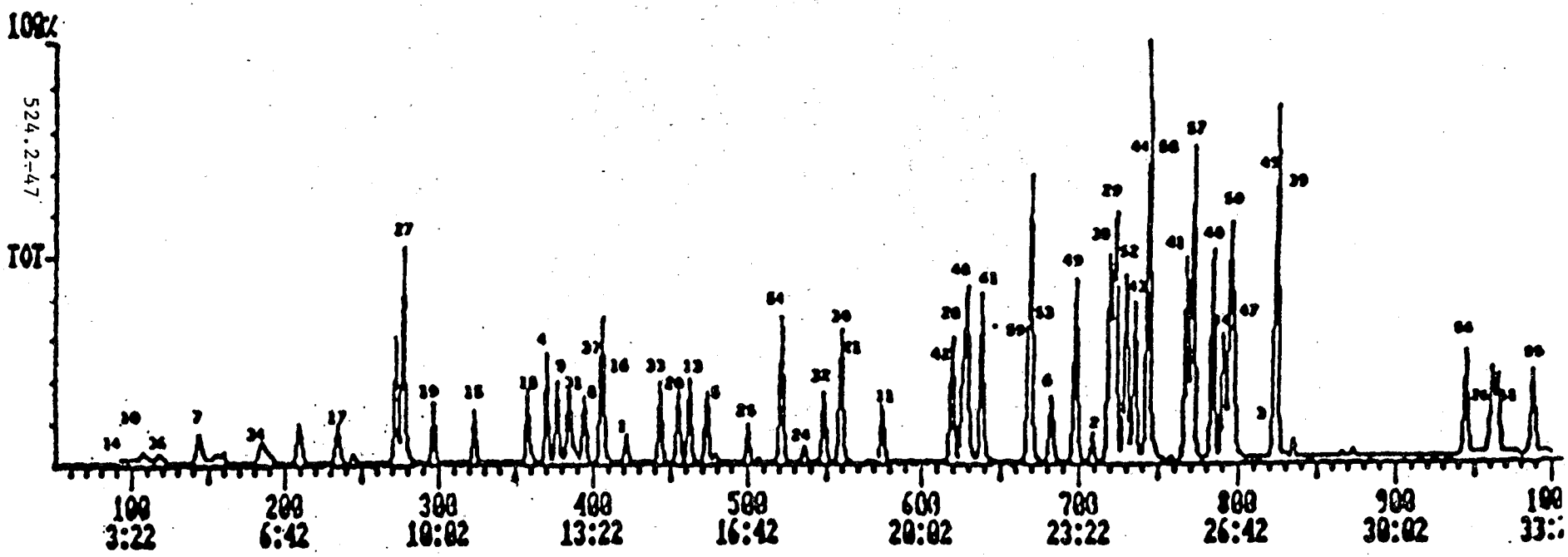
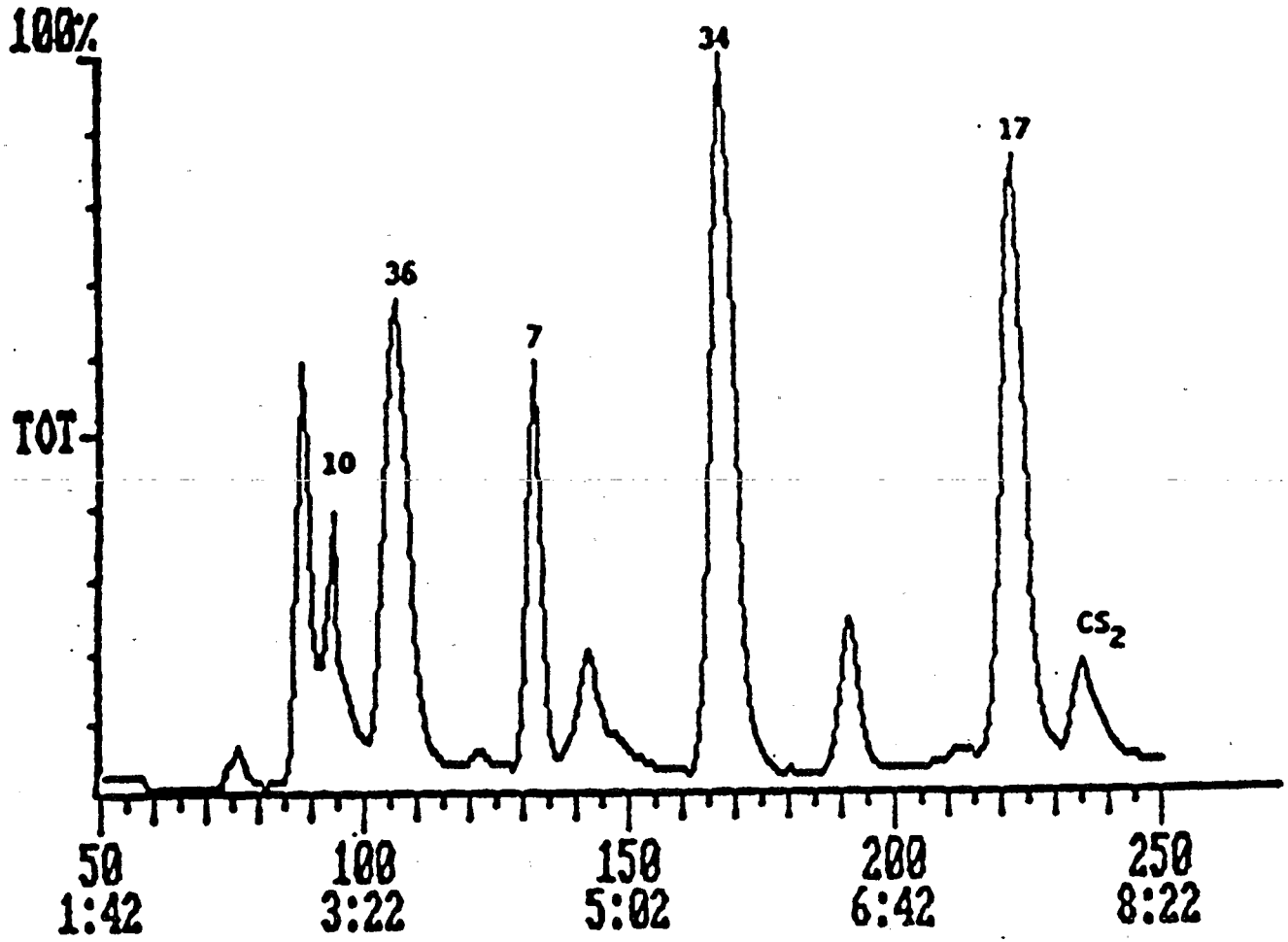


FIGURE 4. AMPLIFIED FIRST EIGHT MINUTES OF A TOTAL ION CURRENT CHROMATOGRAM FROM A VOLATILE COMPOUND CALIBRATION MIXTURE CONTAINING 25 ng (5 µg/L) OF EACH COMPONENT. THE COMPOUND IDENTIFICATION NUMBERS ARE GIVEN IN TABLE 6.



METHOD 525.2 DETERMINATION OF ORGANIC COMPOUNDS IN DRINKING WATER BY LIQUID-SOLID EXTRACTION AND CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Revision 1.1

J.W. Eichelberger, T.D. Behymer, W.L. Budde - Method 525, Revision 1.0, 2.0, 2.1 (1988)

J.W. Eichelberger, T.D. Behymer, and W.L. Budde - Method 525.1 Revision 2.2 (July 1991)

J.W. Eichelberger, J.W. Munch, and J.A. Shoemaker Method 525.2 Revision 1.0 (February, 1994)

J.W. Munch - Method 525.2, Revision 2.0 (1995)

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METHOD 525.2

DETERMINATION OF ORGANIC COMPOUNDS IN DRINKING WATER BY LIQUID-SOLID EXTRACTION AND CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

1. SCOPE AND APPLICATION

1.1 This is a general purpose method that provides procedures for determination of organic compounds in finished drinking water, source water, or drinking water in any treatment stage. The method is applicable to a wide range of organic compounds that are efficiently partitioned from the water sample onto a C_{18} organic phase chemically bonded to a solid matrix in a disk or cartridge, and sufficiently volatile and thermally stable for gas chromatography. Single-laboratory accuracy and precision data have been determined with two instrument systems using both disks and cartridges for most of the following compounds:

Analyte	MW[1]	Chemical Abstracts Service Registry Number
Acenaphthylene	152	208-96-8
Alachlor	269	15972-60-8
Aldrin	362	309-00-2
Ametryn	227	834-12-8
Anthracene	178	120-12-7
Atraton	211	1610-17-9
Atrazine	215	1912-24-9
Benz[a]anthracene	228	56-55-3
Benzo[b]fluoranthene	252	205-82-3
Benzo[k]fluoranthene	252	207-08-9
Benzo[a]pyrene	252	50-32-8
Benzo[g,h,i]perylene	276	191-24-2
Bromacil	260	314-40-9
Butachlor	311	23184-66-9
Butylate	217	2008-41-5
Butylbenzylphthalate	312	85-68-7
Carboxin[2]	235	5234-68-4
Chlordane components		
Alpha-chlordane	406	5103-71-9
Gamma-chlordane	406	5103-74-2
Trans nonachlor	440	39765-80-5
Chlorneb	206	2675-77-6
Chlorobenzilate	324	510-15-6
Chlorpropham	213	101-21-3
Chlorothalonil	264	1897-45-6
Chlorpyrifos	349	2921-88-2
2-Chlorobiphenyl	188	2051-60-7

Chrysene	228	218-01-9
Cyanazine	240	21725-46-2
Cycloate	215	1134-23-2
Dacthal(DCPA)	330	1861-32-1
DDD, 4,4'-	318	72-54-8
DDE, 4,4'-	316	72-55-9
DDT, 4,4'-	352	50-29-3
Diazinon[2]	304	333-41-5
Dibenz[a,h]anthracene	278	53-70-3
Di-n-butylphthalate	278	84-74-2
2,3-Dichlorobiphenyl	222	16605-91-7
Dichlorvos	220	62-73-7
Dieldrin	378	60-57-1
Diethylphthalate	222	84-66-2
Di(2-ethylhexyl)adipate	370	103-23-1
Di(2-ethylhexyl)phthalate	390	117-81-7
Dimethylphthalate	194	131-11-3
2,4-Dinitrotoluene	182	121-14-2
2,6-Dinitrotoluene	182	606-20-2
Diphenamid	239	957-51-7
Disulfoton[2]	274	298-04-4
Disulfoton sulfoxide[2]	290	2497-07-6
Disulfoton sulfone	306	2497-06-5
Endosulfan I	404	959-98-8
Endosulfan II	404	33213-65-9
Endosulfan sulfate	420	1031-07-8
Endrin	378	72-20-8
Endrin aldehyde	378	7421-93-4
EPTC	189	759-94-4
Ethoprop	242	13194-48-4
Etridiazole	246	2593-15-9
Fenamiphos[2]	303	22224-92-6
Fenarimol	330	60168-88-9
Fluorene	166	86-73-7
Fluridone	328	59756-60-4
Heptachlor	370	76-44-8
Heptachlor epoxide	386	1024-57-3
2,2',3,3',4,4',6-Heptachlorobiphenyl	392	52663-71-5
Hexachlorobenzene	282	118-74-1
2,2',4,4',5,6'-Hexachlorobiphenyl	358	60145-22-4
Hexachlorocyclohexane, alpha	288	319-84-6
Hexachlorocyclohexane, beta	288	319-85-7
Hexachlorocyclohexane, delta	288	319-86-8
Hexachlorocyclopentadiene	270	77-47-4
Hexazinone	252	51235-04-2
Indeno[1,2,3,c,d]pyrene	276	193-39-5
Isophorone	138	78-59-1
Lindane	288	58-89-9
Merphos[2]	298	150-50-5
Methoxychlor	344	72-43-5

Methyl paraoxon	247	950-35-6
Metolachlor	283	51218-45-2
Metribuzin	214	21087-64-9
Mevinphos	224	7786-34-7
MGK 264	275	113-48-4
Molinate	187	2212-67-1
Napropamide	271	15299-99-7
Norflurazon	303	27314-13-2
2,2',3,3',4,5',6,6'-Octa-chlorobiphenyl	426	40186-71-8
Pebulate	203	1114-71-2
2,2',3',4,6-Pentachloro-biphenyl	324	60233-25-2
Pentachlorophenol	264	87-86-5
Phenanthrene	178	85-01-8
Permethrin, cis-	390	54774-45-7
Permethrin, trans	390	51877-74-8
Prometon	225	1610-18-0
Prometryn	241	7287-19-6
Pronamide	255	23950-58-5
Propachlor	211	1918-16-7
Propazine	229	139-40-2
Pyrene	202	129-00-0
Simazine	201	122-34-9
Simetryn	213	1014-70-6
Stirofos	364	22248-79-9
Tebuthiuron	228	34014-18-1
Terbacil	216	5902-51-2
Terbufos[2]	288	13071-79-9
Terbutryn	241	886-50-0
2,2',4,4'-Tetrachlorobiphenyl	290	2437-79-8
Toxaphene		8001-35-2
Triademefon	293	43121-43-3
2,4,5-Trichlorobiphenyl	256	15862-07-4
Tricyclazole	189	41814-78-2
Trifluralin	335	1582-09-8
Vernolate	203	1929-77-7
Aroclor 1016		12674-11-2
Aroclor 1221		11104-28-2
Aroclor 1232		11141-16-5
Aroclor 1242		53469-21-9
Aroclor 1248		12672-29-6
Aroclor 1254		11097-69-1
Aroclor 1260		11096-82-5

[1]Monoisotopic molecular weight calculated from the atomic masses of the isotopes with the smallest masses.

[2]Only qualitative identification of these analytes is possible because of their instability in aqueous matrices. Merphos, carboxin, disulfoton, and disulfoton sulfoxide showed instability within 1 h of fortification. Diazinon, fenamiphos, and terbufos showed significant losses within 7 days under the sample storage conditions specified in this method.

Attempting to determine all of the above analytes in all samples is not practical and not necessary in most cases. If all the analytes must be determined, multiple calibration mixtures will be required.

1.2 Method detection limit (MDL) is defined as the statistically calculated minimum amount that can be measured with 99% confidence that the reported value is greater than zero (1). The MDL is compound dependent and is particularly dependent on extraction efficiency and sample matrix. MDLs for all method analytes are listed in Tables 3 through 6. The concentration calibration range demonstrated in this method is 0.1 µg/L to 10 µg/L for most analytes.

2. SUMMARY OF METHOD

Organic compound analytes, internal standards, and surrogates are extracted from a water sample by passing 1 L of sample water through a cartridge or disk containing a solid matrix with a chemically bonded C_{18} organic phase (liquid-solid extraction, LSE). The organic compounds are eluted from the LSE cartridge or disk with small quantities of ethyl acetate followed by methylene chloride, and this extract is concentrated further by evaporation of some of the solvent. The sample components are separated, identified, and measured by injecting an aliquot of the concentrated extract into a high resolution fused silica capillary column of a gas chromatography/mass spectrometry (GC/MS) system. Compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a data base. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for samples. The concentration of each identified component is measured by relating the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by a compound that is used as an internal standard. Surrogate analytes, whose concentrations are known in every sample, are measured with the same internal standard calibration procedure.

3. DEFINITIONS

3.1 INTERNAL STANDARD (IS) -- A pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same solution. The internal standard must be an analyte that is not a sample component.

3.2 SURROGATE ANALYTE (SA) -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample

aliquot in known amount(s) before extraction or other processing, and is measured with the same procedures used to measure other sample components. The purpose of the SA is to monitor method performance with each sample.

3.3 LABORATORY DUPLICATES (LD1 and LD2) -- Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.4 FIELD DUPLICATES (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances, and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

3.5 LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.6 FIELD REAGENT BLANK (FRB) -- An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.7 INSTRUMENT PERFORMANCE CHECK SOLUTION (IPC) -- A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.8 LABORATORY FORTIFIED BLANK (LFB) -- An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.9 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be

determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.10 STOCK STANDARD SOLUTION (SSS) -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

3.11 PRIMARY DILUTION STANDARD SOLUTION (PDS) -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.12 CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.13 QUALITY CONTROL SAMPLE (QCS) -- A solution of method analytes of known concentrations which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

4. INTERFERENCES

4.1 During analysis, major contaminant sources are reagents and liquid-solid extraction devices. Analyses of field and laboratory reagent blanks provide information about the presence of contaminants.

4.2 Interfering contamination may occur when a sample containing low concentrations of compounds is analyzed immediately after a sample containing relatively high concentrations of compounds. Syringes and splitless injection port liners must be cleaned carefully or replaced as needed. After analysis of a sample containing high concentrations of compounds, a laboratory reagent blank should be analyzed to ensure that accurate values are obtained for the next sample.

5. SAFETY

5.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are cited (2-4).

5.2 Some method analytes have been tentatively classified as known or suspected human or mammalian carcinogens. Pure standard materials and stock standard solutions of these compounds should be handled with suitable protection to skin, eyes, etc.

6. **EQUIPMENT AND SUPPLIES** (All specifications are suggested. Catalog numbers are included for illustration only.)

6.1 All glassware must be meticulously cleaned. This may be accomplished by washing with detergent and water, rinsing with water, distilled water, or solvents, air-drying, and heating (where appropriate) in a muffle furnace. Volumetric glassware should never be heated to the temperatures obtained in a muffle furnace.

6.2 Sample containers. 1-L or 1-qt amber glass bottles fitted with Teflon-lined screw caps. Amber bottles are highly recommended since some of the method analytes are very sensitive to light and are oxidized or decomposed upon exposure.

6.3 Volumetric flasks, various sizes.

6.4 Laboratory or aspirator vacuum system. Sufficient capacity to maintain a minimum vacuum of approximately 13 cm (5 in.) of mercury for cartridges. A greater vacuum (66 cm [26 in.] of mercury) may be used with disks.

6.5 Micro syringes, various sizes.

6.6 Vials. Various sizes of amber vials with Teflon-lined screw caps.

6.7 Drying column. The drying tube should contain about 5 to 7 grams of anhydrous sodium sulfate to prohibit residual water from contaminating the extract. Any small tube may be used, such as a syringe barrel, a glass dropper, etc. as long as no sodium sulfate passes through the column into the extract.

6.8 Analytical balance. Capable of weighing 0.0001 g accurately.

6.9 Fused silica capillary gas chromatography column. Any capillary column that provides adequate resolution, capacity, accuracy, and precision (Sect. 10) can be used. Medium polar, low bleed columns are recommended for use with this method to provide adequate chromatography and minimize column bleed. A 30 m X 0.25 mm id fused silica capillary column coated with a 0.25 µm bonded film of polyphenylmethylsilicone (J&W DB-5.MS) was used to develop this method. Any column which provides analyte separations equivalent to or better than this column may be used.

6.10 Gas chromatograph/mass spectrometer/data system (GC/MS/DS).

6.10.1 The GC must be capable of temperature programming and be equipped for splitless/split injection. On-column capillary injection is acceptable if all the quality control specifications in Sect. 9 and Sect. 10 are met. The injection tube liner should be quartz and about 3 mm in diameter. The injection system must not allow the analytes

to contact hot stainless steel or other metal surfaces that promote decomposition.

6.10.2 The GC/MS interface should allow the capillary column or transfer line exit to be placed within a few mm of the ion source. Other interfaces, for example the open split interface, are acceptable as long as the system has adequate sensitivity (see Sect. 10 for calibration requirements).

6.10.3 The mass spectrometer must be capable of electron ionization at a nominal electron energy of 70 eV to produce positive ions. The spectrometer must be capable of scanning at a minimum from 45 to 450 amu with a complete scan cycle time (including scan overhead) of 1.0 sec or less. (Scan cycle time = total MS data acquisition time in sec divided by number of scans in the chromatogram). The spectrometer must produce a mass spectrum that meets all criteria in Table 1 when an injection of approximately 5 ng of DFTPP is introduced into the GC. An average spectrum across the DFTPP GC peak may be used to test instrument performance. The scan time should be set so that all analytes have a minimum of 5 scans across the chromatographic peak.

6.10.4 An interfaced data system is required to acquire, store, reduce, and output mass spectral data. The computer software must have the capability of processing stored GC/MS data by recognizing a GC peak within any given retention time window, comparing the mass spectrum from the GC peak with spectral data in a user-created data base, and generating a list of tentatively identified compounds with their retention times and scan numbers. The software must also allow integration of the ion abundance of any specific ion between specified time or scan number limits, calculation of response factors as defined in Sect. 10.2.6 (or construction of a linear regression calibration curve), calculation of response factor statistics (mean and standard deviation), and calculation of concentrations of analytes using either the calibration curve or the equation in Sect. 12.

6.11 Standard Filter Apparatus, ALL GLASS OR TEFLON LINED. These should be used to carry out disk extractions when no automatic system or manifold is utilized.

6.12 A manifold system or an automatic or robotic commercially available sample preparation system designed for either cartridges or disks may be utilized in this method if all quality control requirements discussed in Sect. 9 are met.

7. REAGENTS AND STANDARDS

7.1 Helium carrier gas, as contaminant free as possible.

7.2 Liquid-solid extraction (LSE) cartridges. Cartridges are inert non-leaching plastic, for example polypropylene, or glass, and must not contain plasticizers, such as phthalate esters or adipates, that leach into the ethyl acetate and methylene chloride eluant. The cartridges are packed with about 1 gram of silica, or other inert inorganic support, whose surface is modified by chemically bonded octadecyl (C_{18}) groups. The packing must have a narrow size distribution and must not leach organic compounds into the eluting solvent. One liter of water should pass through the cartridge in about 2 h with the assistance of a slight vacuum of about 13 cm (5 in.) of mercury. Sect. 9 provides criteria for acceptable LSE cartridges which are available from several commercial suppliers.

The extraction disks contain octadecyl bonded silica uniformly enmeshed in an inert matrix. The disks used to generate the data in this method were 47 mm in diameter and 0.5 mm in thickness. Other disk sizes are acceptable and larger disks may be used for special problems or when sample compositing is carried out. As with cartridges, the disks should not contain any organic compounds, either from the matrix or the bonded silica, which will leach into the ethyl acetate and methylene chloride eluant. One liter of reagent water should pass through the disks in 5-20 min using a vacuum of about 66 cm (26 in.) of mercury. Sect. 9 provides criteria for acceptable LSE disks which are available commercially.

7.3 Solvents

7.3.1 Methylene chloride, ethyl acetate, acetone, toluene and methanol. High purity pesticide quality or equivalent.

7.3.2 Reagent water. Water in which an interference is not observed at the method detection limit of the compound of interest. Prepare reagent water by passing tap water through a filter bed containing about 0.5 kg of activated carbon or by using a water purification system. Store in clean, narrow-mouth bottles with Teflon-lined septa and screw caps.

7.4 Hydrochloric acid. 6N.

7.5 Sodium sulfate, anhydrous. (Soxhlet extracted with methylene chloride for a minimum of 4 h or heated to 400°C for 2 h in a muffle furnace.)

7.6 Stock standard solutions. Individual solutions of surrogates, internal standards, and analytes, or mixtures of analytes, may be purchased from commercial suppliers or prepared from pure materials. To prepare, add 10 mg (weighed on an analytical balance to 0.1 mg) of the pure material to 1.9 mL of methanol, ethyl acetate, or acetone in a 2-mL volumetric flask, dilute to the mark, and transfer the solution to an amber glass vial. If the analytical standard is available only in quantities smaller than 10 mg, reduce the volume of solvent accordingly. Some polycyclic aromatic hydrocarbons are

not soluble in methanol, ethyl acetate, or acetone, and their stock standard solutions are prepared in toluene. Methylene chloride should be avoided as a solvent for standards because its high vapor pressure leads to rapid evaporation and concentration changes. Methanol, ethyl acetate, and acetone are not as volatile as methylene chloride, but their solutions must also be handled with care to avoid evaporation. If compound purity is confirmed by the supplier at >96%, the weighed amount can be used without correction to calculate the concentration of the solution (5 μg/μL). Store the amber vials at 4° C or less.

7.7 Primary dilution standard solution. The stock standard solutions are used to prepare a primary dilution standard solution that contains multiple analytes. Mixtures of these analytes to be used as primary dilution standards may be purchased from commercial suppliers. Do not put every method analyte in a single primary dilution standard because chromatographic separation will be extremely difficult, if not impossible. Two or three primary dilution standards would be more appropriate. The recommended solvent for these standards is acetone or ethyl acetate. Aliquots of each of the stock standard solutions are combined to produce the primary dilution in which the concentration of the analytes is at least equal to the concentration of the most concentrated calibration solution, that is, 10 ng/μL. Store the primary dilution standard solution in an amber vial at 4° C or less, and check frequently for signs of degradation or evaporation, especially just before preparing calibration solutions.

7.8 Fortification solution of internal standards and surrogates. Prepare an internal standard solution of acenaphthene-D_{10}, phenanthrene-D_{10}, and chrysene-D_{12}, in methanol, ethyl acetate, or acetone at a concentration of 500 μg/mL of each. This solution is used in the preparation of the calibration solutions. Dilute a portion of this solution by 10 to a concentration of 50 μg/mL and use this solution to fortify the actual water samples (see Sect. 11.1.3 and Sect. 11.2.3). Similarly, prepare both surrogate compound solutions (500μg/mL for calibration, 50 μg/mL for fortification). Surrogate compounds used in developing this method are 1,3-dimethyl-2-nitrobenzene, perylene-D_{12}, and triphenylphosphate. Other surrogates, for example pyrene-D_{10} may be used in this solution as needed (a 100-μL aliquot of this 50 μg/mL solution added to 1 L of water gives a concentration of 5 μg/L of each internal standard or surrogate). Store these solutions in an amber vial at 4° C or less. These two solutions may be combined or made as a single solution.

7.9 GC/MS performance check solution. Prepare a solution in methylene chloride of the following compounds at 5 ng/μL of each: DFTPP and endrin, and 4,4'-DDT. Store this solution in an amber vial at 4° C or less. DFTPP is less stable in acetone or ethyl acetate than it is in methylene chloride.

7.10 Calibration solutions (CAL1 through CAL6). Prepare a series of six concentration calibration solutions in ethyl acetate which contain analytes of interest (except pentachlorophenol, toxaphene, and the Aroclor compounds) at suggested concentrations of 10, 5, 2, 1, 0.5, and 0.1 ng/μL, with a constant concentration of 5 ng/μL of each internal standard and surrogate in each CAL solution. It should be noted that CAL1 through CAL6 are prepared by combining appropriate aliquots of a primary dilution standard solution (Sect. 7.7) and the fortification solution (500 μg/mL) of internal standards and surrogates (Sect. 7.8). All calibration solutions should contain at least 80% ethyl acetate to avoid gas chromatographic problems. IF ALL METHOD ANALYTES ARE TO BE DETERMINED, TWO OR THREE SETS OF CALIBRATION SOLUTIONS WILL LIKELY BE REQUIRED. Pentachlorophenol is included in this solution at a concentration four times the other analytes. Toxaphene CAL solutions should be prepared as separate solutions at concentrations of 250, 200, 100, 50, 25, and 10 ng/μL. Aroclor CAL solutions should be prepared individually at concentrations of 25, 10, 5, 2.5, 1., 0.5 and 0.2 ng/μL. Store these solutions in amber vials in a dark cool place. Check these solutions regularly for signs of degradation, for example, the appearance of anthraquinone from the oxidation of anthracene.

7.11 Reducing agent. Sodium sulfite, anhydrous. Sodium thiosulfate is not recommended as it may produce a residue of elemental sulfur that can interfere with some analytes.

7.12 Fortification solution for recovery standard. Prepare a solution of terphenyl-D_{14} at a concentration of 500 μg/mL in methylene chloride or ethyl acetate. These solutions are also commercially available. An aliquot of this solution should be added to each extract to check on the recovery of the internal standards in the extraction process.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample collection. When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 2 min). Adjust the flow to about 500 mL/min and collect samples from the flowing stream. Keep samples sealed from collection time until analysis. When sampling from an open body of water, fill the sample container with water from a representative area. Sampling equipment, including automatic samplers, must be free of plastic tubing, gaskets, and other parts that may leach interfering analytes into the water sample. Automatic samplers that composite samples over time should use refrigerated glass sample containers if possible.

8.2 Sample dechlorination and preservation. All samples should be iced or refrigerated at 4°C and kept in the dark from the time of collection until extraction. Residual chlorine should be reduced at the sampling site by addition of 40-50 mg of sodium sulfite (this may be added as a solid with stirring or shaking until dissolved) to each water sample. It is very important that the sample be

dechlorinated prior to adding acid to lower the pH of the sample. Adding sodium sulfite and HCl to the sample bottles prior to shipping to the sampling site is not permitted. Hydrochloric acid should be used at the sampling site to retard the microbiological degradation of some analytes in water. The sample pH is adjusted to <2 with 6 N hydrochloric acid. This is the same pH used in the extraction, and is required to support the recovery of acidic compounds like pentachlorophenol.

8.2.1 If cyanizine is to be determined, a separate sample must be collected. Cyanazine degrades in the sample when it is stored under acidic conditions or when sodium sulfite is present in the stored sample. Samples collected for cyanazine determination MUST NOT be dechlorinated or acidified when collected. They should be iced or refrigerated as described above and analyzed within 14 days. However, these samples MUST be dechlorinated and acidified immediately prior to fortification with internal standards and surrogates, and extraction using the same quantities of acid and sodium sulfite described above.

8.2.2 Atraton and prometon are not efficiently extracted from water at pH 2 due to what appears to be their ionization in solution under acidic conditions. In order to determine these analytes accurately, a separate sample must be collected and dechlorinated with sodium sulfite, but no acid should be added. At neutral pH, these two compounds are recovered from water with efficiencies greater than 90%. The data in Tables 3, 4, 5, 6, and 8 are from samples extracted at pH 2.

8.3 Holding time. Results of the time/storage study of all method analytes showed that all but six compounds are stable for 14 days in water samples when the samples are dechlorinated, preserved, and stored as described in Sect. 8.2. Therefore, samples must be extracted within 14 days. If the following analytes are to be determined, the samples cannot be held for 14 days but must be extracted immediately after collection and preservation: carboxin, diazinon, disulfoton, disulfoton sulfoxide, fenamiphos, and terbufos. Sample extracts may be stored at 4° C for up to 30 days after sample extraction.

8.4 Field blanks.

8.4.1 Processing of a field reagent blank (FRB) is recommended along with each sample set, which is composed of the samples collected from the same general sample site at approximately the same time. At the laboratory, fill a sample container with reagent water, seal, and ship to the sampling site along with the empty sample containers. Return the FRB to the laboratory with the filled sample bottles.

8.4.2 When sodium sulfite and hydrochloric acid are added to samples, use the same procedure to add the same amounts to the FRB.

9. QUALITY CONTROL

9.1 Quality control (QC) requirements are the initial demonstration of laboratory capability followed by regular analyses of laboratory reagent blanks, laboratory fortified blanks, and laboratory fortified matrix samples. A MDL should be determined for each analyte of interest. The laboratory must maintain records to document the quality of the data generated. Additional quality control practices are recommended.

9.2 Initial demonstration of low disk or cartridge system background. Before any samples are analyzed, or any time a new supply of cartridges or disks is received from a supplier, it must be demonstrated that a laboratory reagent blank (LRB) is reasonably free of contamination that would prevent the determination of any analyte of concern. In this same experiment, it must be demonstrated that the particle size and packing of the LSE cartridges or the preparation of the disks are acceptable. Consistent flow rate with all samples is an indication of acceptable particle size distribution, packing, and proper preparation.

9.2.1 A source of potential contamination is the liquid-solid extraction (LSE) cartridge or disk which could contain phthalate esters, silicon compounds, and other contaminants that could prevent the determination of method analytes (5). Although disks are generally made of an inert matrix, they may still contain phthalate material. Generally, phthalate esters can be leached from the cartridges into ethyl acetate and methylene chloride and produce a variable background in the water sample. If the background contamination is sufficient to prevent accurate and precise measurements, the condition must be corrected before proceeding with the initial demonstration.

9.2.2 Other sources of background contamination are solvents, reagents, and glassware. Background contamination must be reduced to an acceptable level before proceeding with the next section. In general, background from method analytes should be below the method detection limits.

9.2.3 One liter of water should pass through a cartridge in about 2 h with a partial vacuum of about 13 cm (5 in.) of mercury. Using full aspirator or pump vacuum, approximately 5-20 min will normally be required to pass one liter of drinking water through a disk. The extraction time should not vary unreasonably among LSE cartridges or disks.

9.3 Initial demonstration of laboratory accuracy and precision. Analyze four to seven replicates of a laboratory fortified blank containing each analyte of concern at a suggested concentration in the range of 2-5 µg/L. This concentration should be approximately in the middle of the calibration range, and will be dependent on the sensitivity of the instrumentation used.

9.3.1 Prepare each replicate by adding sodium sulfite and HCl according to Sect. 8.2, then adding an appropriate aliquot of the primary dilution standard solution, or certified quality control sample, to reagent water. Analyze each replicate according to the procedures described in Sect. 11.

9.3.2 Calculate the measured concentration of each analyte in each replicate, the mean concentration of each analyte in all replicates, and mean accuracy (as mean percentage of true value) for each analyte, and the precision (as relative standard deviation, RSD) of the measurements for each analyte.

9.3.3 For each analyte and surrogate, the mean accuracy, expressed as a percentage of the true value, should be 70-130% and the RSD should be <30%. If these criteria are not met, locate the source of the problem, and repeat with freshly prepared LFBs.

9.3.4 Analyze seven replicate laboratory fortified blanks which have been fortified with all analytes of interest at approximately 0.5 µg/L. Calculate the MDL of each analyte using the procedure described in Sect. 13.1.2 (1). It is recommended that these analyses be performed over a period of three or four days to produce more realistic method detection limits.

9.3.5 Develop and maintain a system of control charts to plot the precision and accuracy of analyte and surrogate measurements as a function of time. Charting of surrogate recoveries is an especially valuable activity since these are present in every sample and the analytical results will form a significant record of data quality.

9.4 Monitor the integrated areas of the quantitation ions of the internal standards and surrogates in continuing calibration checks (see Sect. 10.3). In laboratory fortified blanks or samples, the integrated areas of internal standards and surrogates will not be constant because the volume of the extract will vary (and is difficult to keep constant). But the ratios of the areas should be reasonably constant in laboratory fortified blanks and samples. The addition of 10 µL of the recovery standard, terphenyl-D_{14} (500 µg/mL), to the extract is recommended to be used to monitor the recovery of the internal standards in laboratory fortified blanks and samples. Internal standard recovery should be in excess of 70%.

9.5 With each batch of samples processed as a group within a 12 h work shift, analyze a laboratory reagent blank to determine the background system contamination. Any time a new batch of LSE cartridges or disks is received, or new supplies of other reagents are used, repeat the demonstration of low background described in Sect. 9.2.

9.6 With each batch of samples processed as a group within a work shift, analyze a single laboratory fortified blank (LFB) containing each analyte of concern at a concentration as determined in Sect. 9.3. If more than 20 samples are included in a batch, analyze a LFB for every 20 samples. Use the procedures described in Sect. 9.3.3 to evaluate the accuracy of the measurements. If acceptable accuracy cannot be achieved, the problem must be located and corrected before additional samples are analyzed. Add the results to the on-going control charts to document data quality.

Note: If the LFB for each batch of samples contains the individual PCB congeners listed in Section 1, then a LFB for each Aroclor is not required. At least one LFB containing toxaphene should be extracted for each 24 hr period during which extractions are performed. Toxaphene should be fortified in a separate LFB from other method analytes.
If individual PCB congeners are not part of the LFB, then it is suggested that one multi-component analyte (toxaphene, chlordane or an Aroclor) LFB be analyzed with each sample set. By selecting a different multi-component analyte for this LFB each work shift, LFB data can be obtained for all of these analytes over the course of several days.

9.7 Determine that the sample matrix does not contain materials that adversely affect method performance. This is accomplished by analyzing replicates of laboratory fortified matrix samples and ascertaining that the precision, accuracy, and method detection limits of analytes are in the same range as obtained with laboratory fortified blanks. If a variety of different sample matrices are analyzed regularly, for example, drinking water from groundwater and surface water sources, matrix independence should be established for each. Over time, LFM data should be documented for all routine sample sources for the laboratory. A laboratory fortified sample matrix should be analyzed for every 20 samples processed in the same batch. If the recovery data for a LFM does not meet the criteria in Sect. 9.3.3., and LFBs show the laboratory to be in control , then the samples from that matrix (sample location) are documented as suspect due to matrix effects.

9.8 With each set of samples, a field reagent blank (FRB) should be analyzed. The results of this analysis will help define contamination resulting from field sampling and transportation activities.

9.9 At least quarterly, analyze a quality control sample from an external source. If measured analyte concentrations are not of acceptable accuracy (Sect. 9.3.3), check the entire analytical procedure to locate and correct the problem source.

9.10 Numerous other quality control measures are incorporated into other parts of this procedure, and serve to alert the analyst to potential problems.

10. CALIBRATION AND STANDARDIZATION

10.1 Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed and is required intermittently throughout sample analysis as dictated by results of continuing calibration checks. After initial calibration is successful, a continuing calibration check is required each day or at the beginning of each period in which analyses are performed not to exceed 12 h. Additional periodic calibration checks are good laboratory practice. It is recommended that an additional calibration check be performed at the end of each period of continuous instrument operation, so that all field sample analyses are bracketed by a calibration check standard.

10.2 Initial calibration

10.2.1 Calibrate the mass and abundance scales of the MS with calibration compounds and procedures prescribed by the manufacturer with any modifications necessary to meet the requirements in Sect. 10.2.2.

10.2.2 Inject into the GC/MS system a 1 μL aliquot of the 5 ng/μL solution of DFTPP, endrin and 4,4'-DDT. If desired, the endrin and DDT degradation checks may be performed simultaneously with the DFTPP check or in a separate injection. Acquire a mass spectrum that includes data for m/z 45-450. Use GC conditions that produce a narrow (at least five scans per peak) symmetrical peak for each compound (Sect. 10.2.3.1 and Sect. 10.2.3.2). If the DFTPP mass spectrum does not meet all criteria in Table 1, the MS must be retuned and adjusted to meet all criteria before proceeding with calibration. A single spectrum or an average spectrum across the GC peak may be used to evaluate the performance of the system. Locate any degradation products of endrin (endrin ketone [EK] and endrin aldehyde [EA]) and 4,4'-DDT (4,4'-DDE and 4,4'-DDD) at their appropriate retention times and quantitation ions (Table 2). Endrin ketone can be located at ≈1.1 to 1.2 times the endrin retention time with prominent m/z 67 and 317 ions in the mass spectrum. If degradation of either endrin or DDT exceeds 20%, maintenance is required on the GC injection port and possibly other areas of the system before proceeding with the

calibration. Calculate percent breakdown using peak areas based on total ion current (TIC) as follows:

% 4,4'-DDT breakdown=

$$\frac{\Sigma \text{ TIC area of DDT degradation peaks (DDE+DDD)}}{\Sigma \text{ TIC area of total DDT peaks (DDT+DDE+DDD)}} \times 100$$

% endrin breakdown=

$$\frac{\Sigma \text{ TIC area of endrin degradation peaks (EA+EK)}}{\Sigma \text{ TIC area of total endrin peaks (endrin+EA+EK)}} \times 100$$

10.2.3 Inject a 1-μL aliquot of a medium concentration calibration solution, for example 0.5-2 μg/L, and acquire and store data from m/z 45-450 with a total cycle time (including scan overhead time) of 1.0 sec or less. Cycle time should be adjusted to measure at least five or more spectra during the elution of each GC peak. Calibration standards for toxaphene and Aroclors must be injected individually.

10.2.3.1 The following are suggested multi-ramp temperature program GC conditions. Adjust the helium carrier gas flow rate to about 33 cm/sec. Inject at 45°C and hold in splitless mode for 1 min. Heat rapidly to 130°C. At 3 min start the temperature program: 130-180°C at 12°/min; 180-240°C at 7°/min; 240-320°C at 12°/min. Start data acquisition at 4 min.

10.2.3.2 Single ramp linear temperature program suggested GC conditions. Adjust the helium carrier gas flow rate to about 33 cm/sec. Inject at 40°C and hold in splitless mode for 1 min. Heat rapidly to 160°C. At 3 min start the temperature program: 160-320°C at 6°/min; hold at 320° for 2 min. Start data acquisition at 3 min.

10.2.4 Performance criteria for the calibration standards. Examine the stored GC/MS data with the data system software.

10.2.4.1 GC performance. Anthracene and phenanthrene should be separated by baseline. Benz[a]anthracene and chrysene should be separated by a valley whose height is less than 25% of the average peak height of these two compounds. If the valley between benz[a]anthracene and chrysene exceeds 25%, the GC column requires maintenance. See Sect. 10.3.6.

10.2.4.2 MS sensitivity. The GC/MS/DS peak identification software should be able to recognize a GC peak in

the appropriate retention time window for each of the compounds in the calibration solution, and make correct identifications. If fewer than 99% of the compounds are recognized, system maintenance is required. See Sect. 10.3.6.

10.2.5 If all performance criteria are met, inject a 1-μL aliquot of each of the other CAL solutions using the same GC/MS conditions. Calibration standards of toxaphene and Aroclors must be injected individually.

10.2.5.1 Some GC/MS systems may not be sensitive enough to detect some of the analytes in the two lowest concentration CAL solutions. In this case, the analyst should prepare additional CAL solutions at slightly higher concentrations to obtain at least 5 calibration points that bracket the expected analyte concentration range.

10.2.6 Calculate a response factor (RF) for each analyte of interest and surrogate for each CAL solution using the internal standard whose retention time is nearest the retention time of the analyte or surrogate. Table 2 contains suggested internal standards for each analyte and surrogate, and quantitation ions for all compounds. This calculation is supported in acceptable GC/MS data system software (Sect. 6.10.4), and many other software programs. The RF is a unitless number, but units used to express quantities of analyte and internal standard must be equivalent.

Note: To calibrate for multi-component analytes (toxaphene and Aroclors), one of the following methods should be used.
Option 1- Calculate an average response factor or linear regression equation for each multi-component analyte from the combined area of all its component peaks identified in the calibration standard chromatogram, using 2-3 of the suggested quantitation ions in Table 2.
Option 2- Calculate an average response factor or linear regression equation for each multi-component analyte using the combined areas of 3-6 of the most intense and reproducible peaks in each of the calibration standard chromatograms. Use an appropriate quantitation ion for each peak.

$$RF = \frac{(A_x)(Q_{is})}{(A_{is})(Q_x)}$$

where:

A_x = integrated abundance of the quantitation ion of the analyte.

A_{is} = integrated abundance of the quantitation ion internal standard.

Q_x = quantity of analyte injected in ng or concentration units.

Q_{is} = quantity of internal standard injected in ng or concentration units.

10.2.6.1 For each analyte and surrogate, calculate the mean RF from the analyses of the six CAL solutions. Calculate the standard deviation (SD) and the relative standard deviation (RSD) from each mean: RSD = 100 (SD/M). If the RSD of any analyte or surrogate mean RF exceeds 30%, either analyze additional aliquots of appropriate CAL solutions to obtain an acceptable RSD of RFs over the entire concentration range, or take action to improve GC/MS performance. See Sect. 10.3.6.

10.2.7 As an alternative to calculating mean response factors, use the GC/MS data system software or other available software to generate a linear regression calibration by plotting A_x / A_{is} vs. Q_x.

10.3 Continuing calibration check. Verify the MS tune and initial calibration at the beginning of each 12 h work shift during which analyses are performed using the following procedure.

10.3.1 Inject a 1-µL aliquot of the 5 ng/µL solution of DFTPP, endrin, and 4,4'-DDT. Acquire a mass spectrum for DFTPP that includes data for m/z 45-450. Ensure that all criteria in Sect. 10.2.2 are met.

10.3.2 Inject a 1-µL aliquot of a calibration solution and analyze with the same conditions used during the initial calibration. It is recommended that the concentration of calibration solution be varied, so that the calibration can be verified at more than one point. Note: If the continuing calibration check standard contains the PCB congeners listed in Section 1, calibration verification is not required for each Aroclor. Calibration verification of toxaphene should be performed at least once each 24 hr period.

10.3.3 Demonstrate acceptable performance for the criteria shown in Sect. 10.2.4.

10.3.4 Determine that the absolute areas of the quantitation ions of the internal standards and surrogate(s) have not changed by more than 30% from the areas measured in the most recent continuing calibration check, or by more than 50% from the

areas measured during initial calibration. If these areas have decreased by more than these amounts, adjustments must be made to restore system sensitivity. These adjustments may require cleaning of the MS ion source, or other maintenance as indicated in Sect. 10.3.6, and recalibration. Control charts are useful aids in documenting system sensitivity changes.

10.3.5 Calculate the RF for each analyte and surrogate from the data measured in the continuing calibration check. The RF for each analyte and surrogate must be within 30% of the mean value measured in the initial calibration. Alternatively, if a linear regression is used, the calculated amount for each analyte must be ± 30% of the true value. If these conditions do not exist, remedial action should be taken which may require recalibration. Any field sample extracts that have been analyzed since the last acceptable calibration verification should be reanalyzed after adequate calibration has been restored.

10.3.5.1 Because of the large number of compounds on the analyte list, it is possible for a few analytes of interest to be outside the continuing calibration criteria. If analytes that missed the calibration check are detected in samples, they may be quantified using a single point calibration. The single point standards should be prepared at concentrations that produce responses close (±20%) to those of the unknowns. If the same analyte misses the continuing calibration check on three consecutive work shifts, remedial action MUST be taken. If more than 10% of the analytes of interest miss the continuing calibration check on a single day, remedial action MUST be taken.

10.3.6 Some possible remedial actions. Major maintenance such as cleaning an ion source, cleaning quadrupole rods, replacing filament assemblies, etc. require returning to the initial calibration step.

10.3.6.1 Check and adjust GC and/or MS operating conditions; check the MS resolution, and calibrate the mass scale.

10.3.6.2 Clean or replace the splitless injection liner; silanize a new injection liner.

10.3.6.3 Flush the GC column with solvent according to manufacturer's instructions.

10.3.6.4 Break off a short portion (about 1 meter) of the column from the end near the injector; or replace GC

column. This action will cause a change in retention times.

10.3.6.5 Prepare fresh CAL solutions, and repeat the initial calibration step.

10.3.6.6 Clean the MS ion source and rods (if a quadrupole).

10.3.6.7 Replace any components that allow analytes to come into contact with hot metal surfaces.

10.3.6.8 Replace the MS electron multiplier, or any other faulty components.

11. PROCEDURE

11.1 CARTRIDGE EXTRACTION

11.1.1 This procedure may be carried out in the manual mode or in the automated mode (Sect. 6.12) using a robotic or automatic sample preparation device. If an automatic system is used to prepare samples, follow the manufacturer's operating instructions, but follow this procedure. If the manual mode is used, a suggested setup of the extraction apparatus is shown in Figure 1A. The reservoir is not required, but recommended for convenient operation. Water drains from the reservoir through the LSE cartridge and into a syringe needle which is inserted through a rubber stopper into the suction flask. A slight vacuum of approximately 13 cm (5 in.) of mercury is used during all operations with the apparatus. About 2 h should be required to draw a liter of water through the cartridge.

11.1.2 Elute each cartridge with a 5 mL aliquot of ethyl acetate followed by a 5 mL aliquot of methylene chloride. Let the cartridge drain dry after each flush. Then elute the cartridge with a 10 mL aliquot of methanol, but DO NOT allow the methanol to elute below the top of the cartridge packing. From this point, do not allow the cartridge to go dry. Add 10 mL of reagent water to the cartridge, but before the reagent water level drops below the top edge of the packing, begin adding sample to the solvent reservoir.

11.1.3 Pour the water sample into the 2-L separatory funnel with the stopcock closed, add 5 mL methanol, and mix well. If a vacuum manifold is used instead of the separatory funnel, the sample may be transferred directly to the cartridge after the methanol is added to the sample. (Residual chlorine should not be present as a reducing agent should have been added at the time of sampling. Also the pH of the sample should be about 2. If residual chlorine is present and/or the pH is >2, the sample may be invalid.) Add a 100-μL aliquot of the

fortification solution (50 μg/mL) for internal standards and surrogates, and mix immediately until homogeneous. The resulting concentration of these compounds in the water should be 5 μg/L.

11.1.4 Periodically transfer a portion of the sample into the solvent reservoir. The water sample will drain into the cartridge, and from the exit into the suction flask. Maintain the packing material in the cartridge immersed in water at all times. After all of the sample has passed through the LSE cartridge, draw air or nitrogen through the cartridge for 10 min.

11.1.5 Transfer the 125-mL solvent reservoir and LSE cartridge (from Figure 1A) to the elution apparatus if used (Figure 1B). The same 125-mL solvent reservoir is used for both apparatus. Rinse the inside of the 2-L separatory funnel and the sample jar with 5 mL of ethyl acetate and elute the cartridge with this rinse into the collection tube. Wash the inside of the separatory funnel and the sample jar with 5 mL methylene chloride and elute the cartridge, collecting the rinse in the same collection tube. Small amounts of residual water from the sample container and the LSE cartridge may form an immiscible layer with the eluate. Pass the eluate through the drying column (Sect. 6.7) which is packed with approximately 5 to 7 grams of anhydrous sodium sulfate and collect in a second vial. Wash the sodium sulfate with at least 2 mL methylene chloride and collect in the same vial. Concentrate the extract in a warm water bath under a gentle stream of nitrogen. Do not concentrate the extract to less than 0.5 mL, as this will result in losses of analytes. Make any volume adjustments with ethyl acetate. It is recommended that an aliquot of the recovery standard be added to the concentrated extract to check the recovery of the internal standards (see Sect. 7.12).

11.2 DISK EXTRACTION

11.2.1 This procedure was developed using the standard 47 mm diameter disks. Larger disks (90 mm diameter) may be used if sample compositing is being done or special matrix problems are encountered. If larger disks are used, the washing solvent volume is 15 mL, the conditioning solvent volume is 15 mL, and the elution solvent volume is two 15 mL aliquots.

11.2.1.1 Extractions using the disks may be carried out either in the manual or automatic mode (Sect. 6.12) using an automatic sample preparation device. If an automatic system is used to prepare samples, follow the manufacturer's operating instructions, but follow this procedure. Insert the disk into the filter apparatus (Figure 2) or sample preparation

unit. Wash the disk with 5 mL of a 1:1 mixture of ethyl acetate (EtAc) and methylene chloride (MeCl2) by adding the solvent to the disk, drawing about half through the disk, allowing it to soak the disk for about a minute, then drawing the remaining solvent through the disk. (NOTE: Soaking the disk may not be desirable when disks other than Teflon are used. Instead, apply a constant, low vacuum in this Section and Sect. 11.2.1.2 to ensure adequate contact time between solvent and disk.)

11.2.1.2 Pre-wet the disk with 5 mL methanol (MeOH) by adding the MeOH to the disk and allowing it to soak for about a minute, then drawing most of the remaining MeOH through. A layer of MeOH must be left on the surface of the disk, which should not be allowed to go dry from this point until the end of the sample extraction. THIS IS A CRITICAL STEP FOR A UNIFORM FLOW AND GOOD RECOVERY.

11.2.1.3 Rinse the disk with 5 mL reagent water by adding the water to the disk and drawing most through, again leaving a layer on the surface of the disk.

11.2.2 Add 5 mL MeOH per liter of water to the sample. Mix well. (Residual chlorine should not be present as a reducing agent should have been added at the time of sampling. Also the pH of the sample should be about 2. If residual chlorine is present and/or the pH is >2, the sample may be invalid.)

11.2.3 Add 100 µL of the internal standard and surrogate compound fortification solution (50 µg/mL) to the sample and shake or mix until the sample is homogeneous. The resulting concentration of these compounds in the water should be 5 µg/L.

11.2.4 Add the water sample to the reservoir and apply full vacuum to begin the extraction. Particulate-free water may pass through the disk in as little as 5 min without reducing analyte recoveries. Extract the entire sample, draining as much water from the sample container as possible. Dry the disk by maintaining vacuum for about 10 min.

11.2.5 Remove the filtration top, but do not disassemble the reservoir and fritted base. If a suction flask is being used, empty the water from the flask, and insert a suitable collection tube to contain the eluant. The only constraint on the sample tube is that it fit around the drip tip of the fritted base. Reassemble the apparatus.

11.2.6 Add 5 mL of ethyl acetate to the sample bottle, and rinse the inside walls thoroughly. Allow the solvent to settle to the bottom of the bottle, then transfer it to the disk. A disposable pipet or syringe may be used to do this, rinsing the sides of the glass filtration reservoir in the process.

Draw about half of the solvent through the disk, release the vacuum, and allow the disk to soak for a minute. Draw the remaining solvent through the disk. (NOTE: Soaking the disk may not be desirable if disks other than Teflon are used. Instead, apply a constant, low vacuum in this Section and Sect. 11.2.7 to ensure adequate contact time between solvent and disk.)

11.2.7 Repeat the above step (Sect. 11.2.6) with methylene chloride.

11.2.8 Using a syringe or disposable pipet, rinse the filtration reservoir with two 3 mL portions of 1:1 EtAc:MeCl2. Draw the solvent through the disk and into the collector tube. Pour the combined eluates (Sect. 11.2.6, Sect. 11.2.7, and Sect. 11.2.8) through the drying tube (Sect. 6.7) containing about 5 to 7 grams of anhydrous sodium sulfate. Rinse the drying tube and sodium sulfate with two 3 mL portions of 1:1 EtAc:MeCl2 mixture. Collect all the extract and washings in a concentrator tube.

11.2.9 While gently heating the extract in a water bath or a heating block, concentrate to between 0.5 and 1 mL under a gentle stream of nitrogen. Do not concentrate the extract to less than 0.5 mL, since this will result in losses of analytes. Make any volume adjustments with ethyl acetate. It is recommended that an aliquot of the recovery standard be added to the concentrated extract to check the recovery of the internal standards (see Sect. 7.12).

11.3 Analyze a 1 µL aliquot with the GC/MS system under the same conditions used for the initial and continuing calibrations (Sect. 10.2.3).

11.4 At the conclusion of data acquisition, use the same software that was used in the calibration procedure to tentatively identify peaks in predetermined retention time windows of interest. Use the data system software to examine the ion abundances of components of the chromatogram.

11.5 Identification of analytes. Identify a sample component by comparison of its mass spectrum (after background subtraction) to a reference spectrum in the user-created data base. The GC retention time of the sample component should be within 5 sec of the retention time observed for that same compound in the most recently analyzed continuing calibration check standard.

11.5.1 In general, all ions that are present above 10% relative abundance in the mass spectrum of the standard should be present in the mass spectrum of the sample component and should agree within absolute 20%. For example, if an ion has a relative abundance of 30% in the standard spectrum, its abundance in the sample spectrum should be in the range of 10

to 50%. Some ions, particularly the molecular ion, are of special importance, and should be evaluated even if they are below 10% relative abundance.

11.5.2 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), appropriate analyte spectra and background spectra can be selected by examining plots of characteristic ions for tentatively identified components. When analytes coelute (i.e., only one GC peak is apparent), the identification criteria can be met but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

11.5.3 Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different GC retention times. See Sect. 10.2.4.1. Acceptable resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the average height of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. Benzo[b] and benzo[k]fluoranthene may be measured as an isomeric pair. MGK 264 is made up of two structural isomers. These are listed separately in the data tables.

11.5.4 Each multi-component analyte can be identified by the presence of its individual components in a characteristic pattern based on the relative amounts of each component present. Chromatograms of standard materials of multi-component analytes should be carefully evaluated, so that these patterns can be recognized by the analyst.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Complete chromatographic resolution is not necessary for accurate and precise measurements of analyte concentrations if unique ions with adequate intensities are available for quantitation. In validating this method, concentrations were calculated by measuring the characteristic ions listed in Table 2. If the response of any analyte exceeds the calibration rage established in Section 10, dilute the extract and reanalyze.

12.1.1 Calculate analyte and surrogate concentrations, using the multipoint calibration established in Sect. 10. Do not use daily calibration verification data to quantitate analytes in samples.

$$C_x = \frac{(A_x)(Q_{is})}{(A_{is})\ RF\ V}$$

where:

C_x = concentration of analyte or surrogate in µg/L in the water sample.
A_x = integrated abundance of the quantitation ion of the analyte in the sample.
A_{is} = integrated abundance of the quantitation ion of the internal standard in the sample.
Q_{is} = total quantity (in micrograms) of internal standard added to the water sample.
V = original water sample volume in liters.
RF = mean response factor of analyte from the initial calibration. RF is a unitless value.

12.1.2 Alternatively, use the GC/MS system software or other available proven software to compute the concentrations of the analytes and surrogates from the linear regression established in Sect. 10. Do not use daily calibration verification data to quantitate analytes in samples.

12.1.3 Calculations should utilize all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty). Experience indicates that three significant figures may be used for concentrations above 99 µg/L, two significant figures for concentrations between 1-99 µg/L, and one significant figure for lower concentrations.

12.2 To quantitate multi-component analytes (toxaphene and Aroclors), one of the following methods should be used.

Option 1 - Calculate an average RF or linear regression equation for each multi-component analyte from the combined area of all its component peaks identified in the calibration standard chromatogram, using 2-3 of the suggested quantitation ions in Table 2.

Option 2 - Calculate an average response factor or linear regression equation for each multi-component analyte using the combined areas of 3-6 of the most intense and reproducible peaks in each of the calibration standard chromatograms.

When quantifying multi-component analytes in samples, the analyst should use caution to include only those peaks from the sample that are attributable to the multi-component analyte. Option 1 should not be used if there are significant interference peaks within the Aroclor or toxaphene pattern. Option 2 was used to generate the data in Table 6.

13. METHOD PERFORMANCE

13.1 Single laboratory accuracy and precision data (Tables 3-6) for each listed analyte (except multi-component analytes) were obtained at a

concentration of 0.5 µg/L and/or 5 µg/L in reagent water utilizing both the disk and the cartridge technology and two different GC/MS systems, an ion trap and a quadrupole mass spectrometer. Table 8 lists accuracy and precision data from replicate determinations of method analytes in tap water using liquid-solid cartridge extractions and the ion trap mass spectrometer. Any type of GC/MS system may be used to perform this method if it meets the requirement in Sect. 6.10 and the quality control criteria in Sect. 9. The multi-component analytes (i.e. toxaphene and Aroclors) are presented in Tables 5 and 6. The average recoveries in the tables represent six to eight replicate analyses done over a minimum of a 2 day period.

13.1.2 With these data, the method detection limits (MDL) in the tables were calculated using the formula:

$$MDL = S\ t_{(n-1,1-alpha = 0.99)}$$

where:

$t_{(n-1,1-alpha = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom
n = number of replicates
S = standard deviation of replicate analyses.

13.2 Problem compounds

13.2.1 Some polycyclic aromatic hydrocarbons (PAH), including the labeled PAHs used in this method as internal standards, are rapidly oxidized and/or chlorinated in water containing residual chlorine. Therefore, residual chlorine must be reduced at the time of sampling. These same types of compounds, especially anthracene, benz[a]anthracene, and benzo[a]pyrene, are susceptible to photodegradation. Therefore, care should be taken to avoid exposing standards, samples, and extracts to direct light. Low recoveries of some PAH compounds have been observed when the cartridge or disk was air dried longer than 10 min (Sect. 11.1.4 and Sect. 11.2.4). Drying times longer than 10 min should be avoided, or nitrogen may be used to dry the cartridge or disk to minimize the possible oxidation of these analytes during the drying step.

13.2.2 Merphos is partially converted to DEF in aqueous matrices, and also when introduced into a hot gas chromatographic injection system. The efficiency of this conversion appears to be unpredictable and not reproducible. Therefore, merphos cannot be quantified and can only be identified by the presence of DEF in the sample.

13.2.3 Several of the nitrogen and/or phosphorus containing pesticides listed as method analytes are difficult to

chromatograph and appear as broad, asymmetrical peaks. These analytes, whose peak shapes are typically poor, are listed in Table 7. The method performance for these analytes is strongly dependent on chromatographic efficiency and performance. Poor peak shapes will affect the linearity of the calibration curves and result in poor accuracy at low concentrations. Also listed in Table 7 are data generated at a mid-concentration level for these analytes. In most cases, the data at this concentration meet the quality control criteria requirements of the method.

13.2.4 Phthalate esters and other background components appear in variable quantities in laboratory and field reagent blanks, and generally cannot be accurately measured at levels below about 2 µg/L. Subtraction of the concentration in the blank from the concentration in the sample at or below the 2 µg/L level is not recommended because the concentration of the background in the blank is highly variable.

13.2.5 Atraton and prometon are not efficiently extracted from the water at pH 2 due to what appears to be their ionization occurring in solution under acidic conditions. In order to determine these analytes accurately, a separate sample must be collected and dechlorinated with sodium sulfite, but no HCl should be added at the time of collection. At neutral pH, these two compounds are recovered from water with efficiencies greater than 90%. The data in Tables 3, 4, 5, 6, and 8 are from samples extracted at pH 2.

13.2.6 Carboxin, disulfoton, and disulfoton sulfoxide were found to be unstable in water and began to degrade almost immediately. These analytes may be identified by this method but not accurately measured.

13.2.7 Low recoveries of metribuzin were observed in samples fortified with relatively high concentrations of additional method analytes. In samples fortified with approximately 80 analytes at 5 µg/L each, metribuzin was recovered at about 50% efficiency. This suggests that metribuzin may break through the C-18 phase in highly contaminated samples resulting in low recoveries.

13.2.8 If cyanazine is to be determined, a separate sample must be collected. Cyanazine degrades in the sample when it is stored under acidic conditions or when sodium sulfite is present in the stored sample. Samples collected for cyanazine determination MUST NOT be dechlorinated or acidified when collected. They should be iced or refrigerated and analyzed within 14 days. However, these samples MUST be dechlorinated and acidified immediately prior to fortification with internal standards and surrogates, and extraction using the same quantities of acid and sodium sulfite described in Sect. 8.

14. POLLUTION PREVENTION

14.1 This method utilizes liquid-solid extraction (LSE) technology to remove the analytes from water. It requires the use of very small volumes of organic solvent and very small quantities of pure analytes, thereby eliminating the potential hazards to both the analyst and the environment involved with the use of large volumes of organic solvents in conventional liquid-liquid extractions.

14.2 For information about pollution prevention that may be applicable to laboratory operations, consult "Less Is Better: Laboratory Chemical Management for Waste Reduction" available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C., 20036.

15. WASTE MANAGEMENT

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions. The laboratory using this method has the responsibility to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations. For further information on waste management, see "The Waste Management Manual for Laboratory Personnel," also avail-able from the American Chemical Society at the address in Sect. 14.2.

16. REFERENCES

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17. TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. ION ABUNDANCE CRITERIA FOR BIS(PERFLUOROPHENYL)PHENYL PHOSPHINE (DECAFLUOROTRIPHENYLPHOSPHINE, DFTPP)

Mass (M/z)	Relative Abundance Criteria	Purpose of Checkpoint[1]
51	10-80% of the base peak	low mass sensitivity
68	<2% of mass 69	low mass resolution
70	<2% of mass 69	low mass resolution
127	10-80% of the base peak	low-mid mass sensitivity
197	<2% of mass 198	mid-mass resolution
198	base peak or >50% of 442	mid-mass resolution and sensitivity
199	5-9% of mass 198	mid-mass resolution and isotope ratio
275	10-60% of the base peak	mid-high mass sensitivity
365	>1% of the base peak	baseline threshold
441	Present and < mass 443	high mass resolution
442	base peak or >50% of 198	high mass resolution and sensitivity
443	15-24% of mass 442	high mass resolution and isotope ratio

[1]All ions are used primarily to check the mass measuring accuracy of the mass spectrometer and data system, and this is the most important part of the performance test. The three resolution checks, which include natural abundance isotope ratios, constitute the next most important part of the performance test. The correct setting of the baseline threshold, as indicated by the presence of low intensity ions, is the next most important part of the performance test. Finally, the ion abundance ranges are designed to encourage some standardization to fragmentation patterns.

TABLE 2. RETENTION TIME DATA, QUANTITATION IONS, AND INTERNAL STANDARD REFERENCES FOR METHOD ANALYTES

Compound	Retention Time (min:sec) A[a]	Retention Time (min:sec) B[b]	Quantitation Ion	IS Reference #
Internal Standards				
acenaphthene-d10 (#1)	7:47	7:01	164	
chrysene-d12 (#2)	21:33	18:09	240	
phenanthrene-d10 (#3)	11:37	10:13	188	
Surrogates				
1,3-dimethyl-2-nitrobenzene	5:16	4:33	134	1
perylene-d12	26:60	21:31	264	3
triphenylphosphate	20:25	17:25	326/325	3
Target Analytes				
acenaphthylene	7:30	6:46	152	1
alachlor	12:59	11:24	160	2
aldrin	14:24	12:31	66	2
ametryn	13:11	11:35	227/170	2
anthracene	11:50	10:24	178	2
Aroclor 1016		7:30-14:00	152/256/292	2
Aroclor 1221		6:38-11:25	152/222/256	2
Aroclor 1232		6:38-13:54	152/256/292	2
Aroclor 1242		6:38-15:00	152/256/292	2
Aroclor 1248		8:47-15:00	152/256/292	2
Aroclor 1254		11:00-18:00	220/326/360	2
Aroclor 1260		13:10-21:00	326/360/394	2
atraton	10:31	9:25	196/169	1
atrazine	10:49	9:38	200/215	1/2
benz[a]anthracene	21:31	18:08	228	3
benzo[b]fluoranthene	25:33	20:44	252	3
benzo[k]fluoranthene	25:45	20:48	252	3
benzo[g,h,i]perylene	31:16	24:18	276	3
benzo[a]pyrene	25:24	21:25	252	3
bromacil	13:46	12:03	205	2
butachlor	16:25	14:16	176/160	2
butylate	6:60	6:23	57/146	1
butylbenzylphthalate	19:39	16:53	149	2/3
carboxin	17:37	15:13	143	2

TABLE 2. RETENTION TIME DATA, QUANTITATION IONS, AND INTERNAL STANDARD REFERENCES FOR METHOD ANALYTES (CONTINUED)

Compound	Retention Time (min:sec) A[a]	Retention Time (min:sec) B[b]	Quantitation Ion	IS Reference #
chlordane, (alpha-chlordane)	16:43	14:28	375/373	2/3
chlordane, (gamma-chlordane)	16:19	14:05	373	2/3
chlordane, (trans-nonachlor)	16:47	14:30	409	2/3
chlorneb	7:47	7:05	191	1
chlorobenzilate	18:22	15:52	139	2
2-chlorobiphenyl	7:53	7:08	188	1
chlorpropham	9:33	8:36	127	1
chlorpyrifos	14:10	12:23	197/97	2
chlorothalonil	11:38	10:15	266	2
chrysene	21:39	18:13	228	3
cyanazine	14:14	12:28	225/68	2
cycloate	9:23	8:26	83/154	1
DCPA	14:20	12:30	301	2
4,4'-DDD	18:40	16:05	235/165	2
4,4'-DDE	17:20	14:59	246	2
4,4'-DDT	19:52	17:00	235/165	2
DEF	17:24	15:05	57 /169	2
diazinon	11:19	10:05	137/179	2
dibenz[[a,h]anthracene	30:32	23:47	278	3
di-n-butylphthalate	13:49	12:07	149	2
2,3-dichlorobiphenyl	10:20	9:12	222/152	1
dichlorvos	5:31	4:52	109	1
dieldrin	17:35	15:09	79	2
di(2-ethylhexyl)adipate	20:11	17:19	129	2/3
di(2-ethylhexyl)phthalate	22:11	18:39	149	2/3
diethylphthalate	8:68	7:53	149	1
dimethylphthalate	7:13	6:34	163	1
2,4-dinitrotoluene	8:08	7:22	165	1
2,6-dinitrotoluene	7:19	6:40	165	1
diphenamid	14:52	12:58	72/167	2
disulfoton	11:43	10:22	88	2
disulfoton sulfone	16:28	14:17	213/153	2
disulfoton sulfoxide	6:09	5:31	97	1

TABLE 2. RETENTION TIME DATA, QUANTITATION IONS, AND INTERNAL STANDARD REFERENCES FOR METHOD ANALYTES (CONTINUED)

Compound	Retention Time (min:sec) A[a]	Retention Time (min:sec) B[b]	Quantitation Ion	IS Reference #
endosulfan I	16:44	14:26	195	2
endosulfan II	18:35	15:59	195	2
endosulfan sulfate	19:47	16:54	272	2
endrin	18:15	15:42	67/81	2
endrin aldehyde	19:02	16:20	67	2
EPTC	6:23	5:46	128	1
ethoprop	9:19	8:23	158	1
etridiazole	7:14	6:37	211/183	1
fenamiphos	16:48	14:34	303/154	2
fenarimol	23:26	19:24	139	3
fluorene	8:59	8:03	166	1
fluridone	26:51	21:26	328	3
HCH, alpha	10:19	9:10	181	1
HCH, beta	10:57	9:41	181	2
HCH, delta	11:57	10:32	181	2
HCH, gamma (Lindane)	11:13	9:54	181	2
heptachlor	13:19	11:37	100	2
heptachlor epoxide	15:34	13:29	81	2
2,2′,3,3′,4,4′,6-heptachlorobiphenyl	21:23	18:04	394/396	3
hexachlorobenzene	10:27	9:15	284	1
2,2′,4,4′,5,6′-hexachlorobiphenyl	17:32	15:09	360	2
hexachlorocyclopentadiene	5:16	5:38	237	1
hexazinone	20:00	17:06	171	2
indeno[1,2,3-cd]pyrene	30:26	23:43	276	3
isophorone	4:54	4:10	82	1
merphos	15:38	13:35	209/153	2
methoxychlor	21:36	18:14	227	3
methyl paraoxon	11:57	10:22	109	2
metolachlor	14:07	12:20	162	2
metribuzin	12:46	11:13	198	2
mevinphos	5:54	6:19	127	1
MGK 264 - isomer a	15:18	13:00	164/66	2
MGK 264 - isomer b	14:55	13:19	164	2

TABLE 2. *RETENTION TIME* DATA, QUANTITATION IONS, AND INTERNAL STANDARD REFERENCES FOR METHOD ANALYTES (CONTINUED)

Compound	Retention Time (min:sec) A[a]	Retention Time (min:sec) B[b]	Quantitation Ion	IS Reference #
molinate	8:19	7:30	126	1
napropamide	16:53	14:37	72	2
norflurazon	19:31	16:46	145	2
2,2′,3,3′,4,5′,6,6′-octachlorobiphenyl	21:33	18:11	430/428	3
pebulate	7:18	6:40	128	1
2,2′,3′,4,6-pentachlorobiphenyl	15:37	13:33	326	2
pentachlorophenol	11:01	9:45	266	2
permethrin, cis	24:25	20:01	183	3
permethrin, trans	24:39	20:10	183	3
phenanthrene	11:41	10:16	178	2
prometon	10:39	9:32	225/168	2
prometryn	13:15	11:39	241/184	2
pronamide	11:19	10:02	173	2
propachlor	9:00	8:07	120	1
propazine	10:54	9:43	214/172	2
pyrene	16:41	14:24	202	2
simazine	10:41	9:33	201/186	2
simetryn	13:04	11:29	213	2
stirofos	16:20	14:11	109	2
tebuthiuron	8:00	7:16	156	1
terbacil	11:44	10:24	161	2
terbufos	11:14	9:58	57	2
terbutryn	13:39	11:58	226/185	2
2,2′,4,4′-tetrachlorobiphenyl	14:02	12:14	292	2
toxaphene		13:00-21:00	159	2
triademefon	14:30	12:40	57	2
2,4,5-trichlorobiphenyl	12:44	10:53	256	2
tricyclazole	17:15	14:51	189	2
trifluralin	9:31	8:37	306	1
vernolate	7:10	6:32	128	1

[a] Single-ramp linear temperature program conditions (Sect. 10.2.3.2).

[b] Multi-ramp linear temperature program conditions (Sect. 10.2.3.1).

TABLE 3. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Surrogates					
1,3-dimethyl-2-nitrobenzene	5.0	4.7	3.9	94	
perylene-d12	5.0	4.9	4.8	98	
triphenylphosphate	5.0	5.5	6.3	110	
Target Analytes					
acenaphthylene	0.50	0.45	8.2	91	0.11
alachlor	0.50	0.47	12	93	0.16
aldrin	0.50	0.40	9.3	80	0.11
ametryn	0.50	0.44	6.9	88	0.092
anthracene	0.50	0.53	4.3	106	0.068
Aroclor 1016	ND	ND	ND	ND	ND
Aroclor 1221	ND	ND	ND	ND	ND
Aroclor 1232	ND	ND	ND	ND	ND
Aroclor 1242	ND	ND	ND	ND	ND
Aroclor 1448	ND	ND	ND	ND	ND
Aroclor 1254	ND	ND	ND	ND	ND
Aroclor 1260	ND	ND	ND	ND	ND
atraton[4]	0.50	0.35	15	70	0.16
atrazine	0.50	0.54	4.8	109	0.078
benz[a]anthracene	0.50	0.41	16	82	0.20
benzo[b]fluoranthene	0.50	0.49	20	98	0.30
benzo[k]fluoranthene	0.50	0.51	35	102	0.54
benzo[g,h,i]perylene	0.50	0.72	2.2	144	0.047
benzo[a]pyrene	0.50	0.58	1.9	116	0.032
bromacil	0.50	0.54	6.4	108	0.10
butachlor	0.50	0.62	4.1	124	0.076
butylate	0.50	0.52	4.1	105	0.064
butylbenzylphthalate	0.50	0.77	11	154	0.25
carboxin	5.0	3.8	12	76	1.4
chlordane (alpha-chlordane)	0.50	0.36	11	72	0.12
chlordane (gamma-chlordane)	0.50	0.40	8.8	80	0.11
chlordane (trans-nonachlor)	0.50	0.43	17	87	0.22

TABLE 3. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING *LIQUID-SOLID* C-18 CARTRIDGE EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER (CONTINUED)

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
chlorneb	0.50	0.51	5.7	102	0.088
chlorobenzilate	5.0	6.5	6.9	130	1.3
2-chlorobiphenyl	0.50	0.40	7.2	80	0.086
chlorpropham	0.50	0.61	6.2	121	0.11
chlorpyrifos	0.50	0.55	2.7	110	0.044
chlorothalonil	0.50	0.57	6.9	113	0.12
chrysene	0.50	0.39	7.0	78	0.082
cyanazine	0.50	0.71	8.0	141	0.17
cycloate	0.50	0.52	6.1	104	0.095
DCPA	0.50	0.55	5.8	109	0.094
4,4'-DDD	0.50	0.54	4.4	107	0.071
4,4'-DDE	0.50	0.40	6.3	80	0.075
4,4'-DDT	0.50	0.79	3.5	159	0.083
diazinon	0.50	0.41	8.8	83	0.11
dibenz[a,h]anthracene	0.50	0.53	0.5	106	0.010
di-n-butylphthalate	ND	ND	ND	ND	ND
2,3-dichlorobiphenyl	0.50	0.40	11	80	0.14
dichlorvos	0.50	0.55	9.1	110	0.15
dieldrin	0.50	0.48	3.7	96	0.053
di-(2-ethylhexyl)adipate	0.50	0.42	7.1	84	0.090
di(2-ethylhexyl)phthalate	ND	ND	ND	ND	ND
diethylphthalate	0.50	0.59	9.6	118	0.17
dimethylphthalate	0.50	0.60	3.2	120	0.058
2,4-dinitrotoluene	0.50	0.60	5.6	119	0.099
2,6-dinitrotoluene	0.50	0.60	8.8	121	0.16
diphenamid	0.50	0.54	2.5	107	0.041
disulfoton	5.0	3.99	5.1	80	0.62
disulfoton sulfone	0.50	0.74	3.2	148	0.070
disulfoton sulfoxide	0.50	0.58	12	116	0.20
endosulfan I	0.50	0.55	18	110	0.30
endosulfan II	0.50	0.50	29	99	0.44
endosulfan sulfate	0.50	0.62	7.2	124	0.13

TABLE 3. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER (CONTINUED)

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
endrin	0.50	0.54	18	108	0.29
endrin aldehyde	0.50	0.43	15	87	0.19
EPTC	0.50	0.50	7.2	100	0.11
ethoprop	0.50	0.62	6.1	123	0.11
etridiazole	0.50	0.69	7.6	139	0.16
fenamiphos	5.0	5.2	6.1	103	0.95
fenarimol	5.0	6.3	6.5	126	1.2
fluorene	0.50	0.46	4.2	93	0.059
fluridone	5.0	5.1	3.6	102	0.55
HCH, alpha	0.50	0.51	13	102	0.20
HCH, beta	0.50	0.51	20	102	0.31
HCH, delta	0.50	0.56	13	112	0.21
HCH, gamma (Lindane)	0.50	0.63	8.0	126	0.15
heptachlor	0.50	0.41	12	83	0.15
heptachlor epoxide	0.50	0.35	5.5	70	0.058
2,2′,3,3′,4,4′,6-heptachlorobiphenyl	0.50	0.35	10	71	0.11
hexachlorobenzene	0.50	0.39	11	78	0.13
2,2′,4,4′,5,6′-hexachlorobiphenyl	0.50	0.37	9.6	73	0.11
hexachlorocyclopentadiene	0.50	0.43	5.6	86	0.072
hexazinone	0.50	0.70	5.0	140	0.11
indeno[1,2,3-cd]pyrene	0.50	0.69	2.7	139	0.057
isophorone	0.50	0.44	3.2	88	0.042
methoxychlor	0.50	0.62	4.2	123	0.077
methyl paraoxon	0.50	0.57	10	115	0.17
metolachlor	0.50	0.37	8.0	75	0.090
metribuzin	0.50	0.49	11	97	0.16
mevinphos	0.50	0.57	12	114	0.20
MGK 264 - isomer a	0.33	0.39	3.4	116	0.040
MGK 264 - isomer b	0.17	0.16	6.4	96	0.030
molinate	0.50	0.53	5.5	105	0.087
napropamide	0.50	0.58	3.5	116	0.060
norflurazon	0.50	0.63	7.1	126	0.13

TABLE 3. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER (CONTINUED)

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
2,2′,3,3′,4,5′,6,6′-octachlorobiphenyl	0.50	0.50	8.7	101	0.13
pebulate	0.50	0.49	5.4	98	0.080
2,2′,3′,4,6-pentachlorobiphenyl	0.50	0.30	16	61	0.15
pentachlorophenol	ND	ND	ND	ND	ND
permethrin, cis	0.25	0.30	3.7	121	0.034
permethrin, trans	0.75	0.82	2.7	109	0.067
phenathrene	0.50	0.46	4.3	92	0.059
prometon[a]	0.50	0.30	42	60	0.38
prometryn	0.50	0.46	5.6	92	0.078
pronamide	0.50	0.54	5.9	108	0.095
propachlor	0.50	0.49	7.5	98	0.11
propazine	0.50	0.54	7.1	108	0.12
pyrene	0.50	0.38	5.7	77	0.066
simazine	0.50	0.55	9.1	109	0.15
simetryn	0.50	0.52	8.2	105	0.13
stirofos	0.50	0.75	5.8	149	0.13
tebuthiuron	5.0	6.8	14	136	2.8
terbacil	5.0	4.9	14	97	2.1
terbufos	0.50	0.53	6.1	106	0.096
terbutryn	0.50	0.47	7.6	95	0.11
2,2′,4,4′-tetrachlorobiphenyl	0.50	0.36	4.1	71	0.044
toxaphene	ND	ND	ND	ND	ND
triademefon	0.50	0.57	20	113	0.33
2,4,5-trichlorobiphenyl	0.50	0.38	6.7	75	0.075
tricyclazole	5.0	4.6	19	92	2.6
trifluralin	0.50	0.63	5.1	127	0.096
vernolate	0.50	0.51	5.5	102	0.084

ND = Not Determined

[a] Data from samples extracted at pH 2 - for accurate determination of this analyte, a separate sample must be extracted at ambient pH.

TABLE 4. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Surrogates					
1,3-dimethyl-2-nitrobenzene	5.0	4.6	2.6	93	
perylene-d12	5.0	4.8	1.6	95	
triphenylphosphate	5.0	5.0	2.5	101	
Target Analytes					
acenaphthylene	0.50	0.47	8.4	94	0.12
alachlor	0.50	0.50	5.8	100	0.087
aldrin	0.50	0.39	13	78	0.16
ametryn	0.50	0.38	28	76	0.32
anthracene	0.50	0.49	13	98	0.18
Aroclor 1016	ND	ND	ND	ND	ND
Aroclor 1221	ND	ND	ND	ND	ND
Aroclor 1232	ND	ND	ND	ND	ND
Aroclor 1242	ND	ND	ND	ND	ND
Aroclor 1248	ND	ND	ND	ND	ND
Aroclor 1254	ND	ND	ND	ND	ND
Aroclor 1260	ND	ND	ND	ND	ND
atraton[a]	0.50	0.07	139	19	0.29
atrazine	0.50	0.60	3.7	119	0.065
benz[a]anthracene	0.50	0.38	6.1	76	0.070
benzo[b]fluoranthene	0.50	0.61	2.5	121	0.046
benzo[k]fluoranthene	0.50	0.61	27	122	0.50
benzo[g,h,i]perylene	0.50	0.69	1.4	138	0.029
benzo[a]pyrene	0.50	0.58	6.1	116	0.11
bromacil	0.50	0.49	23	99	0.34
butachlor	0.50	0.63	2.1	127	0.039
butylate	0.50	0.50	4.9	99	0.073
butylbenzylphthalate	0.50	0.78	5.5	156	0.13
carboxin	5.0	2.7	12	54	0.98
chlordane (alpha-chlordane)	0.50	0.37	5.5	74	0.061
chlordane (gamma-chlordane)	0.50	0.40	4.2	80	0.050
chlordane (trans-nonachlor)	0.50	0.45	7.8	90	0.11

TABLE 4. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER (CONTINUED)

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
chlorneb	0.50	0.51	7.3	100	0.11
chlorobenzilate	5.0	7.9	8.4	156	2.0
2-chlorobiphenyl	0.50	0.42	1.9	84	0.023
chlorpropham	0.50	0.68	5.4	134	0.11
chlorpyrifos	0.50	0.61	6.5	119	0.12
chlorothalonil	0.50	0.59	6.5	116	0.11
chrysene	0.50	0.35	3.6	71	0.038
cyanazine	0.50	0.68	15	136	0.31
cycloate	0.50	0.53	4.9	106	0.077
DCPA	0.50	0.55	4.5	110	0.073
4,4'-DDD	0.50	0.67	14	137	0.28
4,4'-DDE	0.50	0.48	4.9	96	0.070
4,4'-DDT	0.50	0.93	3.2	187	0.090
diazinon	0.50	0.56	6.8	109	0.11
dibenz[a,h]anthracene	0.50	0.61	15	122	0.28
di-n-butylphthalate	ND	ND	ND	ND	ND
2,3-dichlorobiphenyl	0.50	0.46	8.1	93	0.11
dichlorvos	0.50	0.54	5.6	108	0.092
dieldrin	0.50	0.52	7.8	104	0.12
di-(2-ethylhexyl)adipate	ND	ND	ND	ND	ND
di(2-ethylhexyl)phthalate	ND	ND	ND	ND	ND
diethylphthalate	0.50	0.66	10	132	0.20
dimethylphthalate	0.50	0.57	8.3	114	0.14
2,4-dinitrotoluene	0.50	0.54	5.7	109	0.093
2,6-dinitrotoluene	0.50	0.48	4.9	96	0.071
diphenamid	0.50	0.60	3.8	118	0.067
disulfoton	5.0	4.8	9.4	96	1.3
disulfoton sulfone	0.50	0.82	2.8	164	0.070
disulfoton sulfoxide	0.50	0.68	8.9	136	0.18
endosulfan I	0.50	0.65	10	132	0.20
endosulfan II	0.50	0.60	21	122	0.38
endosulfan sulfate	0.50	0.67	6.1	133	0.12

TABLE 4. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER (CONTINUED)

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
endrin	0.50	0.58	18	116	0.31
endrin aldehyde	0.50	0.51	16	101	0.24
EPTC	0.50	0.50	3.8	100	0.056
ethoprop	0.50	0.69	2.3	138	0.048
etridiazole	0.50	0.74	4.0	149	0.090
fenamiphos	5.0	6.3	8.8	124	1.6
fenarimol	5.0	7.5	5.5	150	1.2
fluorene	0.50	0.47	8.1	94	0.11
fluridone	5.0	5.7	4.5	114	0.77
HCH, alpha	0.50	0.54	12	107	0.20
HCH, beta	0.50	0.57	17	112	0.28
HCH, delta	0.50	0.61	8.2	120	0.15
HCH, gamma (Lindane)	0.50	0.62	6.6	124	0.12
heptachlor	0.50	0.40	12	80	0.14
heptachlor epoxide	0.50	0.36	8.7	71	0.093
2,2′,3,3′,4,4′,6-heptachlorobiphenyl	0.50	0.36	13	71	0.14
hexachlorobenzene	0.50	0.47	8.3	95	0.12
2,2′,4,4′,5,6′-hexachlorobiphenyl	0.50	0.41	11	83	0.13
hexachlorocyclopentadiene	0.50	0.42	12	84	0.16
hexazinone	0.50	0.85	5.6	169	0.14
indeno[1,2,3-cd]pyrene	0.50	0.69	2.4	138	0.050
isophorone	0.50	0.41	4.2	83	0.052
methoxychlor	0.50	0.58	1.9	117	0.033
methyl paraoxon	0.50	0.62	14	122	0.25
metolachlor	0.50	0.38	7.5	75	0.084
metribuzin	0.50	0.54	3.9	107	0.062
mevinphos	0.50	0.72	3.7	143	0.079
MGK 264 - isomer a	0.33	0.40	8.8	119	0.10
MGK 264 - isomer b	0.17	0.17	5.9	103	0.030
molinate	0.50	0.53	3.2	105	0.050
napropamide	0.50	0.64	5.9	126	0.11
norflurazon	0.50	0.70	4.2	141	0.089

TABLE 4. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER (CONTINUED)

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
2,2′,3,3′,4,5′,6,6′-octachlorobiphenyl	0.50	0.51	4.2	102	0.064
pebulate	0.50	0.48	5.8	96	0.084
2,2′,3′,4,6-pentachlorobiphenyl	0.50	0.35	4.2	70	0.044
pentachlorophenol	2.0	1.9	16	95	.89
permethrin,cis	0.25	0.32	3.3	126	0.031
permethrin,trans	0.75	0.89	1.9	118	0.051
phenathrene	0.50	0.48	5.0	95	0.071
prometon[a]	0.50	0.21	66	45	0.44
prometryn	0.50	0.46	24	93	0.33
pronamide	0.50	0.58	7.1	113	0.12
propachlor	0.50	0.49	5.4	98	0.079
propazine	0.50	0.59	5.0	117	0.088
pyrene	0.50	0.40	3.2	79	0.038
simazine	0.50	0.60	10	120	0.18
simetryn	0.50	0.41	15	83	0.19
stirofos	0.50	0.84	3.2	168	0.081
tebuthiuron	5.0	9.3	8.6	187	2.4
terbacil	5.0	5.0	11	100	1.7
terbufos	0.50	0.62	4.2	123	0.077
terbutryn	0.50	0.46	23	94	0.32
2,2′,4,4′-tetrachlorobiphenyl	0.50	0.40	7.4	79	0.088
toxaphene	ND	ND	ND	ND	ND
triademefon	0.50	0.73	7.2	145	0.16
2,4,5-trichlorobiphenyl	0.50	0.44	5.3	89	0.071
tricyclazole	5.0	6.8	12	137	2.4
trifluralin	0.50	0.62	2.6	124	0.048
vernolate	0.50	0.51	3.4	100	0.051

ND = Not Determined

[a] Data from samples extracted at pH 2 - for accurate determination of this analyte, a separate sample must be extracted at ambient pH.

TABLE 5. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Surrogates					
1,3-dimethyl-2-nitrobenzene	5.0	4.9	8.4	98	
perylene-d12	5.0	4.3	18	86	
triphenylphosphate	5.0	4.8	13	96	
Target Analytes					
acenaphthylene	0.50	0.50	8.8	100	0.13
alachlor	0.50	0.58	4.0	115	0.069
aldrin	0.50	0.42	3.5	85	0.045
ametryn	0.50	0.46	3.3	91	0.045
anthracene	0.50	0.42	3.8	84	0.048
Aroclor 1016	1.0	1.1	4.4	113	0.15
Aroclor 1221	ND	ND	ND	ND	ND
Aroclor 1232	ND	ND	ND	ND	ND
Aroclor 1242	ND	ND	ND	ND	ND
Aroclor 1248	ND	ND	ND	ND	ND
aroclor 1254[a]	1.0	1.1	17	110	0.56
aroclor 1260	1.0	0.96	9.3	96	0.27
atraton[c]	0.50	0.35	11	70	0.12
atrazine	0.50	0.55	5.0	109	0.081
benz[a]anthracene	0.50	0.43	7.3	85	0.093
benzo[b]fluoranthene	0.50	0.44	16	88	0.21
benzo[k]fluoranthene	0.50	0.34	22	68	0.23
benzo[g,h,i]perylene	0.50	0.38	31	76	0.35
benzo[a]pyrene	0.50	0.36	21	73	0.23
bromacil	0.50	0.45	9.1	90	0.12
butachlor	0.50	0.67	12	133	0.24
butylate	0.50	0.52	5.2	104	0.082
butylbenzylphthalate[b]	5.0	5.7	7.7	114	1.4
carboxin	0.50	0.58	22	117	0.38
chlordane, (alpha-chlordane)	0.50	0.47	12	95	0.17
chlordane, (gamma-chlordane)	0.50	0.50	10	99	0.16
chlordane, (trans-nonachlor)	0.50	0.48	11	96	0.16

TABLE 5. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER *(CONTINUED)*

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
chlorneb	0.50	0.51	8.1	103	0.13
chlorobenzilate	0.50	0.61	9.7	123	0.17
2-chlorobiphenyl	0.50	0.47	4.8	94	0.068
chlorpropham	0.50	0.55	8.1	109	0.13
chlorpyrifos	0.50	0.50	2.4	99	0.035
chlorothalonil	0.50	0.62	5.3	123	0.098
chrysene	0.50	0.50	9.2	99	0.14
cyanazine	0.50	0.49	13	97	0.19
cycloate	0.50	0.52	7.6	103	0.12
DCPA	0.50	0.55	7.2	109	0.12
4,4'-DDD	0.50	0.52	3.6	103	0.055
4,4'-DDE	0.50	0.41	5.8	81	0.070
4,4'-DDT	0.50	0.54	2.4	108	0.039
diazinon	0.50	0.37	2.7	75	0.030
dibenz[a,h]anthracene	0.50	0.37	29	74	0.32
di-n-butylphthalate[b]	5.0	6.2	4.6	124	0.89
2,3-dichlorobiphenyl	0.50	0.45	5.8	90	0.079
dichlorvos	0.50	0.53	8.0	106	0.13
dieldrin	0.50	0.50	10	100	0.15
di(2-ethylhexyl)adipate	0.50	0.59	18	117	0.31
di(2-ethylhexyl)phthalate[b]	5.0	6.5	6.6	130	1.3
diethylphthalate	0.50	0.63	15	126	0.28
dimethylphthalate	0.50	0.51	9.5	102	0.14
2,4-dinitrotoluene	0.50	0.45	18	91	0.24
2,6-dinitrotoluene	0.50	0.40	17	80	0.20
diphenamid	0.50	0.55	6.5	111	0.11
disulfoton	0.50	0.62	9.8	124	0.18
disulfoton sulfone	0.50	0.64	3.5	128	0.068
disulfoton sulfoxide	0.50	0.57	8.6	114	0.15
endosulfan I	0.50	0.60	6.1	121	0.11
endosulfan II	0.50	0.64	3.9	128	0.074
endosulfan sulfate	0.50	0.58	5.4	116	0.093

TABLE 5. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER (CONTINUED)

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
endrin	0.50	0.62	18	124	0.34
endrin aldehyde	0.50	0.58	8.7	116	0.15
EPTC	0.50	0.53	7.7	105	0.12
ethoprop	0.50	0.62	10	124	0.19
etridiazole	0.50	0.61	6.5	122	0.12
fenamiphos	0.50	0.67	12	133	0.24
fenarimol	0.50	0.74	11	148	0.25
fluorene	0.50	0.49	9.0	98	0.13
fluridone	5.0	5.2	2.5	105	0.39
HCH, alpha	0.50	0.55	6.8	109	0.11
HCH, beta	0.50	0.54	5.3	107	0.085
HCH, delta	0.50	0.52	3.1	105	0.049
HCH, gamma (Lindane)	0.50	0.53	5.3	105	0.084
heptachlor	0.50	0.50	4.1	100	0.061
heptachlor epoxide	0.50	0.54	8.2	108	0.13
2,2′,3,3′,4,4′,6-heptachlorobiphenyl	0.50	0.45	11	90	0.15
hexachlorobenzene	0.50	0.41	6.0	82	0.074
2,2′,4,4′,5,6′-hexachlorobiphenyl	0.50	0.40	15	80	0.18
hexachlorocyclopentadiene	0.50	0.34	13	68	0.13
hexazinone	0.50	0.80	5.6	159	0.14
indeno[1,2,3-cd]pyrene	0.50	0.36	28	71	0.30
isophorone	0.50	0.54	7.9	107	0.13
methoxychlor	0.50	0.58	7.7	115	0.13
methyl paraoxon	0.50	0.85	3.7	170	0.094
metolachlor	0.50	0.58	4.8	117	0.085
metribuzin	0.50	0.54	14	108	0.22
mevinphos	0.50	0.47	12	95	0.17
MGK 264 - isomer a	0.33	0.38	9.5	113	0.11
MGK 264 - isomer b	0.16	0.18	5.4	105	0.029
molinate	0.50	0.55	5.2	111	0.086
napropamide	0.50	0.63	10	127	0.20
norflurazon	0.50	0.82	3.8	165	0.093

TABLE 5. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER *(CONTINUED)*

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
2,2′,3,3′,4,5′,6,6′-octachlorobiphenyl	0.50	0.49	19	99	0.28
pebulate	0.50	0.56	6.1	112	0.10
2,2′,3′,4,6-pentachlorobiphenyl	0.50	0.43	8.7	86	0.11
pentachlorophenol	2.0	2.4	10	119	0.72
permethrin,cis	0.25	0.45	3.2	179	0.043
permethrin,trans	0.75	1.1	2.2	153	0.074
phenanthrene	0.50	0.48	4.8	96	0.069
prometon[c]	0.50	0.24	27	48	0.20
prometryn	0.50	0.46	3.0	92	0.041
pronamide	0.50	0.56	5.3	113	0.089
propachlor	0.50	0.56	8.6	112	0.14
propazine	0.50	0.52	4.3	103	0.066
pyrene	0.50	0.47	11	95	0.16
simazine	0.50	0.48	8.8	96	0.13
simetryn	0.50	0.48	2.9	96	0.042
stirofos	0.50	0.80	3.9	160	0.093
tebuthiuron	0.50	0.67	7.4	134	0.15
terbacil	0.50	0.59	12	119	0.22
terbufos	0.50	0.46	11	92	0.15
terbutryn	0.50	0.48	2.6	97	0.038
2,2′,4,4′-tetrachlorobiphenyl	0.50	0.40	6.4	81	0.077
toxaphene	10	11	4.9	118	1.7
triademefon	0.50	0.73	6.4	146	0.14
2,4,5-trichlorobiphenyl	0.50	0.44	3.3	88	0.043
tricyclazole	0.50	0.63	16	127	0.31
trifluralin	0.50	0.62	13	124	0.24
vernolate	0.50	0.50	9.3	101	0.14

[a] Seven replicates

[b] Seven replicates in fortified tap water.

[c] Data from samples extracted at pH 2 - for accurate determination of this analyte, a separate sample must be extracted at ambient pH.

TABLE 6. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Surrogates					
1,3-dimethyl-2-nitrobenzene	5.0	4.9	10	98	
perylene-d12	5.0	4.9	4.5	98	
triphenylphosphate	5.0	5.9	8.1	117	
Target Analytes					
acenaphthylene	0.50	0.51	4.5	102	0.068
alachlor	0.50	0.54	6.6	108	0.11
aldrin	0.50	0.45	6.3	90	0.085
ametryn	0.50	0.41	23	82	0.29
anthracene	0.50	0.39	15	79	0.18
Aroclor 1016	0.20	0.25	4.7	123	0.040
Aroclor 1221	0.20	0.26	6.1	130	0.054
Aroclor 1232	0.20	0.24	4.7	121	0.042
Aroclor 1242	0.20	0.26	4.9	129	0.043
Aroclor 1248	0.20	0.24	4.1	118	0.038
Aroclor 1254	0.20	0.22	3.7	110	0.028
Aroclor 1260[a]	0.20	0.21	2.2	108	0.018
atraton[a]	0.50	0.10	46	21	0.14
atrazine	0.50	0.56	4.6	111	0.076
benz[a]anthracene	0.50	0.44	7.4	88	0.098
benzo[b]fluoranthene	0.50	0.50	9.1	100	0.14
benzo[k]fluoranthene	0.50	0.46	2.2	91	0.031
benzo[g,h,i]perylene	0.50	0.47	7.9	95	0.11
benzo[a]pyrene	0.50	0.44	12	89	0.16
bromacil	0.50	0.49	4.4	99	0.066
butachlor	0.50	0.66	5.1	132	0.10
butylate	0.50	0.50	5.4	100	0.082
butylbenzylphthalate[b]	5.0	5.7	7.7	114	1.4
carboxin	0.50	0.40	38.1	79	0.45
chlordane, (alpha-chlordane)	0.50	0.50	4.3	101	0.065
chlordane, (gamma-chlordane)	0.50	0.51	7.2	102	0.11
chlordane, (trans-nonachlor)	0.50	0.52	6.2	104	0.097

TABLE 6. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING *LIQUID-SOLID C-18 DISK EXTRACTION* AND THE ION TRAP MASS SPECTROMETER (CONTINUED)

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
chlorneb	0.50	0.54	6.3	108	0.10
chlorobenzilate	0.50	0.59	9.7	117	0.17
2-chlorobiphenyl	0.50	0.50	4.7	100	0.070
chlorpropham	0.50	0.55	4.7	111	0.079
chlorpyrifos	0.50	0.54	11	109	0.18
chlorothalonil	0.50	0.59	4.4	119	0.079
chrysene	0.50	0.48	6.1	96	0.088
cyanazine	0.50	0.52	8.3	105	0.13
cycloate	0.50	0.51	4.1	102	0.063
DCPA	0.50	0.53	3.2	105	0.051
4,4'-DDD	0.50	0.63	16	127	0.31
4,4'-DDE	0.50	0.48	3.7	96	0.054
4,4'-DDT	0.50	0.58	7.2	117	0.13
diazinon	0.50	0.50	4.5	101	0.068
dibenz[a,h]anthracene	0.50	0.47	9.9	94	0.14
di-n-butylphthalate[b]	5.0	5.7	3.3	115	0.59
2,3-dichlorobiphenyl	0.50	0.50	2.6	100	0.039
dichlorvos	0.50	0.50	8.7	99	0.13
dieldrin	0.50	0.53	7.0	106	0.11
di(2-ethylhexyl)adipate[b]	5.0	5.4	7.5	107	1.3
di(2-ehtylhexyl)phthalate[b]	5.0	5.7	2.6	114	0.46
diethylphthalate	0.50	0.68	5.0	137	0.10
dimethylphthalate	0.50	0.51	5.0	102	0.077
2,4-dinitrotoluene	0.50	0.30	8.1	59	0.072
2,6-dinitrotoluene	0.50	0.28	6.4	56	0.054
diphenamid	0.50	0.56	6.4	112	0.11
disulfoton	0.50	0.70	5.3	139	0.11
disulfoton sulfone	0.50	0.64	5.9	128	0.11
disulfoton sulfoxide	0.50	0.60	3.8	119	0.068
endosulfan I	0.50	0.61	4.9	122	0.089
endosulfan II	0.50	0.66	6.1	131	0.12
endosulfan sulfate	0.50	0.57	9.0	115	0.16

TABLE 6. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE ION TRAP MASS SPECTROMETER (CONTINUED)

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
endrin	0.50	0.68	7.9	137	0.16
endrin aldehyde	0.50	0.57	2.8	114	0.048
EPTC	0.50	0.48	5.2	97	0.076
ethoprop	0.50	0.61	7.5	122	0.14
etridiazole	0.50	0.54	4.2	108	0.067
fenamiphos	0.50	0.67	10	133	0.20
fenarimol	0.50	0.59	5.8	118	0.10
fluorene	0.50	0.53	3.4	106	0.054
fluridone	5.0	5.2	2.3	104	0.16
HCH, alpha	0.50	0.55	5.0	110	0.083
HCH, beta	0.50	0.54	4.1	109	0.068
HCH, delta	0.50	0.53	3.6	106	0.058
HCH, gamma (Lindane)	0.50	0.50	3.2	100	0.047
heptachlor	0.50	0.49	4.0	98	0.059
heptachlor epoxide	0.50	0.50	3.2	100	0.048
2,2′,3,3′,4,4′,6-heptachlorobiphenyl	0.50	0.46	7.3	92	0.10
hexachlorobenzene	0.50	0.49	3.4	97	0.049
2,2′,4,4′,5,6′-hexachlorobiphenyl	0.50	0.50	5.3	99	0.079
hexachlorocyclopentadiene	0.50	0.37	9.3	73	0.10
hexazinone	0.50	0.75	4.2	150	0.094
indeno[1,2,3-cd]pyrene	0.50	0.48	7.3	96	0.10
isophorone	0.50	0.51	4.3	102	0.066
methoxychlor	0.50	0.52	6.7	104	0.10
methyl paraoxon	0.50	0.75	4.5	151	0.10
metolachlor	0.50	0.57	3.2	114	0.054
metribuzin	0.50	0.53	5.7	107	0.090
mevinphos	0.50	0.56	6.2	112	0.10
MGK 264 - isomer a	0.33	0.38	6.7	113	0.076
MGK 264 - isomer b	0.16	0.18	5.3	110	0.029
molinate	0.50	0.53	3.8	105	0.060
napropamide	0.50	0.58	7.9	116	0.14
norflurazon	0.50	0.71	4.3	142	0.091

TABLE 6. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE ION TRAP MASS SPECTROMETER (CONTINUED)

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
2,2',3,3',4,5',6,6'-octachlorobiphenyl	0.50	0.47	5.3	94	0.076
pebulate	0.50	0.56	7.1	112	0.11
2,2',3',4,6-pentachlorobiphenyl	0.50	0.49	4.0	97	0.059
pentachlorophenol	2.0	2.2	15	111	1.0
permethrin,cis	0.25	0.37	3.1	149	0.035
permethrin,trans	0.75	0.84	1.6	112	0.039
phenanthrene	0.50	0.49	6.3	97	0.092
prometon[d]	0.50	0.16	63	32	0.30
prometryn	0.50	0.46	23	91	0.32
pronamide	0.50	0.56	3.9	111	0.064
propachlor	0.50	0.58	5.7	115	0.098
propazine	0.50	0.53	4.7	106	0.074
pyrene	0.50	0.52	5.2	104	0.080
simazine	0.50	0.54	2.8	107	0.045
simetryn	0.50	0.36	20	71	0.22
stirofos	0.50	0.72	3.7	144	0.080
tebuthiuron	0.50	0.67	7.9	133	0.16
terbacil	0.50	0.64	12	129	0.23
terbufos	0.50	0.57	6.8	113	0.11
terbutryn	0.50	0.46	24	93	0.34
2,2',4,4'-tetrachlorobiphenyl	0.50	0.46	7.4	91	0.10
toxaphene[c]	10	12	2.7	122	1.0
triademefon	0.50	0.71	7.3	142	0.16
2,4,5-trichlorobiphenyl	0.50	0.48	4.5	97	0.066
tricyclazole	0.50	0.65	14	130	0.27
trifluralin	0.50	0.59	7.8	117	0.14
vernolate	0.50	0.50	3.2	99	0.047

[a] Six replicates

[b] Seven replicates in fortified tap water.

[c] Seven replicates

[d] Data from samples extracted at pH 2 - for accurate determination of this analyte, a separate sample must be extracted at ambient pH.

TABLE 7. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS AT 5 µg/L IN REAGENT WATER OF POORLY CHROMATOGRAPHED NITROGEN AND PHOSPHOROUS CONTAINING PESTICIDES

Compound	Ion Trap Mass Spectrometer				Quadrupole Mass Spectrometer			
	Cartridge		Disk		Cartridge		Disk	
	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	Relative Standard Deviation (&)	Mean Method Accuracy (% of True Conc.)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)
fenamiphos	7.7	99	4.5	108	6.1	103	8.8	124
fenarimol	2.0	104	10	110	6.5	126	5.5	150
fluridone	2.5	105	2.3	104	3.6	102	4.5	114
hexazinone	4.2	106	9.7	116	5.3	104	8.3	127
norflurazon	4.1	111	9.6	119	3.2	98	11.1	113
stirofos	8.2	114	12	124	4.1	110	11.1	125
tebuthiuron	9.5	119	5.3	145	13	136	8.6	182
triademeton	7.8	113	10	128	3.7	100	9.8	118
tricyclazole	16	81	9.5	99	19	92	12	137

TABLE 8. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN TAP WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc.	Mean	% RSD	% REC
acenaphthylene	5.0	5.2	5.3	104
alachlor	5.0	5.5	6.9	110
aldrin	5.0	4.4	14	88
ametryn	5.0	4.2	3.4	83
anthracene	5.0	4.3	5.2	87
Aroclor 1016	ND	ND	ND	ND
Aroclor 1221	ND	ND	ND	ND
Aroclor 1232	ND	ND	ND	ND
Aroclor 1242	ND	ND	ND	ND
Aroclor 1248	ND	ND	ND	ND
Aroclor 1254	ND	ND	ND	ND
Aroclor 1260	ND	ND	ND	ND
atraton[a]	5.0	2.2	28	43
atrazine	5.0	5.6	6.2	111
benz[a]anthracene	5.0	4.9	8.8	97
benzo[b]fluoranthene	5.0	5.7	7.5	114
benzo[k]fluoranthene	5.0	5.7	2.9	113
benzo[g,h,i]perylene	5.0	5.6	7.1	113
benzo[a]pyrene	5.0	6.1	4.6	121
bromacil	5.0	3.5	5.1	69
butachlor	5.0	5.4	7.5	109
butylate	5.0	5.1	4.5	102
butylbenzylphthalate	5.0	7.2	8.3	144
carboxin	5.0	1.0	23	20
chlordane, (alpha-chlordane)	5.0	5.2	8.9	104
chlordane, (gamma-chlordane)	5.0	5.1	8.0	102
chlordane, (trans-nonachlor)	5.0	5.6	7.4	111
chlorneb	5.0	5.2	3.0	105
chlorobenzilate	5.0	5.7	4.4	114
2-chlorobiphenyl	5.0	5.8	5.4	115
chlorpropham	5.0	6.3	4.9	127
chlorpyrifos	5.0	5.3	7.2	107
chlorthalonil	5.0	5.4	9.9	108
chrysene	5.0	5.5	3.9	110

TABLE 8. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN TAP WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER (CONTINUED)

Compound	True Conc.	Mean	% RSD	% REC
cyanazine	5.0	6.1	13	122
cycloate	5.0	5.6	1.5	112
DCPA	5.0	5.4	5.0	107
4,4'-DDD	5.0	5.3	6.5	105
4,4'-DDE	5.0	5.2	6.6	104
4,4'-DDT	5.0	5.6	9.6	111
diazinon	5.0	4.9	8.7	98
dibenz[a,h]anthracene	5.0	5.9	7.5	118
di-n-butylphthalate	5.0	6.2	4.6	124
2,3-dichlorobiphenyl	5.0	5.3	7.4	106
dichlorvos	5.0	2.8	7.3	56
dieldrin	5.0	5.3	7.2	105
di(2-ethylhexyl)adipate	5.0	6.7	10	134
di(2-ethylhexyl)phthalate	5.0	6.5	6.6	130
diethylphthalate	5.0	6.4	7.4	127
dimethylphthalate	5.0	5.8	7.1	116
2,4-dinitrotoluene	5.0	4.2	8.7	84
2,6-dinitrotoluene	5.0	4.1	8.5	82
diphenamid	5.0	5.2	7.7	104
disulfoton	5.0	2.5	33	50
disulfoton sulfone	5.0	5.5	7.4	110
disulfoton sulfoxide	5.0	9.4	11	188
endosulfan I	5.0	5.5	11	109
endosulfan II	5.0	5.3	9.6	106
endosulfan sulfate	5.0	5.3	7.8	106
endrin	5.0	6.1	3.9	121
endrin aldehyde	5.0	5.1	9.1	102
EPTC	5.0	5.1	2.1	102
ethoprop	5.0	6.3	4.2	125
etridiazole	5.0	5.8	7.5	117
fenamiphos	5.0	5.9	22	119
fenarimol	5.0	7.1	3.3	141
fluorene	5.0	5.7	5.2	114
fluridone	5.0	6.2	9.0	125
HCH, alpha	5.0	5.9	2.6	118

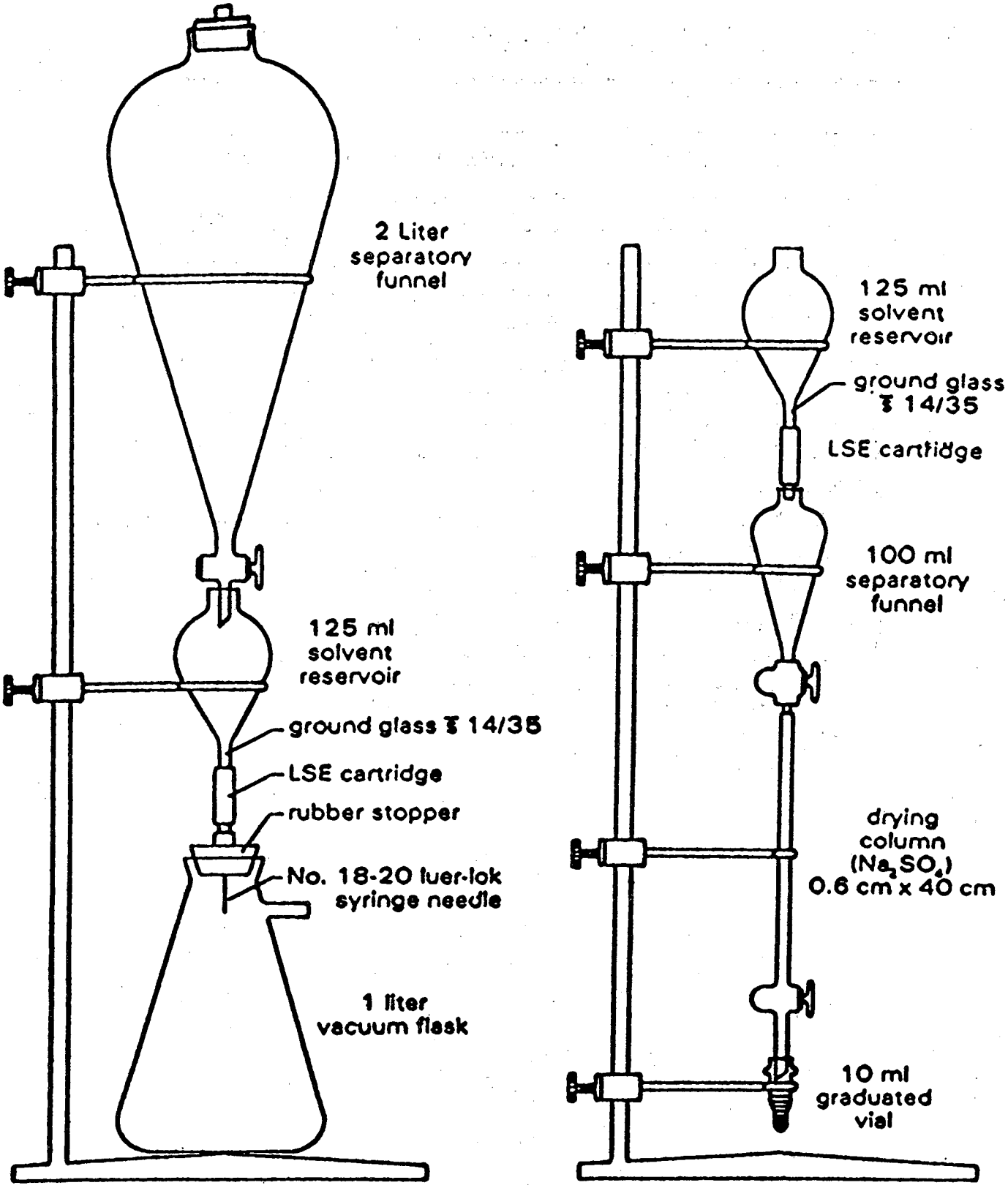
TABLE 8. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN TAP WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER (CONTINUED)

Compound	True Conc.	Mean	% RSD	% REC
HCH, beta	5.0	5.3	8.4	106
HCH, delta	5.0	5.3	5.2	106
HCH, gamma (Lindane)	5.0	5.3	6.9	107
heptachlor	5.0	4.7	8.7	93
heptachlor epoxide	5.0	5.2	7.7	105
2,2',3,3',4,4',6-heptachlorobiphenyl	5.0	5.1	6.9	103
hexachlorobenzene	5.0	4.6	7.4	93
2,2',4,4',5,6'-hexachlorobiphenyl	5.0	5.6	8.1	112
hexachlorocyclopentadiene	5.0	6.0	4.8	120
hexazinone	5.0	6.9	6.3	138
indeno[1,2,3-cd]pyrene	5.0	6.8	7.7	135
isophorone	5.0	4.9	12	99
methoxychlor	5.0	5.6	4.9	112
methyl paraoxon	5.0	5.6	11	111
metolachlor	5.0	5.6	7.7	111
metribuzin	5.0	2.1	5.8	42
mevinphos	5.0	3.3	1.6	67
MGK 264 - isomer a	3.3	3.6	6.2	107
MGK 264 - isomer b	1.7	1.8	7.6	110
molinate	5.0	5.5	1.5	110
napropamide	5.0	5.3	8.9	106
norflurazon	5.0	6.7	7.2	135
2,2',3,3',4,5',6,6'-octaclorobiphenyl	5.0	4.9	6.9	97
pebulate	5.0	5.3	3.1	106
2,2',3',4,6-pentachlorobiphenyl	5.0	5.3	8.1	107
pentachlorophenol	20.	33	4.9	162
permethrin, cis	5.0	3.3	3.5	130
permethrin, trans	5.0	8.5	2.2	113
phenanthrene	5.0	5.5	4.0	109
prometona[a]	5.0	2.0	25	40
prometryn	5.0	4.5	4.3	89
pronamide	5.0	5.7	5.3	115
propachlor	5.0	6.2	4.0	124
propazine	5.0	5.6	4.9	113
pyrene	5.0	5.2	6.7	104

TABLE 8. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN TAP WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER (CONTINUED)

Compound	True Conc.	Mean	% RSD	% REC
simazine	5.0	6.0	9.0	120
simetryn	5.0	3.9	7.0	78
stirofos	5.0	6.1	12	121
tebuthiuron	5.0	6.5	9.7	130
terbacil	5.0	4.0	5.5	79
terbufos	5.0	4.5	8.4	90
terbutryn	5.0	4.3	6.5	86
2,2',4,4'-tetrachlorobiphenyl	5.0	5.3	4.3	106
toxaphene	ND	ND	ND	ND
triademefon	5.0	6.0	12	121
2,4,5-trichlorobiphenyl	5.0	5.2	5.1	103
tricyclazole	5.0	4.8	5.2	96
trifluralin	5.0	5.9	7.8	119
vernolate	5.0	5.4	3.3	108

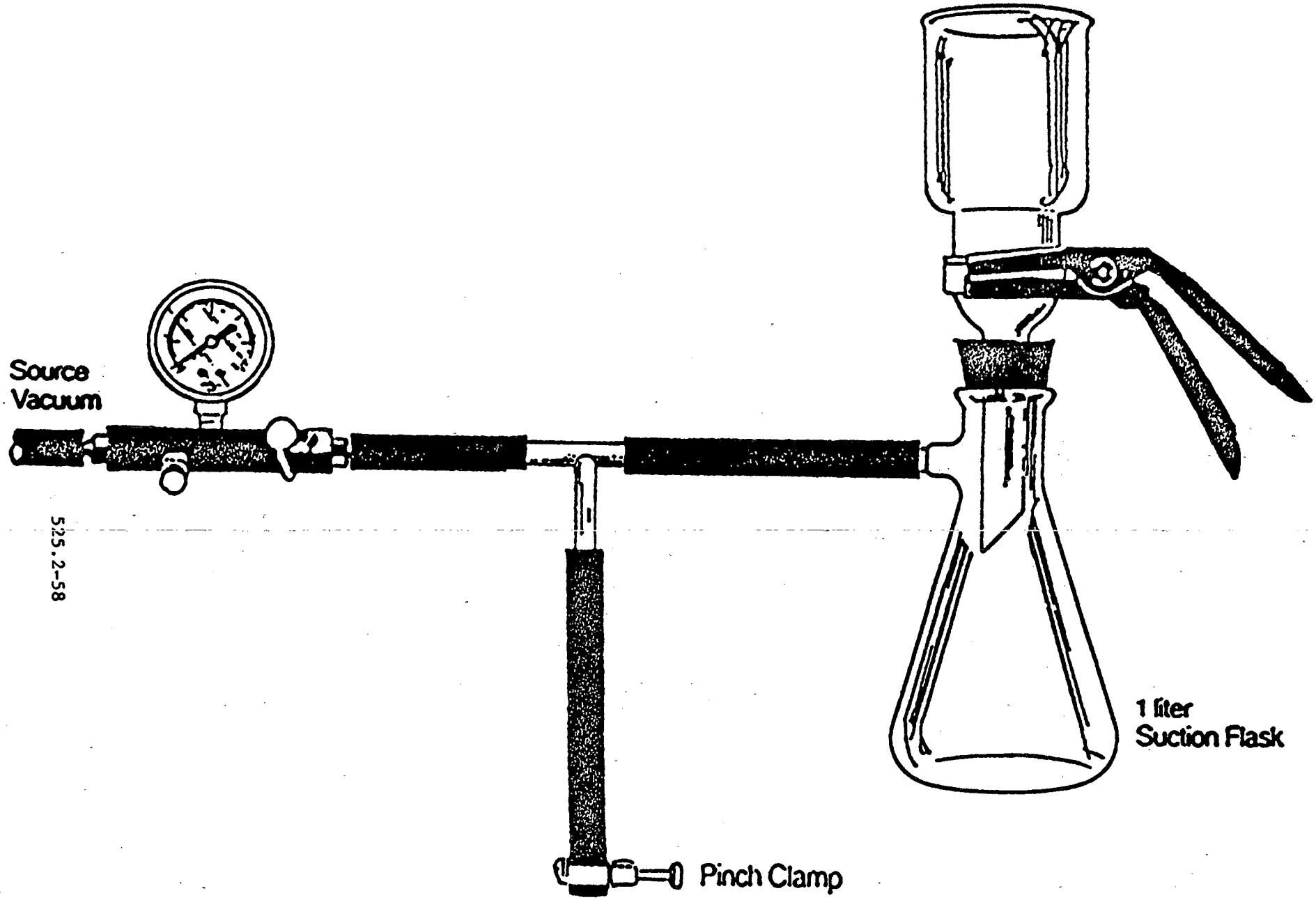
* Data from samples extracted at pH 2 - for accurate determination of this analyte, a separate sample must be extracted at ambient pH.



A. Extraction apparatus

B. Elution apparatus

FIGURE 1. CARTRIDGE EXTRACTION APPARATUS


Source
Vacuum
1 liter
Suction Flask
Pinch Clamp

METHOD 531.1. MEASUREMENT OF N-METHYLCARBAMOYLOXIMES AND N-METHYLCARBAMATES IN WATER BY DIRECT AQUEOUS INJECTION HPLC WITH POST COLUMN DERIVATIZATION

Revision 3.1

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D.L. Foerst - Method 531, Revision 1.0 (1985)

T. Engel (Battelle Columbus Laboratories) - National Pesticide Survey Method 5, Revision 2.0 (1987)

R.L. Graves - Method 531.1, Revision 3.0 (1989)

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METHOD 531.1

MEASUREMENT OF N-METHYLCARBAMOYLOXIMES AND N-METHYLCARBAMATES IN WATER BY DIRECT AQUEOUS INJECTION HPLC WITH POST COLUMN DERIVATIZATION

1. SCOPE AND APPLICATION

1.1 This is a high performance liquid chromatographic (HPLC) method applicable to the determinations of certain N-methylcarbamoyloximes and N-methylcarbamates in ground water and finished drinking water. The following compounds can be determined using this method:

Analyte	Chemical Abstract Services Registry Number
Aldicarb	116-06-3
Aldicarb sulfone	1646-88-4
Aldicarb sulfoxide	1646-87-3
Baygon	114-26-1
Carbaryl	63-25-2
Carbofuran	1563-66-2
3-Hydroxycarbofuran	16655-82-6
Methiocarb	2032-65-7
Methomyl	16752-77-5
Oxamyl	23135-22-0

1.2 This method has been validated in a single laboratory and estimated detection limits (EDLs) and method detection limits (MDLS) have been determined for the analytes above. Observed detection limits may vary between ground waters, depending upon the nature of interferences in the sample matrix and the specific instrumentation used.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of liquid chromatography and in the interpretation of liquid chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Sect. 9.3.

1.4 When this method is used to analyze unfamiliar samples for any or all of the analytes above, analyte identifications should be confirmed by at least one additional qualitative technique (1).

2. SUMMARY OF METHOD

2.1 The water sample is filtered and a 400-μL aliquot is injected into a reverse phase HPLC column. Separation of the analytes is achieved using gradient elution chromatography. After elution from the HPLC column, the analytes are hydrolyzed with 0.05 N sodium hydroxide (NaOH) at 95°C. The methyl amine formed during hydrolysis is

reacted with o-phthalaldehyde (OPA) and 2-mercaptoethanol to form a highly fluorescent derivative which is detected by a fluorescence detector (2). Analytes are quantitated using procedural standard calibration (Sect. 3.14)

3. DEFINITIONS

3.1 INTERNAL STANDARD -- A pure analyte(s) added to a solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same solution. The internal standard must be an analyte that is not a sample component.

3.2 SURROGATE ANALYTE -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction and is measured with the same procedures used to measure other sample components. The purpose of a surrogate analyte is to monitor method performance with each sample.

3.3 LABORATORY DUPLICATES (LD1 and LD2) -- Two sample aliquots taken in the analytical laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.4 FIELD DUPLICATES (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.5 LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.6 FIELD REAGENT BLANK (FRB) -- Reagent water placed in a sample container in the laboratory and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.7 LABORATORY PERFORMANCE CHECK SOLUTION (LPC) -- A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.8 LABORATORY FORTIFIED BLANK (LFB) -- An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

3.9 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.10 STOCK STANDARD SOLUTION -- A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a single analyte prepared in the laboratory with an assayed reference compound. Stock standard solutions are used to prepare primary dilution standards.

3.11 PRIMARY DILUTION STANDARD SOLUTION -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.12 CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution and stock standard solutions of the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.13 QUALITY CONTROL SAMPLE (QCS) -- A sample matrix containing method analytes or a solution of method analytes in a water miscible solvent which is used to fortify reagent water or environmental samples. The QCS is obtained from a source external to the laboratory, and is used to check laboratory performance with externally prepared test materials.

3.14 PROCEDURAL STANDARD CALIBRATION -- A calibration method where aqueous calibration standards are prepared and processed (e.g. purged, extracted, and/or derivatized) in <u>exactly</u> the same manner as a sample. All steps in the process from addition of sampling preservatives through instrumental analyses are included in the calibration. Using procedural standard calibration compensates for any inefficiencies in the processing procedure.

4. INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing apparatus that lead

to discrete artifacts or elevated baselines in liquid chromatograms. Specific sources of contamination have not been identified. All reagents and apparatus must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Sect. 9.2.

4.1.1 Glassware must be scrupulously cleaned.(3) Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot water and detergent and thorough rinsing with tap and reagent water. Drain dry, and heat in an oven or muffle furnace at 400°C for 1 hour. Do not heat volumetric glassware. Thermally stable materials might not be eliminated by this treatment. Thorough rinsing with acetone may be substituted for the heating. After drying and cooling, seal and store glassware in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

4.1.2 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. WARNING: When a solvent is purified, stabilizers added by the manufacturer are removed, thus potentially making the solvent hazardous. Also, when a solvent is purified, preservatives added by the manufacturer are removed, thus potentially reducing the shelf-life.

4.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. A preventive technique is between-sample rinsing of the sample syringe and filter holder with two portions of reagent water. After analysis of a sample containing high concentrations of analytes, one or more laboratory reagent blanks should be analyzed.

4.3 Matrix interference may be caused by contaminants that are present in the sample. The extent of matrix interference will vary considerably from source to source, depending upon the water sampled. Analyte identifications must be confirmed. Positive identification may be made by the use of an alternative detector which operates on a chemical/physical principle different from that originally used; e.g., mass spectrometry, or the use of a second chromatography column. A suggested alternative column is described in Sect. 6.6.3.

5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound must be treated as a potential health hazard. Accordingly, exposure to these chemicals must be reduced to the lowest possible level. 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 also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified (4-6) for the information of the analyst.

5.2 WARNING: When a solvent is purified, stabilizers added by the manufacturer are removed, thus potentially making the solvent hazardous.

6. <u>EQUIPMENT AND SUPPLIES</u> (All specifications are suggested. Catalog numbers are included for illustration only.)

6.1 SAMPLING EQUIPMENT

6.1.1 Grab sample bottle -- 60-mL screw cap vials (Pierce No. 13075 or equivalent) and caps equipped with a PTFE-faced silicone septa (Pierce No. 12722 or equivalent). Prior to use, wash vials and septa as described in Sect. 4.1.1.

6.2 BALANCE -- Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.3 FILTRATION APPARATUS

6.3.1 Macrofiltration -- To filter derivatization solutions and mobile phases used in HPLC. Recommend using 47 mm filters (Millipore Type HA, 0.45 μm for water and Millipore Type FH, 0.5 μm for organics or equivalent).

6.3.2 Microfiltration -- To filter samples prior to HPLC analysis. Use 13 mm filter holder (Millipore stainless steel XX300/200 or equivalent), and 13 mm diameter 0.2 μm polyester filters (Nuclepore 180406 or equivalent).

6.4 SYRINGES AND SYRINGE VALVES

6.4.1 Hypodermic syringe -- 10-mL glass, with Luer-Lok tip.

6.4.2 Syringe valve -- 3-way (Hamilton HV3-3 or equivalent).

6.4.3 Syringe needle -- 7 to 10-cm long, 17-gauge, blunt tip.

6.4.4 Micro syringes -- various sizes.

6.5 MISCELLANEOUS

6.5.1 Solution storage bottles -- Amber glass, 10- to 15-mL capacity with TFE-fluorocarbon-lined screw cap.

6.5.2 Helium, for degassing solutions and solvents.

6.6 HIGH PERFORMANCE LIQUID CHROMATOGRAPH (HPLC)

6.6.1 HPLC system capable of injecting 200- to 400-µL aliquots, and performing binary linear gradients at a constant flow rate. A data system is recommended for measuring peak areas. Table 1 lists retention times observed for method analytes using the columns and analytical conditions described below.

6.6.2 Column 1 (Primary column) -- 150 mm long x 3.9 mm I.D. stainless steel packed with 4 µm NovaPak C18. Mobil Phase is established at 10:90 methanol:water, hold 2 min., then program as a linear gradient to 80:20 methanol:water in 25 min. Alternative columns may be used in accordance with the provisions described in Sect. 9.4.

6.6.3 Column 2 (Alternative column)* -- 250 mm long x 4.6 mm I.D. stainless steel packed with 5 µm Beckman Ultrasphere ODS. Mobile phase is established at 1.0 mL/min as a linear gradient from 15:85 methanol:water to 100 % methanol in 32 min. Data presented in this method were obtained using this column. * Newer manufactured columns have not been able to resolve aldicarb sulfone from oxamyl.

6.6.4 Column 3 (Alternative column) -- 250 mm long x 4.6 mm I.D. stainless steel packed with 5 µm Supelco LC-1. Mobile phase is established at 1.0 mL/min as a linear gradient from 15:85 methanol:water to 100 % methanol in 32 min.

6.6.5 Post column reactor -- Capable of mixing reagents into the mobile phase. Reactor should be constructed using PTFE tubing and equipped with pumps to deliver 0.1 to 1.0 mL/min of each reagent; mixing tees; and two 1.0-mL delay coils, one thermostated at 95°C (ABI URS 051 and URA 100 or equivalent).

6.6.6 Fluorescence detector -- Capable of excitation at 330 nm (nominal) and detection of emission energies greater than 418 nm. A Schoffel Model 970 fluorescence detector was used to generate the validation data presented in this method.

7. **REAGENTS AND STANDARDS** -- WARNING: When a solvent is purified, stabilizers added by the manufacturer are removed, thus potentially making the solvent hazardous. Also, when a solvent is purified, preservatives added by the manufacturer are removed, thus potentially reducing the shelf-life.

7.1 REAGENT WATER -- Reagent water is defined as water that is reasonably free of contamination that would prevent the determination of any analyte of interest. Reagent water used to generate the validation data in this method was distilled water obtained from the Magnetic Springs Water Co., 1801 Lone Eagle St., Columbus, Ohio 43228.

7.2 METHANOL -- Distilled-in-glass quality or equivalent.

7.3 HPLC MOBILE PHASE

7.3.1 Water -- HPLC grade (available from Burdick and Jackson).

7.3.2 Methanol -- HPLC grade. Filter and degas with helium before use.

7.4 POST COLUMN DERIVATIZATION SOLUTIONS

7.4.1 Sodium hydroxide, 0.05 N -- Dissolve 2.0 g of sodium hydroxide (NaOH) in reagent water. Dilute to 1.0 L with reagent water. Filter and degas with helium just before use.

7.4.2 2-Mercaptoethanol (1+1) -- Mix 10.0 mL of 2-mercaptoethanol and 10.0 mL of acetonitrile. Cap. Store in hood (CAUTION -- stench).

7.4.3 Sodium borate (0.05 N) -- Dissolve 19.1 g of sodium borate ($Na_2B_4O_7 \cdot 10H_2O$) in reagent water. Dilute to 1.0 L with reagent water. The sodium borate will completely dissolve at room temperature if prepared a day before use.

7.4.4 OPA reaction solution -- Dissolve 100 ± 10 mg of o-phthalaldehyde (mp 55-58°C) in 10 mL of methanol. Add to 1.0 L of 0.05 N sodium borate. Mix, filter, and degas with helium. Add 100 µL of 2-mercaptoethanol (1+1) and mix. Make up fresh solution daily.

7.5 MONOCHLOROACETIC ACID BUFFER (pH3) -- Prepare by mixing 156 mL of 2.5 M monochloroacetic acid and 100 mL 2.5 M potassium acetate.

7.6 4-BROMO-3,5-DIMETHYLPHENYL N-METHYLCARBAMATE (BDMC) -- 98% purity, for use as internal standard (available from Aldrich Chemical Co.).

7.7 STOCK STANDARD SOLUTIONS (1.00 µg/µL) -- Stock standard solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedure:

7.7.1 Prepare stock standard solutions by accurately weighing approximately 0.0100 g of pure material. Dissolve the material in methanol and dilute to volume in a 10-mL volumetric flask. 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. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.7.2 Transfer the stock standard solutions into TFE-fluorocarbon-sealed screw cap vials. Store at room temperature and protect from light.

7.7.3 Stock standard solutions should be replaced after two months or sooner if comparison with laboratory fortified blanks, or QC samples indicate a problem.

7.8 INTERNAL STANDARD SOLUTION -- Prepare an internal standard fortification solution by accurately weighing approximately 0.0010 g of pure BDMC. Dissolve the BDMC in methanol and dilute to volume in a 10-mL volumetric flask. Transfer the internal standard fortification solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Addition of 5 µL of the internal standard fortification solution to 50 mL of sample results in a final internal standard concentration of 10 µg/L. Solution should be replaced when ongoing QC (Sect. 9) indicates a problem. Note: BDMC has been shown to be an effective internal standard for the method analytes, but other compounds may be used, if the quality control requirements in Sect. 9 are met.

7.9 LABORATORY PERFORMANCE CHECK SOLUTION -- Prepare concentrate by adding 20 µL of the 3-hydroxycarbofuran stock standard solution, 1.0 mL of the aldicarb sulfoxide stock standard solution, 200 µL of the methiocarb stock standard solution, and 1 mL of the internal standard fortification solution to a 10-mL volumetric flask. Dilute to volume with methanol. Thoroughly mix concentrate. Prepare check solution by placing 100 µL of the concentrate solution into a 100-mL volumetric flask. Dilute to volume with buffered reagent water. Transfer to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Solution should be replaced when ongoing QC (Sect. 9) indicates a problem.

8. SAMPLE COLLECTION, PRESERVATION AND HANDLING

8.1 Grab samples must be collected in glass containers. Conventional sampling practices (8) should be followed; however, the bottle must not be prerinsed with sample before collection.

8.2 SAMPLE PRESERVATION/PH ADJUSTMENT -- Oxamyl, 3-hydroxycarbofuran, aldicarb sulfoxide, and carbaryl can all degrade quickly in neutral and basic waters held at room temperature. (6,7) This short term degradation is of concern during the time samples are being shipped and the time processed samples are held at room temperature in autosampler trays. Samples targeted for the analysis of these three analytes must be preserved at pH 3. The pH adjustment also minimizes analyte biodegradation.

8.2.1 Add 1.8 mL of monochloroacetic acid buffer to the 60-mL sample bottle. Add buffer to the sample bottle at the sampling site or in the laboratory before shipping to the sampling site.

8.2.2 If residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample to the sample bottle prior to collecting the sample.

8.2.3 After sample is collected in bottle containing buffer, seal the sample bottle and shake vigorously for 1 min.

8.2.4 Samples must be iced or refrigerated at 4°C from the time of collection until analysis is begun. Although preservation results of up to 28 days indicate method analytes are not labile in water samples when sample pH is adjusted to 3 or less, and samples are shipped and stored at 4°C, analyte lability may be affected by the matrix. Therefore, the analyst should verify that the preservation technique is applicable to the samples under study.

9. QUALITY CONTROL

9.1 Minimum quality control (QC) requirements are initial demonstration of laboratory capability, monitoring internal standard peak area or height in each sample and blank (when internal standard calibration procedures are being employed), analysis of laboratory reagent blanks, laboratory fortified samples, laboratory fortified blanks and QC samples. A MDL for each analyte must also be determined.

9.2 LABORATORY REAGENT BLANKS. Before processing any samples, the analyst must demonstrate that all glassware and reagent interferences are under control. Each time a set of samples is extracted or reagents are changed, a laboratory reagent blank (LRB) must be analyzed. If within the retention time window of any analyte of interest the LRB produces a peak that would prevent the determination of that analyte, determine the source of contamination and eliminate the interference before processing samples.

9.3 INITIAL DEMONSTRATION OF CAPABILITY.

9.3.1 Select a representative concentration, about 10 times EDL, or a concentration that represents a medium concentration calibration standard for each analyte. Prepare a primary dilution standard (in methanol) containing each analyte at 1000 times selected concentration. With a syringe, add 50 µL of the concentrate to each of four to seven 50-mL aliquots of reagent water, and analyze each aliquot according to procedures beginning in Sect. 11.

9.3.2 For each analyte the recovery value for all of these samples must fall in the range of ± 20% of the fortified amount, and the RSD of the measurements must be 20% or less. For those compounds that meet the acceptance criteria, performance is judged acceptable and sample analysis may begin. For those compounds that fail these criteria, this procedure must be

repeated using four samples until satisfactory performance has been demonstrated.

9.3.3 To determine the MDL, analyze a minimum of 7 LFBs prepared at a low concentration. Use the concentrations in Table 3 as a guide, or use calibration data to estimate a concentration that will yield a peak with a signal to noise ratio of approximately 5. Analyze the 7 replicates as described in Sect.11, and on a schedule that results in the analyses being conducted over several days. Calculate the mean accuracy and standard deviation for each analyte. Calculate the MDL using the equation given in Table 3.

9.3.4 The initial demonstration of capability is used primarily to preclude a laboratory from analyzing unknown samples via a new, unfamiliar method prior to obtaining some experience with it. It is expected that as laboratory personnel gain experience with this method the quality of data will improve beyond those required here.

9.4 The analyst is permitted to modify HPLC columns, HPLC conditions, and internal standards to improve separations or lower analytical costs. Each time such method modifications are made, the analyst must repeat the procedures in Sect. 9.3.

9.5 ASSESSING THE INTERNAL STANDARD

9.5.1 When using the internal standard calibration procedure, the analyst must monitor the IS response (peak area or peak height) of all samples during each analysis day. The IS response for any sample chromatogram should not deviate from the daily calibration check standard's IS response by more than 30%.

9.5.2 If >30% deviation occurs with an individual extract, optimize instrument performance and inject a second aliquot.

9.5.2.1 If the reinjected aliquot produces an acceptable internal standard response, report results for that aliquot.

9.5.2.2 If a deviation of greater than 30% is obtained for the reinjected extract, analysis of the sample should be repeated beginning with Sect. 11, provided a duplicate sample is still available. Otherwise, report results obtained from the reinjected extract, but annotate as suspect.

9.5.3 If consecutive samples fail the IS response acceptance criterion, immediately analyze a calibration check standard.

9.5.3.1 If the check standard provides a response for the IS within 20% of the predicted value, then follow procedures itemized in Sect. 9.5.2 for each sample failing the IS response criterion.

9.5.3.2 If the check standard provides a response for the IS which deviates more than 20% of the predicted value, then the analyst must recalibrate, as specified in Sect. 10.

9.6 ASSESSING LABORATORY PERFORMANCE - LABORATORY FORTIFIED BLANKS

9.6.1 The laboratory must analyze at least one laboratory fortified blank (LFB) sample with every 20 samples or one per sample set (all samples analyzed within a 24-h period) whichever is greater. The fortification concentration of each analyte in the LFB should be 10 times EDL or a concentration in the middle of the calibration range. Calculate accuracy as percent recovery (X_i). If the recovery of any analyte falls outside the control limits (see Sect. 9.6.2), that analyte is judged out of control, and the source of the problem must be identified and resolved before continuing analyses.

9.6.2 Until sufficient data become available from within their own laboratory, usually a minimum of results from 20 to 30 analyses, the laboratory should assess laboratory performance against the control limits in Sect. 9.3.2. When sufficient internal performance data becomes available, develop control limits from the mean percent recovery (X) and standard deviation (S) of the percent recovery. These data are used to establish upper and lower control limits as follows:

$$\text{UPPER CONTROL LIMIT} = X + 3S$$
$$\text{LOWER CONTROL LIMIT} = X - 3S$$

After each five to ten new recovery measurements, new control limits should be calculated using only the most recent 20-30 data points. These calculated control limits should <u>not</u> exceed those established in Sect. 9.3.2.

9.6.3 If acceptable accuracy and method detection limits cannot be achieved, the problem must be located and corrected before further samples are analyzed. Data from all field samples analyzed since the last acceptable LFB should be considered suspect, and duplicate samples should be analyzed, if they are available, after the problem has been corrected. LFB results should be added to the on-going control charts to document data quality.

Since the calibration check sample in Sect. 10.2.4 and 10.3.3 and the LFB are made the same way and since procedural

standards are used, the sample analyzed here may also be used as a calibration check as described in those sections.

9.6.4 It is recommended that the laboratory periodically determine and document its detection limit capabilities for analytes of interest.

9.6.5 At least quarterly, analyze a QC sample from an outside source.

9.7 ASSESSING ANALYTE RECOVERY - LABORATORY FORTIFIED SAMPLE MATRIX

9.7.1 The laboratory must add a known concentration to a minimum of 5% of the routine samples or one sample per set, whichever is greater. The concentration should not be less then the background concentration of the sample selected for fortification. Ideally, the concentration should be the same as that used for the laboratory fortified blank (Sect. 9.6). Over time, samples from all routine sample sources should be fortified.

9.7.2 Calculate the percent recovery, P, of the concentration for each analyte, after correcting the analytical result, X, from the fortified sample for the background concentration, b, measured in the unfortified sample, i.e.,:

$$P = 100\ (X - b)\ /\ \text{fortifying concentration},$$

and compare these values to control limits appropriate for reagent water data collected in the same fashion. The value for P must fall in the range of 65%-135% of the fortified amount.

9.7.3 If the recovery of any such analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control (Sect. 9.6), the recovery problem encountered with the dosed sample is judged to be matrix related, not system related. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

9.8 ASSESSING INSTRUMENT SYSTEM - LABORATORY PERFORMANCE CHECK SAMPLE - Instrument performance should be monitored on a daily basis by analysis of the LPC sample. The LPC sample contains compounds designed to monitor instrument sensitivity, column performance (primary column) and chromatographic performance. LPC sample components and performance criteria are listed in Table 4. Inability to demonstrate acceptable instrument performance indicates the need for reevaluation of the instrument system. The sensitivity requirements are set based on the EDLs published in this method. If laboratory EDLs differ from those listed in this method,

concentrations of the LPC standard compounds must be adjusted to be compatible with the laboratory EDLs.

9.9 The laboratory may adopt additional quality control 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. For example, field or laboratory duplicates may be analyzed to assess the precision of the environmental measurements or field reagent blanks may be used to assess contamination of samples under site conditions, transportation and storage.

10. CALIBRATION AND STANDARDIZATION

10.1 Establish HPLC operating parameters equivalent to those indicated in Sect. 6.6. The HPLC system may be calibrated using either the internal standard technique (Sect. 10.2) or the external standard technique (Sect. 10.3).

10.2 INTERNAL STANDARD CALIBRATION PROCEDURE. The analyst must select one or more internal standards similar in analytical behavior to the analytes of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. BDMC has been identified as a suitable internal standard.

10.2.1 Prepare calibration standards at a minimum of three (recommend five) concentration levels for each analyte of interest by adding volumes of one or more of the stock standards to a volumetric flask. Guidance on the number of standards is as follows: A minimum of three calibration standards are required to calibrate a range of a factor of 20 in concentration. For a factor of 50 use at least four standards, and for a factor of 100 at least five standards. The lowest standard should represent analyte concentrations near, but above, their respective MDLs. The remaining standards should bracket the analyte concentrations expected in the sample, or should define the working range of the detector. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with buffered reagent water. To prepare buffered reagent water, add 10 mL of 1.0 M monochloroacetic acid buffer to 1 L of reagent water.

10.2.2 Analyze each calibration standard according to the procedure in Sect. 11. Tabulate peak height or area responses against concentration for each compound and internal standard. Calculate response factors (RF) for each analyte and surrogate using Equation 1.

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)} \quad \text{Equation 1}$$

where:

A_s = Response for the analyte to be measured.
A_{is} = Response for the internal standard.
C_{is} = Concentration of the internal standard $\mu g/L$).
C_s = Concentration of the analyte to be measured $\mu g/L$).

10.2.3 If the RF value over the working range is constant (20% RSD or less), the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios (A_s/A_{is}) vs. C_s.

10.2.4 The working RF or calibration curve must be verified on each working day by the measurement of a minimum of two calibration check standards, one at the beginning and one at the end of the analysis day. These check standards should be at two different concentration levels to verify the concentration curve. For extended periods of analysis (greater than 8 hr), it is strongly recommended that check standards be interspersed with samples at regular intervals during the course of the analyses. If the response for any analyte varies from the predicted response by more than ±20%, the test must be repeated using a fresh calibration standard. If the results still do not agree, generate a new calibration curve.

10.3 EXTERNAL STANDARD CALIBRATION PROCEDURE

10.3.1 Prepare calibration standards as described in Sect 10.2.1 omitting the use of an internal standard.

10.3.2 Starting with the standard of lowest concentration, analyze each calibration standard according to Sect. 11.2 and tabulate responses (peak height or area) versus the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (<20% relative standard deviation), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

10.3.3 The working calibration curve or calibration factor must be verified on each working day as described in Sect. 10.2.4.

10.4 Verify calibration standards periodically, recommend at least quarterly, by analyzing a standard prepared from reference material obtained from an independent source. Results from these analyses must be within the limits used to routinely check calibration (Sect. 10.2.4).

11. PROCEDURE

11.1 PH ADJUSTMENT AND FILTRATION

11.1.1 Add preservative to any samples (LFBs, LRBs, or calibration standards) not previously preserved (Sect. 8). Adjust the pH of the sample or standard to pH 3 ± 0.2 by adding 1.5 mL of 2.5 M monochloroacetic acid buffer to each 50 mL of sample. This step should not be necessary if sample pH was adjusted during sample collection as a preservation precaution. Fill a 50-mL volumetric flask to the mark with the sample. Add 5 µL of the internal standard fortification solution (if the internal standard calibration procedure is being employed) and mix by inverting the flask several times.

11.1.2 Affix the three-way valve to a 10-mL syringe. Place a clean filter in the filter holder and affix the filter holder and the 7- to 10-cm syringe needle to the syringe valve. Rinse the needle and syringe with reagent water. Prewet the filter by passing 5 mL of reagent water through the filter. Empty the syringe and check for leaks. Draw 10 mL of sample into the syringe and expel through the filter. Draw another 10 mL of sample into the syringe, expel through the filter, and collect the last 5 mL for analysis. Rinse the syringe with reagent water. Discard the filter.

11.2 LIQUID CHROMATOGRAPHY

11.2.1 Sect. 6.6 summarizes the recommended operating conditions for the liquid chromatograph. Table 1 lists retention times observed using this method. Other HPLC columns or chromatographic conditions may be used if the requirements of Sect. 9 are met.

11.2.2 Calibrate or verify the system calibration daily as described in Sect. 10. The standards and samples must be in pH 3 buffered water.

11.2.3 Inject 400 µL of the sample. Record the volume injected and the resulting peak size in area units.

11.2.4 If the response for the peak exceeds the working range of the system, dilute the sample with pH 3 buffered reagent water and reanalyze.

11.3 IDENTIFICATION OF ANALYTES

11.3.1 Identify a sample component by comparison of its retention time to the retention time of a reference chromatogram. If the retention time of an unknown compound corresponds, within limits, to the retention time of a standard compound, then identification is considered positive.

11.3.2 The width of the retention time window used to make identifications should be based upon 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.

11.3.3 Identification requires expert judgement when sample components are not resolved chromatographically. When peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), or any time doubt exists over the identification of a peak on a chromatogram, appropriate alternate techniques, to help confirm peak identification, need to be employed. For example, more positive identification may be made by the use of an alternative detector which operates on a chemical/physical principle different from that originally used; e.g., mass spectrometry (1), or the use of a second chromatography column. A suggested alternative column is described in Sect. 6.6.3.

12. CALCULATIONS

Determine the concentration of individual compounds in the sample using the following equation:

$$C_x = \frac{(A_x)}{(A_s)} \frac{(Q_s)}{(RF)},$$

where: C_x = analyte concentration in micrograms per liter;
A_x = response of the sample analyte;
A_s = response of the standard (either internal or external), in units consistent with those used for the analyte response;

RF = response factor (with an external standard, RF = 1, because the standard is the same compound as the measured analyte; with an internal standard RF is a unitless value);

Q_s = concentration of internal standard present or concentration of external standard that produced As, in micrograms per liter.

Use the multi-point calibration established in Section 10 for all calculations. Do not use the daily calibration verification data to quantitate analytes in samples.

13. METHOD PERFORMANCE

13.1 In a single laboratory, analyte recoveries from reagent water were used to determine analyte MDLs and EDLs and demonstrate method range. Analyte recoveries and standard deviation about the percent recoveries at one concentration are given in Table 3.

13.2 In a single laboratory, analyte recoveries from two standard synthetic ground waters were determined at one concentration level. Results were used to demonstrate applicability of the method to different ground water matrices. Analyte recoveries from the two synthetic matrices are given in Table 2.

14. REFERENCES

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*17. TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. RETENTION TIMES FOR METHOD ANALYTES

Analyte	Retention Time[a] (minutes) Primary[1]	Alternative[2]	Alternative[3]
Aldicarb sulfoxide	6.80	15.0	17.5
Aldicarb sulfone	7.77	15.2	12.2
Oxamyl	8.20	17.4	14.6
Methomyl	8.94	18.4	14.8
3-Hydroxycarbofuran	13.65	23.3	19
Aldicarb	16.35	27.0	21.4
Baygon	18.86	29.3	24.4
Carbofuran	19.17	29.6	23.4
Carbaryl	20.29	30.8	25.4
Methiocarb	24.74	34.9	28.6
BDMC	25.28	35.5	

[a] Columns and analytical conditions are described in Sect. 6.6.

(1) Waters NovaPak C18

(2) Beckman Ultrasphere ODS

(3) Supelco LC-1

TABLE 2. SINGLE LABORATORY ACCURACY AND PRECISION FOR ANALYTES FROM REAGENT WATER AND SYNTHETIC GROUND WATERS[a]

Analyte	Fortified Concentration µg/L	Reagent Water R[b]	Reagent Water S_R[c]	Synthetic Water 1[d] R	Synthetic Water 1[d] S_R	Synthetic Water 2[e] R	Synthetic Water 2[e] S_R
Aldicarb	5.0	115	3.5	106	3.2	102	8.2
Aldicarb sulfone	10.	101	4.0	98	3.9	95	9.5
Aldicarb sulfoxide	10.	97	4.9	105	4.2	94	10.3
Baygon	5.0	106	3.2	96	4.8	97	5.8
Carbaryl	10.	97	5.8	94	4.7	104	10.4
Carbofuran	7.5	102	5.1	102	3.1	100	7.0
3-Hydroxycarbofuran	10.	102	4.1	98	4.9	101	10.1
Methiocarb	20.	94	1.9	102	4.1	112	3.4
Methomyl	2.5	105	4.2	98	3.9	105	9.5
Oxamyl	10.	100	4.0	97	2.9	102	10.2

[a] Data corrected for amount detected in blank and represent the mean of 7-8 samples.

[b] R = Average percent recovery.

[c] S_R = Standard deviation of the percent recovery.

[d] Corrected for amount found in blank; Absopure Nature Artesian Spring Water Obtained from the Absopure Water Company in Plymouth, Michigan.

[e] Corrected for amount found in blank; reagent water fortified with fulvic acid at the 1 mg/L concentration level. A well-characterized fulvic acid, available from the International Humic Substances Society (associated with the United States Geological Survey in Denver, Colorado), was used.

TABLE 3. SINGLE LABORATORY ACCURACY, PRECISION, METHOD DETECTION LIMITS (MDLs), AND ESTIMATED DETECTION LIMITS (EDLs) FOR ANALYTES FROM REAGENT WATER

Analytes	Fortified µg/L	N[a]	Recovery %	RSD %	MDL[b] µg/L	EDL[c] µg/L
Aldicarb	1.0	8	107	7	0.22	1.0
Aldicarb sulfone	2.0	8	83	20	1.0	2.0
Aldicarb sulfoxide	2.0	8	47	21	0.59	2.0
Baygon	1.0	7	101	32	1.0	1.0
Carbaryl	2.0	8	97	23	1.3	2.0
Carbofuran	1.5	7	90	12	0.52	1.5
3-Hydroxycarbofuran	2.0	8	108	29	1.9	2.0
Methiocarb	4.0	8	82	19	1.9	4.0
Methomyl	0.50	7	102	18	0.29	0.50
Oxamyl	2.0	8	82	17	0.86	2.0

[a] N = Number of replicates

[b] $MDL = S\ t_{(n-1,1-alpha = 0.99)}$

where:

$t_{(n-1,1-alpha = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom

n = number of replicates

S = standard deviation of replicate analyses.

[c] EDL = estimated detection limit; defined as either MDL (Appendix B to 40 CFR Part 136 - Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11) or a level of compound in a sample yielding a peak in the final extract with signal-to-noise ratio of approximately 5, whichever value is higher.

TABLE 4. LABORATORY PERFORMANCE CHECK SOLUTION

Test	Analyte	Conc. Ng	Requirements
Sensitivity	3-Hydroxycarbofuran	2	Detection of analyte; S/N > 3
Chromatographic performance	Aldicarb sulfoxide	100	0.90 <PGF<1.1[a]
Column performance	Methiocarb	20	Resolution >1.0[b]
	4-Bromo-3,5-dimethylphenyl N-methylcarbamate (IS)	10	

[a] PGF = peak Gaussian factor. Calculated using the equation:

$$PGF = \frac{1.83 \times W(1/2)}{W(1/10)}$$

where W(1/2) is the peak width at half height in secs. and W(1/10) is the peak width in secs. at tenth height.

[b] Resolution between the two peaks as defined by the equation:

$$R = \frac{t}{W}$$

where t is the difference in elution times between the two peaks and W is the average peak width in secs., at the baseline, of the two peaks.

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METHOD 551.1 DETERMINATION OF CHLORINATION DISINFECTION BYPRODUCTS, CHLORINATED SOLVENTS, AND HALOGENATED PESTICIDES/ HERBICIDES IN DRINKING WATER BY LIQUID-LIQUID EXTRACTION AND GAS CHROMATOGRAPHY WITH ELECTRON-CAPTURE DETECTION

Revision 1.0

J.W. Hodgeson, A.L. Cohen - Method 551, (1990)

D.J. Munch (USEPA, Office of Water) and D.P. Hautman (International Consultants, Inc.) - Method 551.1, (1995)

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METHOD 551.1

DETERMINATION OF CHLORINATION DISINFECTION BYPRODUCTS, CHLORINATED SOLVENTS, AND HALOGENATED PESTICIDES/HERBICIDES IN DRINKING WATER BY LIQUID-LIQUID EXTRACTION AND GAS CHROMATOGRAPHY WITH ELECTRON-CAPTURE DETECTION

1. SCOPE AND APPLICATION

1.1 This method (1-9) is applicable to the determination of the following analytes in finished drinking water, drinking water during intermediate stages of treatment, and raw source water. The particular choice of analytes from this list should be a function of the specific project requirements.

	Analyte	CAS No.
Disinfection Byproducts (DBPs):		
Trihalomethanes	Chloroform	67-66-3
	Bromodichloromethane	75-27-4
	Bromoform	75-25-2
	Dibromochloromethane	124-48-1
Haloacetonitriles	Bromochloroacetonitrile	83463-62-1
	Dibromoacetonitrile	3252-43-5
	Dichloroacetonitrile	3018-12-0
	Trichloroacetonitrile	545-06-2
Other DBPs	Chloral Hydrate	75-87-6
	Chloropicrin	76-06-2
	1,1-Dichloro-2-propanone	513-88-2
	1,1,1-Trichloro-2-propanone	918-00-3
Chlorinated Solvents:		
	Carbon Tetrachloride	56-23-5
	1,2-Dibromo-3-chloropropane [DBCP]	96-12-8
	1,2-Dibromoethane [EDB]	106-93-4
	Tetrachloroethylene	127-18-4
	1,1,1-Trichloroethane	71-55-6
	1,1,2-Trichloroethane	79-00-5
	Trichloroethylene	79-01-6
	1,2,3-Trichloropropane	96-18-4
Pesticides/Herbicides:		
	Alachlor	15972-60-8
	Atrazine	1912-24-9
	Bromacil	314-40-9
	Cyanazine	21725-46-2
	Endrin	72-20-8
	Endrin Aldehyde	7421-93-4
	Endrin Ketone	53494-70-5
	Heptachlor	76-44-8
	Heptachlor Epoxide	1024-57-3
	Hexachlorobenzene	118-74-1

Hexachlorocyclopentadiene	77-47-4
Lindane (gamma-BHC)	58-89-9
Metolachlor	51218-45-2
Metribuzin	21087-64-9
Methoxychlor	72-43-5
Trifluralin	1582-09-8

1.2 This analyte list includes twelve commonly observed chlorination disinfection byproducts (3,4), eight commonly used chlorinated organic solvents and sixteen halogenated pesticides and herbicides.

1.3 This method is intended as a stand-alone procedure for either the analysis of only the trihalomethanes (THMs) or for all the chlorination disinfection by-products (DBPs) with the chlorinated organic solvents or as a procedure for the total analyte list. The dechlorination/preservation technique presented in section 8 details two different dechlorinating agents. Results for the THMs and the eight solvents may be obtained from the analysis of samples employing either dechlorinating agent. (Sect. 8.1.2)

1.4 After an analyte has been identified and quantitated in an unknown sample with the primary GC column (Sect. 6.9.2.1) qualitative confirmation of results is strongly recommended by gas chromatography/mass spectrometry (GC/MS) (10,11), or by GC analysis using a dissimilar column (Sect. 6.9.2.2).

1.5 The experimentally determined method detection limits (MDLs) (12) for the above listed analytes are provided in Tables 2 and 8. Actual MDL values will vary according to the particular matrix analyzed and the specific instrumentation employed.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of GC 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 Sect. 9.4.

1.7 Methyl-t-butyl ether (MTBE) is recommended as the primary extraction solvent in this method since it effectively extracts all of the target analytes listed in Sect. 1.1. However, due to safety concerns associated with MTBE and the current use of pentane by some laboratories for certain method analytes, pentane is offered as an optional extraction solvent for all analytes except chloral hydrate. If project requirements specify the analysis of chloral hydrate, MTBE must be used as the extracting solvent. This method includes sections specific for pentane as an optional solvent.

2. SUMMARY OF METHOD

2.1 A 50 mL sample aliquot is extracted with 3 mL of MTBE or 5 mL of pentane. Two μL of the extract is then injected into a GC equipped

with a fused silica capillary column and linearized electron capture detector for separation and analysis. Procedural standard calibration is used to quantitate method analytes.

2.2 A typical sample can be extracted and analyzed by this method in 50 min for the chlorination by-products/chlorinated solvents and 2 hrs. for the total analyte list. Confirmation of the eluted compounds may be obtained using a dissimilar column (6.9.2.2) or by the use of GC-MS. Simultaneous confirmation can be performed using dual primary/confirmation columns installed in a single injection port (Sect. 6.9.3) or a separate confirmation analysis.

3. DEFINITIONS

3.1 INTERNAL STANDARD (IS) -- A pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component.

3.2 SURROGATE ANALYTE (SA) -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added directly to a sample aliquot in known amount(s) before extraction or other processing and is measured with the same procedures used to measure other sample components. The purpose of a surrogate analyte is to monitor method performance with each sample.

3.3 LABORATORY DUPLICATES (LD1 and LD2) -- Two sample aliquots, taken in the laboratory from a single sample bottle, and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures. This method cannot utilize laboratory duplicates since sample extraction must occur in the sample vial and sample transfer is not possible due to analyte volatility.

3.4 FIELD DUPLICATES (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures. Since laboratory duplicates cannot be analyzed, the collection and analysis of field duplicates for this method is critical.

3.5 LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water, or other blank matrix, that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.6 FIELD REAGENT BLANK (FRB) -- Reagent water, or other blank matrix, that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to sampling site, exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.7 LABORATORY FORTIFIED BLANK (LFB) -- An aliquot of reagent water, or other blank matrix, to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise analyte quantitation at various concentrations including the required method detection limit.

3.8 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.9 STOCK STANDARD SOLUTION (SSS) -- A concentrated solution containing one or more method analytes which is prepared in the laboratory using assayed reference materials or purchased as certified from a reputable commercial source.

3.10 PRIMARY DILUTION STANDARD SOLUTION (PDS) -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.11 CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standard(s) and surrogate analyte(s). The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.12 QUALITY CONTROL SAMPLE (QCS) -- A solution of method analytes which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.13 LABORATORY PERFORMANCE CHECK SOLUTION (LPC) -- A solution of selected method analytes, surrogate(s), internal standard(s), or other test substances used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.14 METHOD DETECTION LIMIT (MDL) -- The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero. (Appendix B to 40 CFR Part 136)

3.15 ESTIMATED DETECTION LIMIT (EDL) -- Defined as either the MDL or a level of compound in a sample yielding a peak in the final extract with a signal to noise (S/N) ratio of approximately 5, whichever is greater.

3.16 PROCEDURAL STANDARD CALIBRATION -- A calibration method where aqueous calibration standards are prepared and processed (e.g. purged,extracted, and/or derivatized) in exactly the same manner as a sample. All steps in the process from addition of sampling preservatives through instrumental analyses are included in the calibration. Using procedural standard calibration compensates for any inefficiencies in the processing procedure.

4. INTERFERENCES

4.1 Impurities contained in the extracting solvent usually account for the majority of the analytical problems. Each new bottle of solvent should be analyzed for interferences before use. An interference free solvent is a solvent containing no peaks yielding data at $\geq$ MDL (Tables 2 and 8) at the retention times of the analytes of interest. Indirect daily checks on the extracting solvent are obtained by monitoring the laboratory reagent blanks (Sect. 9.3). Whenever an interference is noted in the reagent blank, the analyst should analyze the solvent separately to determine if the source of the problem is the solvent or another reagent.

4.2 Glassware must be scrupulously cleaned (13). Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot water and detergent and thoroughly rinsing with tap and reagent water. Drain dry, and heat in an oven or muffle furnace at 400°C for 1 hr. Do not muffle volumetric ware but instead rinse three times with HPLC grade or better acetone. Thoroughly rinsing all glassware with HPLC grade or better acetone may be substituted for heating provided method blank analysis confirms no background interferant contamination is present. After drying and cooling, seal and store all glassware in a clean environment free of all potential contamination. To prevent any accumulation of dust or other contaminants, store glassware inverted on clean aluminum foil or capped with aluminum foil.

4.3 Commercial lots of the extraction solvents (both MTBE and pentane) often contain observable amounts of chlorinated solvent impurities, e.g., chloroform, trichloroethylene, carbon tetrachloride. When present, these impurities can normally be removed by double distillation.

4.4 This liquid/liquid extraction technique efficiently extracts a wide boiling range of non-polar and polar organic components of the sample. Thus, confirmation is quite important, particularly at lower analyte concentrations. A confirmatory column (6.9.2.2) is suggested for this purpose. Alternatively, GC/MS may also be used for confirmation if sufficient concentration of analyte is present.

4.5 Special care must be taken in the determination of endrin since it has been reported to breakdown to aldo and keto derivatives upon reaction with active sites in the injection port sleeve (14). The active sites are usually the result of micro fragments of the injector port septa and high boiling sample residual deposited in the injection port sleeve or on the inner wall at the front of the capillary column. The degradation of endrin is monitored using the Laboratory Performance Check Standard (Sect. 9.2).

4.6 Interfering and erratic peaks have been observed in method blanks within the retention windows of metribuzin, alachlor, cyanazine and heptachlor. These are believed to be due to phthalate contamination. This contamination can be reduced by paying special attention to reagent preparation (See solvent rinsing the dry buffer and the dechlorination/ preservative salts, Sect. 7.1.7.5) and elimination of all forms of plastic from the procedure (i.e. HDPE bottles, plastic weighing boats, etc.). After NaCl or Na_2SO_4 is muffled or phosphate buffer and dechlorination/preservative salts are solvent rinsed, they should be stored in sealed glass containers. NaCl, Na_2SO_4, phosphate buffer and dechlorination/ preservative salts should be weighed using glass beakers, never plastic weighing boats.

5. SAFETY

5.1 The toxicity and carcinogenicity of chemicals used in this method have not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available (15-17) for the information of the analyst.

5.2 The following have been tentatively classified as known or suspected human or mammalian carcinogens:

Chloroform, 1,2-Dibromo-3-chloropropane, 1,2-Dibromoethane, heptachlor, and hexachlorobenzene.

5.3 The toxicity of the extraction solvent, MTBE, has not been well defined. Susceptible individuals may experience adverse affects upon skin contact or inhalation of vapors. Therefore, protective clothing and gloves should be used and MTBE should be used only in a chemical fume hood or glove box. The same precaution applies to pure standard materials.

6. <u>EQUIPMENT AND SUPPLIES</u> (All specifications in Sections 6 and 7 are suggested. Catalogue numbers are included for illustration only.)

6.1 SAMPLE CONTAINERS - 60-mL screw cap glass vials (Kimble #60958A-16, Fisher #03-339-5E or equivalent) each equipped with size 24-400 cap and PTFE-faced septa (Kimble #73802-24400, Fisher #03-340-14A or equivalent). Prior to use or following each use, wash vials and septa with detergent and tap water then rinse thoroughly with distilled water. Allow the vials and septa to dry at room temperature, place only the vials in an oven and heat to 400°C for 30 min. After removal from the oven allow the vials to cool in an area known to be free of organics. After rinsing caps with distilled water, rinse in a beaker with HPLC grade or better acetone and place in a drying oven at 80°C for 1 hr.

6.2 VIALS - Autosampler, 2.0-mL vial with screw or crimp cap and a teflon faced septa.

6.3 MICRO SYRINGES - 10 µL, 25 µL, 50 µL, 100 µL, 250 µL, and 1000 µL.

6.4 PIPETTES - 3.0 mL or 5.0 mL, type A, TD, glass.

6.5 VOLUMETRIC FLASK - 10 mL, 100 mL, 250 mL, 500 mL glass stoppered.

6.6 DISPOSABLE PASTEUR PIPETS - 9 inch, used for extract transfer.

6.7 STANDARD SOLUTION STORAGE CONTAINERS - 30-mL Boston round, amber glass bottles with TFE-lined caps or equivalent.

6.8 BALANCE - Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.9 GAS CHROMATOGRAPHY SYSTEM

6.9.1 The GC must be capable of temperature programming and should be equipped with a linearized electron capture detector (ECD), fused silica capillary column, and on-column or splitless injector (splitless mode, 30 sec. delay). If simultaneous confirmation is employed the GC must have a second ECD. An auto-sampler/injector is desirable.

6.9.1.1 SPECIAL PRECAUTION: During method development, a problem was encountered with the syringe on the autosampler. The syringe plunger, after repeated sample extract injections, developed resistance when withdrawn or inserted into the syringe barrel. This resistance was due to salt deposits in the syringe barrel which were left behind following the evaporation of hydrated MTBE. To minimize this problem, a unique syringe wash procedure was employed. After sample injection, the syringe was first rinsed three times with reagent water then

three times with MTBE. This effectively removed all the residual salt after each injection from the syringe and surmounted the problem. Some autosampler designs may not encounter this problem but this precaution has been mentioned to alert the analyst. When pentane was used as the extraction solvent, this was not a problem.

6.9.2 Two GC columns are recommended. Column A is recommended as the primary analytical column unless routinely occurring analytes are not adequately resolved. Column B is recommended for use as a confirmatory column when GC/MS confirmation is not sensitive enough or unavailable. Other GC columns or conditions may be employed provided adequate analyte resolution is attained and all the quality assurance criteria established in Sect. 9 are met.

6.9.2.1 Column A - 0.25 mm ID x 30 m fused silica capillary with chemically bonded methyl polysiloxane phase (J&W, DB-1, 1.0 m film thickness or equivalent). As a result of the different boiling points of MTBE (b.p. 55°C) and pentane (b.p. 35°C), two different GC oven temperature programs are specified in Table 1 for MTBE and Table 12 for pentane. Retention times for target analytes were slightly different using the pentane oven temperature program but elution order, analyte resolution, and total analysis time were not effected. Injector temperature: 200°C equipped with 4 mm ID deactivated sleeve with wool plug (Restek #20781 for HP GC's or equivalent). This sleeve design was found to give better analyte response than the standard 2 mm sleeve. Detector temperature: 290°C.

6.9.2.2 Column B - 0.25 mm ID x 30 m with chemically bonded 6 % cyanopropylphenyl/94 % dimethyl polysiloxane phase (Restek, Rtx-1301, 1.0 µm film thickness or equivalent). The column oven was temperature programmed exactly as indicated for column A (Tables 1 and 12). Injector and detector temperatures at 200°C and 290°C, respectively. The same temperature program was utilized to allow for simultaneous confirmation analysis.

6.9.3 To perform simultaneous confirmation from a single injection onto both the primary and confirmation columns, two injector setups can be employed.

6.9.3.1 Using a two hole graphite ferrule (Restek #20235, or equivalent) both columns can be inserted into one injection port. To ensure the column ends are centered in the injection port sleeve and not angled

to the side, an inlet adaptor fitting is installed at the base of the injection port (Restek #20633, or equivalent). Use caution when installing columns in this manner to ensure the column does not break at the base of the injector due to the two columns twisting as the ferrule nut is tightened. To minimize this hazard, the ferrule nut can be reverse twisted four to five times once the ferrule has been seated.

6.9.3.2 An alternate procedure involves installing a 1 meter portion of 0.25 mm deactivated, uncoated fused silica capillary tubing (Restek #10043, or equivalent) into the injector as a normal single column is installed. Then using a Y-press tight union (Restek #20403 or equivalent) join the 1 meter uncoated column to the primary and secondary columns. Using this procedure will reduce detection limits when compared to the procedure outline in 6.9.3.1 since only one column is positioned in the injection port to receive the injected sample extract.

6.9.4 The analyst is permitted to modify GC columns, GC conditions, internal standard or surrogate compounds. Each time such method modifications are made, the analyst must repeat the procedures in Sect. 9.4.

7. REAGENTS AND STANDARDS

7.1 REAGENTS

7.1.1 MTBE - High purity grade. It may be necessary to double distill the solvent if impurities are observed which coelute with some of the more volatile compounds.

7.1.2 Pentane (optional extraction solvent) - High purity grade. It may be necessary to double distill the solvent if impurities are observed which coelute with some of the more volatile compounds.

7.1.3 Acetone - High purity, demonstrated to be free of analytes.

7.1.4 Methanol - High purity, demonstrated to be free of analytes.

7.1.5 Sodium Chloride, NaCl - ACS Reagent Grade. Before using a batch of NaCl, place in muffle furnace, increase temperature to 400°C and hold for 30 min. Store in a capped glass bottle, not in a plastic container.

7.1.6 Sodium Sulfate, Na_2SO_4 - ACS Reagent Grade. Before using a batch of Na_2SO_4, place in muffle furnace, increase

temperature to 400°C and hold for 30 min. Store in a capped glass bottle not in a plastic container.

7.1.7 Sample Preservation Reagents

7.1.7.1 Phosphate buffer - Used to lower the sample matrix pH to 5.2 in order to inhibit base catalyzed degradation of the haloacetonitriles (7), some of the chlorinated solvents, and to standardize the pH of all samples. Prepare a dry homogeneous mixture of 2.50% Sodium Phosphate, dibasic (Na_2HPO_4)/97.5% Potassium Phosphate, monobasic (KH_2PO_4) by weight (example: 5.00 g Na_2HPO_4 and 195 g KH_2PO_4 to yield a total weight of 200 g) Both of these buffer salts should be in granular form and of ACS grade or better. Powder would be ideal but would require extended cleanup time as outlined below in Sect. 7.1.7.5 to allow for buffer/solvent settling.

7.1.7.2 Ammonium Chloride, NH_4Cl, ACS Reagent Grade. Used to convert free chlorine to monochloramine. Although this is not the traditional dechlorination mechanism, ammonium chloride is categorized as a dechlorinating agent in this method.

7.1.7.3 Sodium Sulfite, Na_2SO_3, ACS Reagent Grade. Used as a dechlorinating agent for chloral hydrate sample analysis.

7.1.7.4 To simplify the addition of 6.0 mg of the dechlorinating agent to the 60 mL vial, the dechlorinating salt is combined with the phosphate buffer as a homogeneous mixture. Two g of the appropriate dechlorinating agent are added to 200 g of the phosphate buffer. When 0.60 g of the buffer/dechlorinating agent mixture are added to the 60-mL sample vial, 6 mg of the dechlorinating agent are included reflecting an actual concentration of 100 mg/L. Two separate mixtures are prepared, one containing ammonium chloride and the other with sodium sulfite.

7.1.7.5 If background contaminants are detected in the salts listed in Sections 7.1.7.1 through 7.1.7.3, a solvent rinse cleanup procedure may be required. These contaminants may coelute with some of the high molecular weight herbicides and pesticides. These salts cannot be muffled since they decompose when heated to 400°C. This solvent rinsing procedure is applied to the homogeneous mixture prepared in Sect. 7.1.7.4.

NOTE: If a laboratory is not conducting analyses for the high molecular weight herbicides and pesticides, this cleanup may not be required if no interfering peaks are observed within the retention time window (Sect.12.2) for any target analytes in the laboratory reagent blank.

SOLVENT RINSE CLEANUP PROCEDURE

Prepare two separate homogeneous mixtures of the phosphate buffer salts (Sect. 7.1.7.1) in a 500-mL beaker. To one, add the correct amount of ammonium chloride and to the other add the correct amount of sodium sulfite. Three separate solvents are then used to rinse the mixture. (This solvent rinsing must be performed in a fume hood or glove box.) First, add approx. 100 mL of methanol, or enough to cover the salt to a depth of approx. 1 cm, and using a clean spatula, stir the solvent salt mixture for 1 minute. Allow the buffer/solvent mixture to settle for 1 minute and then decant the methanol, being careful not to pour off the rinsed buffer. It may be necessary to perform this procedure up to four times with methanol. NOTE: By softly lifting and tapping the base of the beaker against the fume hood counter surface, more of the solvent is brought to the surface of the buffer. Next, perform the identical procedure up to two times using acetone. Finally, perform two final rinses with the appropriate extracting solvent (MTBE or Pentane). After the final solvent rinse, place the "wet" buffer on a hot plate at approx. 60°C for 30 minutes or until dry. Stir the mixture every 5 minutes to aid the evaporation of excess solvent. Once dry, place the buffer in a glass bottle with either a ground glass stopper or TFE faced septum.

7.2 REAGENT WATER - Reagent water is defined as purified water which does not contain any measurable quantities of any target analytes or any other interfering species.

7.2.1 A Millipore Super-Q water system or its equivalent may be used to generate deionized reagent water. Distilled water that has been charcoal filtered may also be suitable.

7.2.2 Test reagent water each day it is used by analyzing according to Sect. 11.

7.3 STOCK STANDARD SOLUTIONS (SSS)- These solutions may be obtained as certified solutions or prepared from neat materials using the following procedures:

7.3.1 For analytes which are solids in their pure form, prepare stock standard solutions (1 mg/mL) by accurately weighing approximately 0.01 g of pure material in a 10-mL volumetric flask. Dilute to volume with acetone. Due to the low solubility of simazine, this stock should be prepared at 0.5 mg/mL by weighing 0.005 g diluted to volume with acetone in a 10-mL volumetric flask. Alternatively, simazine stock standard solutions may be prepared in ethyl acetate at approximately 0.01 g/10 mL. Stock standard solutions for analytes which are liquid in their pure form at room temperature can be accurately prepared in the following manner.

7.3.1.1 Place about 9.8 mL of acetone into a 10-mL ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min to allow solvent film to evaporate from the inner walls of the volumetric flask, and weigh to the nearest 0.1 mg.

7.3.1.2 Use a 10-μL syringe and immediately add 10.0 μL of standard material to the flask by keeping the syringe needle just above the surface of the acetone. Caution should be observed to be sure that the standard material falls dropwise directly into the acetone without contacting the inner wall of the volumetric flask.

7.3.1.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in milligrams per milliliter from the net gain in weight. Final concentration should be between 0.800 - 1.50 mg/mL.

7.3.2 Larger volumes of standard solution may be prepared at the discretion 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.

7.3.3 Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source. When purchasing commercially prepared stock standards, every effort should be made to avoid solutions prepared in methanol (chloral hydrate is an exception, Sect. 7.3.3.1). Methanol can cause degradation of most of the haloacetonitriles. In addition, some commercial suppliers have reported instability with solutions of simazine and atrazine prepared in methanol (18). For these reasons, acetone should be used as the primary solvent for stock standard and primary dilution standard preparation and

all sources of methanol introduction into these acetone solutions should be eliminated.

7.3.3.1 It is extremely difficult to acquire chloral hydrate in its pure form since it is classified as a controlled substance. Consequently, if pure chloral hydrate cannot be acquired, a commercially prepared solution of this analyte (most often at 1.0 mg/mL) must be purchased. Most manufactures provide certified chloral hydrate solutions in methanol. Since chloral hydrate is unstable, standards from a separate vendor must be utilized to confirm the accuracy of the primary supplier's solution.

7.3.4 Outside source stock solutions, which are independently prepared or purchased from an outside source different from the source for the original stock standard solutions, must be used as a means of verifying the accuracy of the original stock standard solutions for all analytes. Prepare a dilution of both stocks in acetone and perform a final dilution in MTBE such that each stock dilution is at the same concentration. Analyze as outlined in Section 11.3. The relative percent difference (RPD as defined below) between the analytes' response (area counts) from both solutions should not exceed 25% for any one analyte. The RPD must be less than 20% for 90% or greater of the total number of target analytes analyzed.

$$RPD = \frac{(DUP\ 1 - DUP\ 2)}{((DUP\ 1 + DUP\ 2) / 2)} \times 100$$

7.3.4.1 If this criteria cannot be met, a third outside source should be purchased and tested in the same manner. When two sources of stock solutions agree, the accuracy of the stock solutions is confirmed. This should be done prior to preparing the primary dilution standards.

7.3.5 Stock Solution of Surrogate - Prepare a stock solution of the surrogate standard in acetone by weighing approx. 0.010 g decafluorobiphenyl in a 10-mL volumetric flask. When diluted to volume this yields a concentration of 1.00 mg/mL. Alternate surrogate analytes may be selected provided they are similar in analytical behavior to the compounds of interest, are highly unlikely to be found in any sample, and do not coelute with target analytes.

7.3.6 Stock Solution of Internal Standard (IS) - Use of an IS is optional when MTBE is the extraction solvent but mandatory if pentane is used. This is due to the high volatility of pentane when compared to MTBE (see boiling points, Sect.

6.9.2.1). Prepare an internal standard stock solution of bromofluorobenzene (BFB) in acetone. Since this compound is a liquid at room temperature, the procedure outlined in Sections 7.3.1.1 through 7.3.1.3 should be followed but add approximately 65 µL of neat BFB rather than 10 µL as specified in 7.3.1.2. When diluted to volume this yields a concentration near 10.0 mg/mL. Alternate internal standard analytes may be selected provided they are highly unlikely to be found in any sample and do not coelute with target analytes.

7.3.7 Transfer the stock standard solutions into Teflon-lined screw cap amber bottles. Store at 4°C or less 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.

7.3.8 When stored in a freezer at < -10°C, the THM stock standards have been shown to be stable for up to six months. The other analyte stock standards, with the exception of chloral hydrate, have been shown to be stable for at least four months when stored in a freezer (<-10°C). Chloral hydrate stock standards, when stored in a freezer (<-10°C), have been shown to be stable for two months, however, since freezers can hold at various temperatures below -10°C, fresh chloral hydrate standards should be initially prepared weekly, until the stability of this analyte is determined for a specific laboratory setting.

7.4 PRIMARY DILUTION STANDARDS (PDS) - Two separate groups of primary dilution standards must be prepared; one set in acetone for all the method analytes except chloral hydrate and the second set in methanol for chloral hydrate. Although preparation of separate chloral hydrate standards may seem laborious, due to the stability problems encountered with this analyte, making fresh chloral hydrate primary dilution standards is more efficient. Prepare primary dilution standards by combining and diluting stock standards in acetone (methanol for chloral hydrate). The primary dilution standards should be prepared such that when 25 µL of this primary dilution standard are added to 50 mL of buffered/dechlorinated reagent water (Sect 10.1.2), aqueous concentrations will bracket the working concentration range. Store the primary dilution standard solutions in vials or bottles, with caps using TFE faced liners, in a freezer (<-10°C) with minimal headspace and check frequently for signs of deterioration or evaporation, especially just before preparing calibration standards. The same comments on storage stability in Sect. 7.3.8 apply to primary dilution standards.

7.4.1 SURROGATE PRIMARY DILUTION STANDARD - Dilute 500 µL of the surrogate stock solution to volume with acetone in a 50-mL volumetric flask. This yields a primary dilution standard at 10.0 µg/mL. Addition of 50 µL of this standard to 50 mL of

aqueous sample yields a final concentration in water of 10.0 µg/L. This solution is fortified into the aqueous sample prior to extraction of all calibration standards (Sect. 10.1.3), quality control samples (Sect. 9), laboratory reagent blanks (Sect. 9.3.1) and actual field samples (Sect. 11.1.3) in the extraction set.

7.4.2 INTERNAL STANDARD (IS) PRIMARY DILUTION STANDARD - Prepare a IS primary dilution standard at 100 µg/mL by diluting the appropriate amount of internal standard stock solution (500 µL if stock is 10.0 mg/mL) to volume with acetone in a 50-mL volumetric flask. When 10 µL of this solution are added to 1.0 mL of extract, the resultant final concentration is 1.00 µg/mL. The internal standard is used in order to perform an internal standard calibration and is added to an analytically precise volume of the extract following extraction. This solution is added to all extracts.

7.4.3 Reserve approximately a 10 mL aliquot of the same lot of both the acetone and methanol used in the preparation of the primary dilution standards. When validating the accuracy of the calibration standards (Sect. 7.3.4), fortify a laboratory reagent blank with 25 µL of both the acetone and the methanol which was used to prepare the primary dilution standards. Analysis of this laboratory reagent blank will confirm no target analyte contamination in the solvents used to prepare the primary dilution standards.

7.5 LABORATORY PERFORMANCE CHECK SOLUTION (LPC) - To insure proper instrument performance, a Laboratory Performance Check Solution is prepared. This solution is prepared in MTBE for direct injection on the GC and is used to evaluate the parameters of instrument sensitivity, chromatographic performance, column performance and analyte breakdown. These parameters are listed in Table 7 along with the method analytes utilized to perform this evaluation, their concentration in MTBE and the acceptance criteria. To prepare this solution at the concentrations listed in Table 7, a double dilution of the analyte stock solutions must be made. First prepare a primary stock dilution mix at 1000 times the concentrations listed in Table 7, by adding the appropriate volume of each stock solution to a single 50-mL volumetric flask containing approximately 25 mL of MTBE. Dilute to volume with MTBE. Then the LPC working solution is prepared in MTBE by diluting 50 µL of the primary stock dilution mix in MTBE to 50-mL in a volumetric flask. The best way to accomplish this is to add approximately 48 mL MTBE to the 50-mL volumetric flask and add 50 µL of the primary stock dilution mix, then dilute to volume with MTBE. Store this solution in a vial or bottle, with TFE faced cap, in a freezer (<-10°C) with minimal headspace and check frequently for signs of deterioration or evaporation.

7.5.1 If a laboratory is not conducting analyses for the high molecular weight pesticides and herbicides, a modified LPC

may be prepared. This modified LPC can omit the endrin analyte breakdown component as well as the resolution requirement for bromacil and alachlor under column performance. In addition, substitute analytes in place of lindane for the sensitivity check and hexachlorocyclopentadiene for chromatographic performance can be selected. These substitute compounds must meet the same criteria as listed in table 7 with the concentration for sensitivity check near the substitute analyte's EDL and the concentration for chromatographic performance near 50 times the substitute analyte's EDL. The column performance criteria for resolution between bromodichloromethane and trichloroethylene cannot be modified.

7.5.2 If pentane is selected as an alternate extraction solvent the LPC must also be prepared in pentane.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 SAMPLE VIAL PREPARATION

8.1.1 To conduct analyses for the total analyte list, two sets of 60-mL vials must be prepared for sampling. One set of vials, prepared for the analysis of all target analytes except chloral hydrate, contains ammonium chloride as a dechlorinating agent. Due to concerns over low recoveries for chloral hydrate in matrices preserved with ammonium chloride (Sect. 8.1.2), a separate sample set must be collected and preserved with sodium sulfite. Both sets of vials are prepared as follows.

8.1.1.1 Using the homogeneous phosphate buffer/dechlorinating agent mixtures prepared in Sect. 7.1.7.4, 0.60 g of the appropriate mixture are added to the corresponding vials.

8.1.2 If the sample assay is for only the THMs and/or solvents, either dechlorinating agent can be added. However, sodium sulfite promotes the decomposition of the haloacetonitriles, 1,1-dichloro-2-propanone, 1,1,1-trichloro-2-propanone and chloropicrin and therefore ammonium chloride must be used as the dechlorination reagent in their analysis. In addition, some fortified matrices, dechlorinated with ammonium chloride, have displayed recoveries of chloral hydrate which have been up to 50% lower than expected, when compared to the same sample matrix dechlorinated with sodium sulfite. In other matrices, recoveries have been consistent regardless of dechlorinating agent. The reason for these differences has not been determined. Due to this uncertainty, a separate sample, dechlorinated with 100 mg/L sodium sulfite must be collected for the analysis of chloral hydrate.

8.1.3 The dechlorinating agents, if not added within the homogeneous mixture of the buffer, must be added to the sampling vials as a dry salt. Solutions of the dechlorinating agents should not be used due to concerns over the stability of these salts dissolved in solution and the potential chemical interactions of aqueous solutions of these salts with the dry phosphate buffer.

8.1.4 Samples must contain either 100 mg/L ammonium chloride or sodium sulfite, as appropriate for the analysis being performed. This amount will eliminate free chlorine residual in typical chlorinated drinking water samples. If high chlorine doses are used, such as in a maximum formation potential test, additional dechlorinating reagent may be required.

8.2 SAMPLE COLLECTION

8.2.1 Collect all samples in duplicate. Fill sample bottles to just overflowing but take care not to flush out the buffer/dechlorination reagents. No air bubbles should pass through the sample as the bottle is filled, or be trapped in the sample when the bottle is sealed.

8.2.2 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 3-5 min). Remove the aerator and adjust the flow so that no air bubbles are visually detected in the flowing stream.

8.2.3 When sampling from an open body of water, fill a 1-quart wide-mouth glass bottle or 1-liter beaker with sample from a representative area, and carefully fill duplicate 60-mL sample vials from the container.

8.2.4 The samples must be chilled to 4°C on the day of collection and maintained at that temperature until analysis. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to ensure they will be at 4°C on arrival at the laboratory. Synthetic ice (i.e. Blue ice) is not recommended.

8.3 SAMPLE STORAGE/HOLDING TIMES

8.3.1 Store samples at 4°C and extracts in a freezer (<-10°C) until analysis. The sample storage area must be free of organic solvent vapors.

8.3.2 Extract all samples within 14 days of collection and analyze within 14 days following extraction. This applies to either MTBE or pentane extracts). Samples not analyzed within these time periods must be discarded and replaced.

9. QUALITY CONTROL

9.1 Each laboratory that uses this method is required to operate a formal quality control (QC) program. Minimum QC requirements include the laboratory performance check standard, initial demonstration of laboratory capability, method detection limit determination, analysis of laboratory reagent blanks, continuing calibration check standard, laboratory fortified sample matrices, field duplicates and monitoring surrogate and/or internal standard peak response in each sample and blank. Additional quality control practices may be added.

9.2 ASSESSING INSTRUMENT SYSTEM - LABORATORY PERFORMANCE CHECK STANDARD (LPC). Prior to any sample analyses, a laboratory performance check standard must be analyzed. The LPC sample contains compounds designed to indicate appropriate instrument sensitivity, endrin breakdown, column performance (primary column), and chromatographic performance. LPC sample components and performance criteria are listed in Table 7. Inability to demonstrate acceptable instrument performance indicates the need for reevaluation of the instrument system. The sensitivity requirement is based on the Estimated Detection Limits (EDLs) published in this method. If laboratory EDLs differ from those listed in this method, concentrations of the LPC standard must be adjusted to be compatible with the laboratory EDLs. If endrin breakdown exceeds 20 %, the problem can most likely be solved by performing routine maintenance on the injection port including replacing the injection port sleeve, and all associated seals and septa. If column or chromatographic performance criteria cannot be met, new columns may need to be installed, column flows corrected, or modifications adapted to the oven temperature program. During early method development work, significant chromatographic and column performance problems were observed while using a DB-1 column which had been used for several years for drinking water extract analysis. By installing a new DB-1 column, these performance problems were overcome. If the columns to be used for this method have been used for several years or have had extended use with extracts from harsh sample matrices (i.e. wastewater, acidified sample extracts, hazardous waste samples) it may be difficult to meet the criteria established for this LPC standard and column replacement may be the best alternative.

9.3 LABORATORY REAGENT BLANKS (LRB). Before processing any samples, the analyst must analyze an LRB to demonstrate that all glassware and reagent interferences are under control. In addition, each time a set of samples is extracted or reagents are changed, a LRB must be analyzed. If the LRB produces a peak within the retention time window of any analyte (Sect. 12.2) preventing the quantitation of

that analyte, determine the source of the contamination and eliminate the interference before processing samples. LRB samples must contain the appropriate buffer for the target analytes (buffered/NH_4Cl dechlorinated and/or buffered/Na_2SO_3 dechlorinated reagent water).

9.3.1 Prepare the two LRBs in the appropriate buffered/dechlorinated reagent water. Add 50 μL of surrogate primary dilution standard (Sect. 7.4.1) to each blank and follow the procedure outlined in Sect. 11.2.

9.4 INITIAL DEMONSTRATION OF CAPABILITY (IDC)

9.4.1 Preparation of the IDC Laboratory Fortified Blank (LFB). Select a concentration for each of the target analyte which is approximately 50 times the EDL or close to the expected levels observed in field samples. Concentrations near analyte levels in Table 3.A are recommended. Prepare a LFB by adding the appropriate concentration of the primary dilution standard (Sect. 7.4) to each of four to seven 50 mL aliquots of buffered/NH_4Cl dechlorinated reagent water. Separate Na_2SO_3 preserved matrices need not be analyzed (Sect. 9.4.1.1). Analyze the aliquots according to the method beginning in Section 11.

9.4.1.1 Chloral hydrate is included in the buffered/NH_4Cl dechlorinated reagent water, containing all the other target analytes since no matrix induced recovery problems have been found from reagent water preserved with NH_4Cl.

9.4.2 Following procedural calibration standard analysis and subsequent instrument calibration, analyze a set of at least seven IDC samples and calculate the mean percent recovery (R) and the relative standard deviation of this recovery (RSD). The percent recovery is determined as the ratio of the measured concentration to the actual fortified concentration. For each analyte, the mean recovery value must fall within the range of 80% to 120% and the RSD must not exceed 15 %. For those compounds that meet these criteria, performance is considered acceptable, and sample analysis may begin. For those compounds that fail these criteria, this procedure must be repeated using eight fresh samples until satisfactory performance has been demonstrated.

9.4.3 The initial demonstration of capability is used primarily to preclude a laboratory from analyzing and reporting unknown samples without obtaining some experience with an unfamiliar method. It is expected that as laboratory personnel gain experience with this method, the quality of data will improve beyond those specified in Sect. 9.4.2.

9.4.4 METHOD DETECTION LIMITS (MDL). Prior to the analysis of any field samples the method detection limits must be determined. Initially, estimate the concentration of an analyte which would yield a peak equal to 5 times the baseline noise and drift. Prepare a primary dilution standard with analyte concentrations at 1000 times this level in acetone (or methanol for chloral hydrate).

9.4.4.1 Prepare a 500 mL aliquot of buffered/ammonium chloride dechlorinated reagent water. Fill a minimum of seven replicate, 60-mL vials with 50 mL of the buffered/dechlorinated (NH_4Cl) reagent water.

9.4.4.2 Fortify the 50 mL buffered/dechlorinated (NH_4Cl) reagent water with 50 μL of both the MDL concentrate prepared in acetone and the chloral hydrate MDL concentrate in methanol. Separate preparation of a reagent water containing Na_2SO_3 as the dechlorinating agent for chloral hydrate MDL determination is not necessary. (See Sect. 9.4.1.1)

9.4.4.3 Extract and analyze these samples as outlined in Section 11. MDL determination can then be performed as discussed in Sect. 13.1.

9.5 LABORATORY FORTIFIED BLANK (LFB). Since this method utilizes procedural calibration standards, which are fortified reagent water, there is no difference between the LFB and the continuing calibration check standard. Consequently, there is not a requirement for the analysis of an LFB. However, the criteria established for the continuing calibration check standard (Sect. 10.4) should be evaluated as the LFB.

9.6 LABORATORY FORTIFIED SAMPLE MATRIX (LFM). The laboratory must add known concentrations of analytes to a minimum of 10% of the routine samples or one fortified sample per sample set, whichever is greater, for both NH_4Cl and Na_2SO_3 dechlorinated sample matrices. The concentrations should be equal to or greater than the background concentrations in the sample selected for fortification. Over time, samples from all routine sample sources should be fortified. By fortifying sample matrices and calculating analyte recoveries, any matrix induced analyte bias is evaluated. When an analyte recovery falls outside the acceptance criteria outlined below, a bias is concluded and that analyte for that matrix is reported to the data user as suspect.

9.6.1 First, follow the procedure outlined in Sect. 11.1

9.6.2 Next, prepare the LFM by adding 50 μL of an acetone based standard solution into the remaining 50 mL of the buffered/ NH_4Cl dechlorinated sample matrix in the vial in which it was

sampled. This sample vial will have had the required amount of aqueous sample removed as specified in Sect. 11.1.2. Add 50 μL of surrogate primary dilution standard (Sect. 7.4.1) and follow procedure outlined in Sections 11 and 12.

9.6.3 When chloral hydrate is being determined, prepare the LFM by adding 50 μL of a methanol based chloral hydrate standard solution into 50 mL of the buffered/Na_2SO_3 dechlorinated sample matrix in the vial in which it was sampled. Add 50 μL of surrogate primary dilution standard (Sect. 7.4.1) and follow procedure outlined in Sections 11 and 12.

9.6.4 Calculate the percent recovery, R, of the concentration for each analyte, after correcting the total measured concentration, A, from the fortified sample for the background concentration, B, measured in the unfortified sample, i.e.:

$$R = 100\ (A - B)\ /\ C,$$

where C is the fortifying concentration. The recoveries of all analytes being determined must fall between 75 % and 125 % and the recoveries of at least 90% of these analytes must fall between 80 % and 120 %. This criteria is applicable to both external and internal standard calibrated quantitation.

9.6.5 If a recovery falls outside of this acceptable range, a matrix induced bias can be assumed for the respective analyte and the data for that analyte in that sample matrix must be reported to the data user as suspect.

9.6.6 If the unfortified matrix has analyte concentrations equal to or greater than the concentration fortified, a duplicate sample vial needs to be fortified at a higher concentration. If no such sample is available the recovery data for the LFM sample should not be reported for this analyte to the data user.

9.7 FIELD DUPLICATES (FD1 and FD2). The laboratory must analyze a field sample duplicate for a minimum of 10% of the total number of field samples or at least one field sample duplicate per sample set, whichever is greater. Duplicate results must not reflect a relative percent difference (RPD as defined below) greater than 25% for any one analyte and the RPD for 90% of the analytes being determined must be less than 20%.

$$RPD = \frac{(FD1 - FD2)}{((FD1 + FD2)\ /\ 2)} \times 100$$

where FD1 and FD2 represent the quantified concentration on an individual analyte for the initial and duplicate field sample analysis, respectively. If this criteria is not met the analysis must be repeated. Upon repeated failure, the sampling must be repeated or the analyte out of control must be reported as suspect to the data user.

9.8 ASSESSING SURROGATE RECOVERY

9.8.1 The surrogate analyte is fortified into the aqueous portion of all calibration standards, quality control samples and field samples. By monitoring the surrogate response, the analyst generates useful quality control information from extraction precision through quantitative analysis. Deviations in surrogate recovery may indicate an extraction problem. If using external standard calibration the surrogate retention time functions as a reference for identification of target analytes.

9.8.2 Using the mean surrogate response from the calibration standard analyses (Cal_{SR}), determine the surrogate percent recovery ($\%REC_S$) in all calibration standards, LFBs, and LFMs, and field samples. This recovery is calculated by dividing the surrogate response from the sample (Sam_{SR}) by the mean response from the initial calibration standards (Sect. 10.2 or 10.3) and multiplying by 100, as shown below.

$$\% \ REC_S = \frac{Sam_{SR}}{Cal_{SR}} \times 100$$

Recoveries must fall within the range of 80% to 120%. If a sample provides a recovery outside of this range, the extract must be reanalyzed. If upon reanalysis, the recovery continues to fall outside the acceptable range a fresh sample should be extracted and analyzed. If this is not possible the data for all the analytes from this sample should be reported to the data user as suspect due to surrogate recovery outside acceptable limits.

9.8.3 If consecutive samples fail the surrogate response acceptance criterion, immediately analyze a continuing calibration standard.

9.8.3.1 If the continuing calibration standard provides a recovery within the acceptable range of 80% to 120%, then follow procedures itemized in Sect. 9.8.2 for each sample failing the surrogate response criterion.

9.8.3.2 If the check standard provides a surrogate recovery which falls outside the acceptable range or fails

the acceptance criteria specified in Sect. 10.4 for the target analytes, then the analyst must recalibrate, as specified in Sect. 10.

9.9 ASSESSING THE INTERNAL STANDARD (IS)

9.9.1 When using the internal standard calibration procedure, the analyst must monitor the internal standard response (peak area or peak height) of all samples during each analysis day. The internal standard response should not deviate from mean internal standard response of the past five continuing calibration standards by more than 20%.

9.9.2 If > 20% deviation occurs with an individual extract, optimize instrument performance and inject a second aliquot of that extract.

9.9.2.1 If the reinjected aliquot produces an acceptable internal standard response, report results for that aliquot.

9.9.2.2 If a deviation of greater than 20% is obtained for the reinjected extract, analysis of a calibration check standard must be performed (Sect. 10.4).

9.9.3 If consecutive samples fail this IS response acceptance criterion, immediately analyze a calibration check standard.

9.9.3.1 If the check standard provides a response factor (RF) within 20% of the predicted value for the internal standard and the criteria for all the target analytes as specified in Sect. 10.4 is met, the previous sample(s) failing the IS response criteria need to be reextracted provided the sample is still available. In the event that reextraction is not possible, report results obtained from the reinjected extract (Sect 9.9.2) but annotate as suspect due to internal standard recovery being outside acceptable limits.

9.9.3.2 If the check standard provides a response factor which deviates more than 20% of the predicted value for the internal standard or the criteria for the target analytes, as specified in Sect 10.4 are not met, then the analyst must recalibrate, as specified in Sect. 10.3 and all samples analyzed since the previous calibration check standard need to be reanalyzed.

9.10 CONFIRMATION COLUMN ANALYSIS. If a positive result is observed on the primary column, a confirmation analysis should be performed using either the confirmation column or by GC/MS.

9.11 The laboratory may adapt additional quality control 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. For example, field reagent blanks may be used to assess contamination of samples under site conditions, transportation and storage.

9.12 Quality control samples (QCS) from an outside source, as defined in Sect. 3.12, should be analyzed at least quarterly.

10. CALIBRATION AND STANDARDIZATION

10.1 PREPARATION OF CALIBRATION STANDARDS

10.1.1 Five calibration standards are required. One should contain the analytes at a concentration near to but greater than the method detection limit (Table 2) for each compound; the others should be evenly distributed throughout the concentration range expected in samples or define the working range of the detector. Guidance on the number of standards is as follows: A minimum of three calibration standards are required to calibrate a range of a factor of 20 in concentration. For a factor of 50 use at least four standards, and for a factor of 100 at least five standards. For example, if the MDL is 0.1 µg/L, and a sample concentrations are expected to range from 1.0 µg/L to 10.0 µg/L, aqueous standards should be prepared at 0.20 µg/L, 0.80 µg/L, 2.0 µg/L, 5.0 µg/L, and 15.0 µg/L.

10.1.2 As a means of eliminating any matrix effects due to the use of the phosphate buffer and dechlorinating agents, the procedural calibration standards are prepared in reagent water which has been buffered to pH 5.2 and dechlorinated with ammonium chloride. To prepare this buffered/dechlorinated reagent water, add 5.0 g of phosphate buffer/dechlorinating agent (Sect 7.1.7.4, ammonium chloride type) to 500 mL of reagent water (Sect. 7.2).

10.1.3 Next, add 25 µL of the desired concentration primary dilution standards (acetone and methanol based, Sect. 7.4) to a 50 mL aliquot of the buffered/dechlorinated reagent water in a 60-mL vial. Use a 50-µL micro syringe and rapidly inject 25 µL of the standard into the middle point of the water volume. Remove the needle as quickly as possible after injection. Next, add 50 µL of the surrogate standard solution (Sect. 7.4.1) in the same manner. Mix by slowly and carefully inverting the sample vial two times with minimal sample agitation. Aqueous standards must be prepared fresh daily and extracted immediately after preparation (Section 11.2).

10.1.3.1 By including chloral hydrate into the total NH_4Cl analyte matrix, a separate calibration standard

analysis for Na_2SO_3 preserved reagent water fortified with chloral hydrate is avoided. Chloral hydrate is included in the buffered/NH_4Cl dechlorinated reagent water, containing all the other target analytes since no matrix induced recovery problems have been found from reagent water preserved with NH_4Cl. **Warning! Do not attempt to analyze chloral hydrate in field samples preserved with NH_4Cl, low recoveries may result due to matrix effects.**

10.1.4 CAUTION - DO NOT prepare procedural calibration standards in a volumetric flask and transfer the sample to an extraction vial either directly for weight determination of volume or into a graduated cylinder with a subsequent additional transfer into the extraction vial. Volatility experiments reflected as much as a 30 % loss in volatile low molecular weight analytes following such transfers. All fortified samples and field samples must be extracted in the vial or bottle in which they were fortified and collected.

10.2 EXTERNAL STANDARD CALIBRATION PROCEDURE

10.2.1 Extract and analyze each calibration standard according to Section 11 and tabulate peak height or area response versus the concentration of the standard. The results are used to prepare a calibration curve for each compound by plotting the peak height or area response versus the concentration. This curve can be defined as either first or second order. Alternatively, if the ratio of response to concentration (response factor) is constant over the working range ($\leq$ 10% relative standard deviation,[RSD]), linearity through the origin can be assumed, and the average ratio or calibration factor can be used in place of a calibration curve.

10.2.2 Surrogate analyte recoveries must be verified as detailed in Sections 9.8.

10.3 INTERNAL STANDARD (IS) CALIBRATION PROCEDURE

10.3.1 Extract each calibration standard according to Section 11. Remove a 1.00 mL portion of the MTBE or pentane extract from the sample extraction vial and place this into a 2.0-mL autosampler vial. To this extract, add the 10 μL of the internal standard primary dilution standard, cap the vial and analyze. Following analysis, tabulate peak height or area responses against concentration for each compound and the internal standard. Calculate relative response factor (RRF) for each compound using Equation 1.

Equation 1

$$RRF = \frac{(A_s)\ (C_{is})}{(A_{is})\ (C_s)}$$

where

A_s = Response for the analyte to be measured
A_{is} = Response for the internal standard
C_{is} = Concentration of the internal standard (µg/L)
C_s = Concentration of the analyte to be measured (µg/L)

If RF value over the working range is constant (< 10% RSD), the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response versus analyte ratios, A_s/A_{is} vs. C_s.

10.4 CONTINUING CALIBRATION CHECK STANDARD

10.4.1 Preceding each analysis set, after every tenth sample analysis and after the final sample analysis, a calibration standard should be analyzed as a continuing calibration check. These check standards should be at two different concentration levels to verify the calibration curve. This criteria is applicable to both external and internal standard calibrated quantitation. Surrogate and internal standard recoveries must be verified as detailed in Sections 9.8 and 9.9, respectively.

10.4.2 In order for the calibration to be considered valid, analyte recoveries for the continuing calibration check standard must fall between 75 % and 125 % for all the target analytes. The recoveries of at least 90% of the analytes determined must fall between 80% and 120%

10.4.3 If this criteria cannot be met, the continuing calibration check standard is reanalyzed in order to determine if the response deviations observed from the initial analysis are repeated. If this criteria still cannot be met then the instrument is considered out of calibration for those specific analytes beyond the acceptance range. The instrument needs to be recalibrated and the previous samples reanalyzed or those analytes out of acceptable range should be reported as suspect to the data user for all the previously analyzed samples.

11. PROCEDURE

11.1 SAMPLE PREPARATION

11.1.1 Remove samples from storage and allow them to equilibrate to room temperature.

11.1.2 Remove the vial caps. Remove a 10 mL volume of the sample. Check the pH of this 10 mL aliquot to verify that it is within a pH range of 4.5 and 5.5. If the pH is out of this range a new sample must be collected. Replace the vial caps and weigh the containers with contents to the nearest 0.1 g and record these weights for subsequent sample volume determination. (See Sect. 11.2.4 for continuation of weighing and calculation of true volume). Alternatively, the sample vials may be precalibrated by weighing in 50 mL of water and scoring the meniscus on the bottle. This will eliminate the gravimetric step above and in Sect. 11.2.4.

11.1.3 Inject 50μL of the surrogate analyte fortification solution (Sect. 7.4.1) into the sample. The aqueous concentration of surrogate analyte must be the same as that used in preparing calibration standards (Sect. 9.1.3). Mix by slowly and carefully inverting the sample vial two times with minimal sample agitation.

11.2 SAMPLE EXTRACTION

11.2.1 WITH MTBE AS EXTRACTION SOLVENT

11.2.1.1 After addition of the surrogate (Sect 11.1.3) add exactly 3.0 mL of MTBE with a type A, TD, transfer or automatic dispensing pipet.

11.2.1.2 Add 10 g NaCl or 20 g Na_2SO_4 to the sample vial. (See Section 13.7 for an important notice concerning the use of NaCl when analyzing for DBPs.) Recap and extract the NaCl or Na_2SO_4 /MTBE/sample mixture by vigorously and consistently shaking the vial by hand for 4 min. Invert the vial and allow the water and MTBE phases to separate (approx. 2 min).

If a series of samples are being prepared for extraction using Na_2SO_4, immediately after the addition of the Na_2SO_4, the sample should be recapped, agitated and placed in a secure horizontal position with the undissolved Na_2SO_4 distributed along the length of the vial. If the vial is left in a vertical position, while additional samples have solvent and salt added, the Na_2SO_4 will solidify in the bottom of the vial and it will not dissolve during sample extraction.

NOTE: Previous versions of this method call for the addition of the salt by "shaking the vial vigorously" before the MTBE has been added. Please make a note that this procedural order has been changed in an effort to minimize volatile analyte losses.

11.2.1.3 By using a disposable Pasteur pipet (Sect. 6.2), transfer a portion of the solvent phase from the 60-mL vial to an autosampler vial (Sect. 6.2). Be certain no water has carried over onto the bottom of the autosampler vial. If a dual phase appears in the autosampler vial, the bottom layer can be easily removed and discarded by using a Pasteur pipet. The remaining MTBE phase may be transferred to a second autosampler vial as a backup extract or for separate confirmation analysis. Approximately 2.5 mL of the solvent phase can be conveniently transferred from the original 3 mL volume.

11.2.1.3.1 If using an internal standard quantitation, the extract transfer into the autosampler vial must be performed in a quantitative manner. This may be done using a 1.00 mL syringe or a 2.00-mL graduated disposable pipet to accurately transfer 1.00 mL of sample extract to the autosampler vial where 10 μL of internal standard primary dilution standard (Sect. 7.4.2) solution can be added.

11.2.2 WITH PENTANE AS EXTRACTION SOLVENT

11.2.2.1 After addition of the surrogate (Sect 11.1.3) add exactly 5.0 mL of pentane with a type A, TD, transfer or automatic dispensing pipet.

11.2.2.2 Add 20 g Na_2SO_4 to the sample vial. Recap and extract the Na_2SO_4/pentane/sample mixture by vigorously and consistently shaking the vial by hand for 4 min. Invert the vial and allow the water and pentane phases to separate (approx. 2 min). NOTE: Previous versions of this method call for the addition of NaCl by "shaking the vial vigorously" before the pentane has been added. Please make a note that this procedural order has been changed in an effort to minimize volatile analyte losses. If a series of samples are being prepared for extraction, immediately after the addition of the Na_2SO_4, the sample should be recapped, agitated and placed in a secure horizontal position with the undissolved Na_2SO_4 distributed along the length of the vial. If the vial is left in a vertical position, while additional samples have solvent and salt added, the Na_2SO_4 will solidify in the bottom of the vial and it will not dissolve during sample extraction.

11.2.2.3 Using a disposable Pasteur pipet, transfer a portion of the solvent phase from the 60-mL vial to an autosampler vial. Be certain no water has carried over onto the bottom of the autosampler vial. If a dual phase appears in the autosampler vial, the bottom layer can be easily removed and discarded using a Pasteur pipet. The remaining pentane phase may be transferred to a second autosampler vial as a backup extract or for separate confirmation analysis.

11.2.2.3.1 The extract transfer into the autosampler vial must be performed in a quantitative manner. This may be done using a 1.00-mL syringe or a 2.00-mL graduated disposable pipet to accurately transfer 1.00 mL of sample extract to the autosampler vial where 10 μL of internal standard primary dilution standard (Sect. 7.4.2) solution can be added.

11.2.3 Discard the remaining contents of the sample vial. Shake off the last few drops with short, brisk wrist movements.

11.2.4 Reweigh the empty vial with the original cap and calculate the net weight of sample by difference to the nearest 0.1 g (Sect. 11.1.2 minus Sect. 11.2.4). This net weight (in grams) is equivalent to the volume of water (in mL) extracted, V_s.

11.2.5 The sample extract may be stored in a freezer (<-10°C) for a maximum of fourteen days before chromatographic analysis but no more than 24 hours at room temperature (i.e. on an autosampler rack). Due to the volatility of the extraction solvent, if the septum on a vial has been pierced, the crimp top or screw cap septum needs to be replaced immediately or the extract cannot be reanalyzed at a later time.

11.3 SAMPLE ANALYSIS

11.3.1 The recommended GC operating conditions are described in 6.9.2.1 and 6.9.2.2 along with recommended primary and confirmation columns. Retention data for the primary and confirmation columns are given in Table 1.

11.3.2 Inject 2 μL of the sample extract and record the resulting peak response. For optimum performance and precision, an autosampler for sample injection and a data system for signal processing are strongly recommended.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Identify sample components by comparison of retention times to retention data from the calibration standard analysis. If the retention time of an unknown compound corresponds, within limits (Sect. 12.2), to the retention time of a standard compound, then identification is considered positive.

12.2 The width of the retention time window used to make identifications should be based upon 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. Use the initial demonstration of capability retention time data as an initial means of determining acceptable retention time windows. Throughout the development of this method a retention time window of 1.0 % of the total analyte retention time was used.

12.3 Identification requires expert judgment when sample components are not resolved chromatographically, that is, when GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima). Whenever doubt exists over the identification of a peak in a chromatogram, confirmation is suggested by the use of a dissimilar column or by GC-MS when sufficient concentrations of analytes are present.

12.4 If the peak response exceeds the linear range of the calibration curve, the final extract should be diluted with the appropriate extraction solvent and reanalyzed. The analyst is not permitted to extrapolate beyond the concentration range of the calibration curve.

12.5 Calculate the uncorrected concentrations (C_i) of each analyte in the sample from the response factors or calibration curves generated in Sect. 10.2.1 or 10.3.1. do not use the daily calibration check standard to calculate amounts of method analytes in samples.

12.6 Calculate the corrected sample concentration as:

$$\text{Concentration, } \mu g/L = C_i \times \frac{50}{Vs},$$

where the sample volume, V_s in mL, is equivalent to the net sample weight in grams determined in Sect. 11.1.2 and Sect. 11.2.4.

13. METHOD PERFORMANCE

13.1 In a single laboratory, analyte recoveries from reagent water with MTBE as the extracting solvent, were determined at three concentration levels, Tables 2A through 4B. Results from the lowest fortified level were used to determine the analyte MDLs (11) listed

in Table 2. These MDLs along with the estimated detection limit (EDL) were determined in the following manner. EDLs are provided for informational purposes.

13.1.1 For each analyte, calculate the mean concentration and the standard deviation of this mean between the seven replicates. Multiply the student's t-value at 99% confidence and n-1 degrees of freedom (3.143 for seven replicates) by this standard deviation to yield a statistical estimate of the detection limit. This estimate is the MDL.

13.1.2 Since the statistical estimate is based on the precision of the analysis, an additional estimate of detection can be determined based upon the noise and drift of the baseline as well as precision. This estimate, known as the "EDL" is defined as either the MDL or a level of compound in a sample yielding a peak in the final extract with a signal to noise (S/N) ratio of approximately 5, whichever is greater.

13.1.3 These MDL determinations were conducted on both the primary (DB-1) and the confirmation (Rtx-1301) columns and are presented in Tables 2.A. through 2.D.

13.2 Analyte recoveries were also determined for reagent water with pentane as the extracting solvent. Two concentration levels were studied and the results are presented in Tables 8 and 9. Results from the lowest fortified level were used to determine the analyte MDLs (11) listed in Table 8. These MDLs along with the estimated detection limit (EDL) were determined in a manner analogous to that described in Sect. 13.1.1 through 13.1.2.

13.3 In a single laboratory, method precision and accuracy were evaluated using analyte recoveries from replicate buffered/dechlorinated (both NH_4Cl and Na_2SO_3) matrices with MTBE as the extracting solvent. The matrices studied included; fulvic acid fortified reagent water and ground water displaying a high $CaCO_3$ content. The results for these are presented in Tables 3.A. through 6.B. These matrices were fortified using outside source analyte solutions (except for the pesticides and herbicides) to assess accuracy and eight replicate analyses were conducted to assess precision.

13.4 Holding time studies were conducted for buffered/dechlorinated reagent water and tap water. Holding studies were also conducted on MTBE sample extracts from these two matrices. Results indicated that analytes were stable in these water matrices stored at 4°C.

13.5 MTBE and pentane extracts holding studies indicated the analytes were stable for 14 days when stored in a freezer at <-10°C.

13.6 Chromatograms of a fortified, buffered/NH_4Cl dechlorinated reagent water extract are presented as Figures 1 through 3. In the chromatograms of Figures 1 and 2, the elution of the method analytes

from a MTBE extract can be seen on the primary DB-1 column and the confirmation Rtx-1301 column, respectively. Figure 3 shows the elution of the method analytes from a pentane extract, using a modified temperature program, on the primary DB-1 column. Analyte numerical peak identification, retention time and fortified concentrations are presented for information purposes only in Tables 10, 11 and 12 for Figures 1, 2 and 3, respectively.

13.7 **IMPORTANT NOTICE:** All demonstration data presented in Section 17 using MTBE as the extracting solvent, was obtained using NaCl as the salt. A recent report (19) indicated elevated recoveries (via synthesis) of some brominated DBPs when NaCl was used in the extraction process, due to the inevitable presence of bromide impurities in the NaCl. This phenomenon has been confirmed by the authors of this method in samples from chlorinated water systems that were not extracted immediately after the NaCl was added. Significant effects can be seen if extraction is delayed for as little as 15 minutes after the addition of the NaCl. For this reason, the use of Na_2SO_4 is strongly recommended over NaCl for MTBE extraction of DBPs. Although less method validation data have been obtained for the Na_2SO_4 option, sufficient data have been collected to indicate that it is equivalent or superior to NaCl in salting out the method analytes, and has no observed negative effect on precision or accuracy.

14. POLLUTION PREVENTION

14.1 This method is a micro-extraction procedure which uses a minimal amount of extraction solvent per sample. This microextraction procedure reduces the hazards involved with handling large volumes of potentially harmful organic solvents needed for conventional liquid-liquid extractions.

14.2 For information about pollution prevention that may be applicable to laboratory operations, consult "Less is Better: Laboratory Chemical Management for Waste Reduction", available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

15. WASTE MANAGEMENT

15.1 Due to the nature of this method, there is little need for waste management. No large volumes of solvents or hazardous chemicals are used. The matrices of concern are finished drinking water or source water. However, the Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations, and that laboratories protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult "The Waste Management

Manual for Laboratory Personnel," also available from the American Chemical Society at the address in Sect. 14.2.

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TABLE 1. RETENTION TIME DATA USING MTBE

ANALYTE	Column A[a] Retention Time minutes	Column B[b] Retention Time minutes
Chloroform	7.04	7.73
1,1,1-Trichloroethane	8.64	7.99
Carbon Tetrachloride	9.94	8.36
Trichloroacetonitrile	10.39	10.35
Dichloroacetonitrile	12.01	25.21
Bromodichloromethane	12.42	15.28
Trichloroethylene	12.61	11.96
Chloral Hydrate	13.41	NR [c]
1,1-Dichloro-2-Propanone	14.96	20.50
1,1,2-Trichloroethane	19.91	25.01
Chloropicrin	23.10	23.69
Dibromochloromethane	23.69	26.32
Bromochloroacetonitrile	24.03	29.86
1,2-Dibromoethane (EDB)	24.56	26.46
Tetrachloroethylene	26.24	24.77
1,1,1-Trichloropropanone	27.55	28.47
Bromoform	29.17	30.36
Dibromoacetonitrile	29.42	32.77
1,2,3-Trichloropropane	30.40	31.73
1,2-Dibromo-3-chloropropane (DBCP)	35.28	36.11
Hexachlorocyclopentadiene	40.33	39.53
Trifluralin	45.17	45.43
Simazine	46.27	48.56[d]
Atrazine	46.55	48.56[d]
Hexachlorobenzene	47.39	46.47
Lindane (gamma-BHC)	47.95	49.68
Metribuzin	50.25	53.92
Bromacil	52.09	59.60

TABLE 1. RETENTION TIME DATA USING MTBE (cont'd)

ANALYTE	Column A[a] Retention Time minutes	Column B[b] Retention Time minutes
Alachlor	52.25	54.38
Cyanazine	53.43	59.89
Heptachlor	53.72	53.15
Metolachlor	55.44	57.07
Heptachlor Epoxide	58.42	59.05
Endrin	64.15	65.24
Endrin Aldehyde	65.46	71.56
Endrin Ketone	72.33	81.28
Methoxychlor	73.53	76.73
Surrogate: Decafluorobiphenyl	36.35	36.28
Internal Standard: Bromofluorobenzene	31.00	31.30

(a) **Column A** - 0.25 mm ID x 30 m fused silica capillary with chemically bonded methyl polysiloxane phase (J&W, **DB-1**, 1.0 µm film thickness or equivalent). The linear velocity of the helium carrier is established at 25 cm/sec at 35°C.

The column oven is temperature programmed as follows:

[1] HOLD at 35°C for 22 min
[2] INCREASE to 145°C at 10°C/min and hold at 145°C for 2 min
[3] INCREASE to 225°C at 20°C/min and hold at 225°C for 15 min
[4] INCREASE to 260°C at 10°C/min and hold at 260°C for 30 min. or until all expected compounds have eluted.

Injector temperature: 200°C
Detector temperature: 290°C

(b) **Column B** - 0.25 mm ID x 30 m with chemically bonded 6 % cyanopropylphenyl/94 % dimethyl polysiloxane phase (Restek, **Rtx-1301**, 1.0 µm film thickness or equivalent). The linear velocity of the helium carrier gas is established at 25 cm/sec at 35°C.

The column oven is temperature programmed exactly as indicated for column A, above. The same temperature program is utilized to allow for simultaneous confirmation analysis.

(c) There is no retention time for this analyte since it does not separate into a discreet peak on the Rtx-1301.

(d) Atrazine and simazine coelute on the confirmation column.

TABLE 2.A. METHOD DETECTION LIMIT USING MTBE
NH_4Cl PRESERVED REAGENT WATER ON PRIMARY DB-1 COLUMN

ANALYTE	Fort. Conc., µg/L	Obser.[a] Conc., µg/L	Avg. %Rec.	% RSD	MDL[b] µg/L	EDL[c] µg/L
Alachlor	0.327	0.384	117	2.13	0.025	0.500
Atrazine	0.633	0.764	121	3.56	0.082	0.324
Bromacil	0.094	0.099	105	10.05	0.030	0.055
Bromochloroacetonitrile	0.010	0.011	110	5.42	0.002	0.009
Bromodichloromethane	0.010	0.012	120	7.50	0.003	0.005
Bromoform	0.010	0.018	180	8.12	0.004	0.006
Carbon Tetrachloride	0.010	0.011	110	6.32	0.002	0.004
Chloral Hydrate	0.025	0.029	116	5.61	0.005	0.011
Chloropicrin	0.010	0.009	90	7.65	0.002	0.014
Chloroform	0.050	0.054	108	34.04	0.055	0.075
Cyanazine	0.567	0.757	134	13.93	0.316	0.685
Dibromoacetonitrile	0.010	0.016	160	12.78	0.006	0.010
Dibromochloromethane	0.010	0.011	110	4.55	0.001	0.007
1,2-Dibromo-3-chloropropane	0.010	0.020	200	15.15	0.009	0.009
1,2-Dibromoethane	0.010	0.020	200	12.54	0.008	0.008
Dichloroacetonitrile	0.010	0.009	90	4.28	0.001	0.005
1,1-Dichloro-2-propanone	0.010	0.011	110	6.22	0.002	0.007
Endrin	0.016	0.023	144	2.57	0.002	0.011
Endrin Aldehyde	0.022	0.023	105	2.25	0.002	0.010
Endrin Ketone	0.016	0.016	100	5.14	0.002	0.020
Heptachlor	0.047	0.062	132	43.65	0.081	0.081
Heptachlor Epoxide	0.044	0.050	114	1.64	0.002	0.030
Hexachlorobenzene	0.006	0.006	100	5.44	0.001	0.006
Hexachlorocyclopentadiene	0.019	0.019	100	31.81	0.018	0.022
Lindane (g-BHC)	0.009	0.015	167	9.89	0.004	0.016
Methoxychlor	0.063	0.057	90	4.85	0.008	0.046
Metolachlor	0.219	0.254	116	3.20	0.024	0.146
Metribuzin	0.062	0.100	161	12.45	0.037	0.037
Simazine	0.625	0.794	127	5.95	0.142	0.431

TABLE 2.A. METHOD DETECTION LIMIT USING MTBE (cont'd)
NH_4Cl PRESERVED REAGENT WATER ON PRIMARY DB-1 COLUMN

ANALYTE	Fort. Conc., µg/L	Obser.[a] Conc., µg/L	Avg. %Rec.	% RSD	MDL[b] µg/L	EDL[c] µg/L
Tetrachloroethylene	0.010	0.012	120	5.04	0.002	0.004
Trichloroacetonitrile	0.010	0.010	100	5.31	0.002	0.004
1,1,1-Trichloroethane	0.010	0.013	130	12.35	0.005	0.005
1,1,2-Trichloroethane	0.140	0.124	89	3.27	0.012	0.040
Trichloroethylene	0.010	0.008	80	8.68	0.002	0.008
1,2,3-Trichloropropane	0.156	0.137	88	1.95	0.008	0.028
1,1,1-Trichloro-2-propanone	0.010	0.027	270	20.53	0.016	0.016
Trifluralin	0.022	0.026	118	3.89	0.003	0.010
Surrogate ===> Decafluorobyphenyl	10.0	10.8	108	2.38		

(a) Based upon the analysis of eight replicate MTBE sample extracts.
(b) MDL designates the statistically derived MDL and is calculated by multiplying the standard deviation of the eight replicates by the student's t-value (2.998) appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.
(c) Estimated Detection Limit (EDL) -- Defined as either the MDL or a level of compound in a sample yielding a peak in the final extract with a signal to noise (S/N) ratio of approximately 5, whichever is greater.

TABLE 2.B. METHOD DETECTION LIMIT USING MTBE
NH_4Cl PRESERVED REAGENT WATER ON CONFIRMATION Rtx-1301 COLUMN

ANALYTE	Fort. Conc., µg/L	Obser.[a] Conc., µg/L	Avg. %Rec.	%RSD	MDL[b] µg/L	EDL[c] µg/L
Alachlor	0.109	0.107	98	1.70	0.005	0.076
Bromacil	0.094	0.134	143	11.65	0.047	0.071
Bromochloroacetonitrile	0.010	0.008	80	9.49	0.002	0.015
Bromodichloromethane	0.010	0.012	120	4.34	0.002	0.006
Bromoform	0.010	0.015	150	29.51	0.013	0.013
Carbon Tetrachloride	0.010	0.011	110	18.70	0.006	0.006
Chloropicrin	0.010	NR [d]	NR	NR	NR	0.062
Chloroform	0.010	0.059	590	2.82	0.005	0.008
Cyanazine	0.189	0.279	148	7.56	0.063	0.065
Dibromoacetonitrile	0.010	0.010	100	4.87	0.001	0.007
Dibromochloromethane	0.010	0.021	210	29.30	0.018	0.018
1,2-Dibromo-3-chloropropane	0.010	0.020	200	9.95	0.006	0.024
1,2-Dibromoethane	0.010	0.039	390	6.44	0.007	0.007
Dichloroacetonitrile	0.010	0.010	100	4.11	0.001	0.003
1,1-Dichloro-2-propanone	0.010	0.009	90	11.65	0.003	0.015
Endrin	0.016	0.025	156	4.09	0.003	0.015
Endrin Aldehyde	0.022	0.034	155	22.45	0.023	0.030
Endrin Ketone	0.047	0.049	104	5.49	0.008	0.047
Heptachlor	0.016	0.018	113	3.79	0.002	0.010
Heptachlor Epoxide	0.044	0.079	180	84.71	0.202	0.202
Hexachlorobenzene	0.006	0.006	100	16.47	0.003	0.011
Hexachlorocyclopentadiene	0.019	NR	NR	NR		0.327
Lindane (g-BHC)	0.009	0.011	122	6.09	0.002	0.009
Methoxychlor	0.188	0.221	118	3.53	0.023	0.041
Metolachlor	0.219	0.280	128	1.45	0.012	0.268
Metribuzin	0.062	0.076	123	2.17	0.005	0.013
Simazine/Atrazine	1.26 [e]	1.619	129	2.48	0.121	0.629
Tetrachloroethylene	0.010	0.012	120	6.97	0.002	0.003
Trichloroacetonitrile	0.010	0.006	60	16.01	0.003	0.010

TABLE 2.B. METHOD DETECTION LIMIT USING MTBE (cont'd)
NH_4Cl PRESERVED REAGENT WATER ON CONFIRMATION Rtx-1301 COLUMN

ANALYTE	Fort. Conc., µg/L	Obser.[a] Conc., µg/L	Avg. %Rec.	%RSD	MDL[b] µg/L	EDL[c] µg/L
1,1,1-Trichloroethane	0.010	0.020	200	19.22	0.012	0.012
1,1,2-Trichloroethane	0.140	0.133	95	3.40	0.014	0.020
Trichloroethylene	0.010	0.009	90	13.77	0.004	0.007
1,2,3-Trichloropropane	0.156	0.160	103	3.11	0.015	0.114
1,1,1-Trichloro-2-propanone	0.010	0.011	110	7.11	0.002	0.010
Trifluralin	0.022	0.024	109	3.07	0.002	0.006
Surrogate ===> Decafluorobyphenyl	10.0	10.6	106	1.78		

(a) Based upon the analysis of eight replicate MTBE sample extracts.
(b) MDL designates the statistically derived MDL and is calculated by multiplying the standard deviation of the eight replicates by the student's t-value (2.998) appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.
(c) Estimated Detection Limit (EDL) -- Defined as either the MDL or a level of compound in a sample yielding a peak in the final extract with a signal to noise (S/N) ratio of approximately 5, whichever is greater.
(d) NR indicates Not Reported since their was no peak detected for the eight replicate MDL determination.
(e) The concentration of atrazine and simazine were added together for this determination since these two peaks coelute on the confirmation column.

TABLE 3.A. PRECISION AND ACCURACY RESULTS USING MTBE[a]
NH_4Cl PRESERVED FORTIFIED REAGENT WATER ON THE PRIMARY DB-1 COLUMN

ANALYTE	Fortified Conc., µg/L	Mean Meas. Conc., µg/L	%RSD	Percent Recovery
Alachlor	2.18	2.40	1.47	110
Atrazine	12.6	12.4	1.71	98
Bromacil	1.88	1.85	3.13	98
Bromochloroacetonitrile	5.00	5.69	0.71	114
Bromodichloromethane	5.00	4.94	1.14	99
Bromoform	5.00	5.07	0.72	101
Carbon Tetrachloride	5.00	5.07	1.72	101
Chloropicrin	5.00	5.32	1.38	106
Chloroform	5.00	5.10	1.30	102
Cyanazine	3.77	3.89	2.85	103
Dibromoacetonitrile	5.00	5.78	1.43	116
Dibromochloromethane	5.00	4.87	0.71	97
1,2-Dibromo-3-chloropropane	5.00	5.11	0.59	102
1,2-Dibromoethane	5.00	4.96	0.73	99
Dichloroacetonitrile	5.00	5.35	0.57	107
1,1-Dichloro-2-propanone	5.00	5.08	0.72	102
Endrin	0.311	0.337	1.40	108
Endrin Aldehyde	0.437	0.503	1.32	115
Endrin Ketone	0.310	0.319	1.52	103
Heptachlor	0.313	0.351	2.84	112
Heptachlor Epoxide	0.875	0.968	0.65	111
Hexachlorobenzene	0.124	0.137	0.89	110
Hexachlorocyclopentadiene	0.374	0.368	1.18	98
Lindane (g-BHC)	0.188	0.199	1.41	106
Methoxychlor	1.26	1.48	2.84	117
Metolachlor	4.39	4.89	0.87	111
Metribuzin	1.24	1.21	3.94	97
Simazine	12.5	13.1	2.02	105
Tetrachloroethylene	5.00	5.07	1.62	101
Trichloroacetonitrile	5.00	5.73	1.34	115

TABLE 3.A. PRECISION AND ACCURACY RESULTS USING MTBE[a] (cont'd)
NH_4Cl PRESERVED FORTIFIED REAGENT WATER ON THE PRIMARY DB-1 COLUMN

ANALYTE	Fortified Conc., µg/L	Mean Meas. Conc., µg/L	%RSD	Percent Recovery
1,1,1-Trichloroethane	5.00	5.02	1.22	100
1,1,2-Trichloroethane	2.80	2.92	0.91	104
Trichloroethylene	5.00	4.87	1.48	97
1,2,3-Trichloropropane	3.12	3.08	0.62	99
1,1,1-Trichloro-2-propanone	5.00	5.30	0.81	106
Trifluralin	0.439	0.503	1.09	115
Surrogate ===> Decafluorobyphenyl	10.0	10.4	1.93	104

(a) Based upon the analysis of eight replicate MTBE sample extracts.

TABLE 3.B. PRECISION AND ACCURACY RESULTS USING MTBE [a]
Na_2SO_3 PRESERVED FORTIFIED REAGENT WATER ON THE PRIMARY DB-1 COLUMN

ANALYTE	Fortified Conc., µg/L	Mean Meas. Conc., µg/L	%RSD	Percent Recovery
Bromodichloromethane	5.00	4.91	1.49	98
Bromoform	5.00	5.05	1.32	101
Carbon Tetrachloride	5.00	5.08	2.24	102
Chloral Hydrate	1.00	0.93	1.81	93
Chloroform	5.00	4.96	1.71	99
Dibromochloromethane	5.00	4.83	1.43	97
1,2-Dibromo-3-chloropropane	5.00	5.07	1.04	101
1,2-Dibromoethane	5.00	4.90	1.02	98
Tetrachloroethylene	5.00	5.06	2.53	101
1,1,1-Trichloroethane	5.00	5.01	2.11	100
Trichloroethylene	5.00	4.81	2.21	96
Surrogate ===> Decafluorobyphenyl	10.0	10.2	1.88	102

(a) Based upon the analysis of eight replicate MTBE sample extracts.

TABLE 3.C. PRECISION AND ACCURACY RESULTS USING MTBE[a]
NH_4Cl PRESERVED FORTIFIED REAGENT WATER ON THE CONFIRMATION
Rtx-1301 COLUMN

ANALYTE	Fortified Conc., µg/L	Mean Meas. Conc., µg/L	%RSD	Percent Recovery
Alachlor	2.18	2.26	0.81	104
Bromacil	1.88	1.77	3.50	94
Bromochloroacetonitrile	5.00	5.59	0.86	112
Bromodichloromethane	5.00	4.92	1.02	98
Bromoform	5.00	5.04	0.73	101
Carbon Tetrachloride	5.00	4.90	1.72	98
Chloropicrin	5.00	5.24	1.20	105
Chloroform	5.00	5.05	1.20	101
Cyanazine	3.77	3.90	2.30	103
Dibromoacetonitrile	5.00	5.47	0.58	109
Dibromochloromethane	5.00	5.04	0.90	101
1,2-Dibromo-3-chloropropane	5.00	5.12	0.54	102
1,2-Dibromoethane	5.00	5.09	1.82	102
Dichloroacetonitrile	5.00	5.30	0.55	106
1,1-Dichloro-2-propanone	5.00	4.94	0.70	99
Endrin	0.310	0.335	2.08	108
Endrin Aldehyde	0.440	0.490	2.13	111
Endrin Ketone	0.310	0.317	1.63	102
Heptachlor	0.310	0.349	1.06	113
Heptachlor Epoxide	0.880	0.978	0.80	111
Hexachlorobenzene	0.124	0.135	0.59	109
Hexachlorocyclopentadiene	0.374	0.474	7.19	127
Lindane (g-BHC)	0.188	0.205	0.75	109
Methoxychlor	1.26	1.42	2.30	113
Metolachlor	4.39	4.57	3.43	104
Metribuzin	1.24	1.29	1.15	104
Simazine/Atrazine	25.1 [b]	30.0	1.11	119
Tetrachloroethylene	5.00	4.93	1.65	99
Trichloroacetonitrile	5.00	5.48	1.31	110

TABLE 3.C. PRECISION AND ACCURACY RESULTS USING MTBE [a] (cont'd)
NH_4Cl PRESERVED FORTIFIED REAGENT WATER ON THE CONFIRMATION
Rtx-1301 COLUMN

ANALYTE	Fortified Conc., µg/L	Mean Meas. Conc., µg/L	%RSD	Percent Recovery
1,1,1-Trichloroethane	5.00	4.87	1.66	97
1,1,2-Trichloroethane	2.80	2.76	1.52	98
Trichloroethylene	5.00	4.87	1.52	97
1,2,3-Trichloropropane	3.12	3.07	0.88	98
1,1,1-Trichloro-2-propanone	5.00	4.90	0.89	98
Trifluralin	0.440	0.486	0.93	110
Surrogate ===> Decafluorobyphenyl	10.0	10.6	1.96	106

(a) Based upon the analysis of eight replicate MTBE sample extracts.
(b) Simazine and atrazine coelute on the confirmation column and therefore there results were added together.

TABLE 3.D. PRECISION AND ACCURACY RESULTS USING MTBE [a]
Na_2SO_3 PRESERVED FORTIFIED REAGENT WATER ON THE CONFIRMATION Rtx-1301 COLUMN

ANALYTE	Fortified Conc., µg/L	Mean Meas. Conc., µg/L	%RSD	Percent Recovery
Bromodichloromethane	5.00	4.88	1.53	98
Bromoform	5.00	5.03	1.19	101
Carbon Tetrachloride	5.00	4.90	2.27	98
Chloroform	5.00	4.90	1.58	98
Dibromochloromethane	5.00	5.15	1.78	103
1,2-Dibromo-3-chloropropane	5.00	5.07	0.94	101
1,2-Dibromoethane	5.00	5.02	0.82	100
Tetrachloroethylene	5.00	4.89	2.47	98
1,1,1-Trichloroethane	5.00	4.84	2.18	97
Trichloroethylene	5.00	4.83	2.06	97
Surrogate ===> Decafluorobyphenyl	10.0	10.3	1.64	103

(a) Based upon the analysis of eight replicate MTBE sample extracts.

TABLE 4.A. PRECISION AND ACCURACY RESULTS USING MTBE[a]
NH_4Cl PRESERVED FORTIFIED REAGENT WATER ON THE PRIMARY DB-1 COLUMN

ANALYTE	Fortified Conc., µg/L	Mean Meas. Conc., µg/L	%RSD	Percent Recovery
Alachlor	0.436	0.515	1.84	118
Atrazine	2.520	2.994	1.95	119
Bromacil	0.376	0.376	3.32	100
Bromochloroacetonitrile	0.250	0.281	1.57	113
Bromodichloromethane	0.250	0.276	1.42	110
Bromoform	0.250	0.260	1.62	104
Carbon Tetrachloride	0.250	0.299	1.60	120
Chloropicrin	0.250	0.285	2.03	114
Chloroform	0.250	0.264	1.94	105
Cyanazine	0.754	0.761	1.97	101
Dibromoacetonitrile	0.250	0.276	1.89	110
Dibromochloromethane	0.250	0.266	1.20	106
1,2-Dibromo-3-chloropropane	0.250	0.261	1.82	104
1,2-Dibromoethane	0.250	0.274	1.89	110
Dichloroacetonitrile	0.250	0.268	1.12	107
1,1-Dichloro-2-propanone	0.250	0.261	0.91	105
Endrin	0.062	0.073	2.65	117
Endrin Aldehyde	0.087	0.108	1.29	123
Endrin Ketone	0.062	0.062	0.76	100
Heptachlor	0.063	0.059	10.29	93
Heptachlor Epoxide	0.175	0.206	0.90	118
Hexachlorobenzene	0.025	0.030	3.77	120
Hexachlorocyclopentadiene	0.075	0.074	3.22	99
Lindane (g-BHC)	0.038	0.047	2.74	125
Methoxychlor	0.252	0.298	3.24	118
Metolachlor	0.878	1.056	1.00	120
Metribuzin	0.248	0.264	2.15	107
Simazine	2.500	2.960	2.71	118
Tetrachloroethylene	0.250	0.263	1.93	105
Trichloroacetonitrile	0.250	0.291	1.02	116

TABLE 4.A. PRECISION AND ACCURACY RESULTS USING MTBE[a] (cont'd)
NH_4Cl PRESERVED FORTIFIED REAGENT WATER ON THE PRIMARY DB-1 COLUMN

ANALYTE	Fortified Conc., µg/L	Mean Meas. Conc., µg/L	%RSD	Percent Recovery
1,1,1-Trichloroethane	0.250	0.291	3.65	116
1,1,2-Trichloroethane	0.560	0.531	0.85	95
Trichloroethylene	0.250	0.252	1.20	101
1,2,3-Trichloropropane	0.624	0.595	0.83	95
1,1,1-Trichloro-2-propanone	0.250	0.286	3.72	114
Trifluralin	0.088	0.106	1.50	121
Surrogate ===> Decafluorobyphenyl	10.0	10.9	2.49	109

(a) Based upon the analysis of eight replicate MTBE sample extracts.

TABLE 4.B. PRECISION AND ACCURACY RESULTS USING MTBE[a]
Na_2SO_3 PRESERVED FORTIFIED REAGENT WATER ON THE PRIMARY DB-1 COLUMN

ANALYTE	Fortified Conc., µg/L	Mean Meas. Conc., µg/L	%RSD	Percent Recovery
Bromodichloromethane	0.250	0.270	1.77	108
Bromoform	0.250	0.257	2.04	103
Carbon Tetrachloride	0.250	0.287	5.18	115
Chloral Hydrate	0.250	0.258	4.12	103
Chloroform	0.250	0.248	1.88	99
Dibromochloromethane	0.250	0.261	1.36	105
1,2-Dibromo-3-chloropropane	0.250	0.258	1.26	103
1,2-Dibromoethane	0.250	0.243	0.90	97
Tetrachloroethylene	0.250	0.256	1.95	102
1,1,1-Trichloroethane	0.250	0.276	5.72	110
Trichloroethylene	0.250	0.246	1.01	98
Surrogate ===> Decafluorobyphenyl	10.0	10.6	3.51	106

(a) Based upon the analysis of eight replicate MTBE sample extracts.

TABLE 5.A. PRECISION AND ACCURACY RESULTS USING MTBE[a]
NH_4Cl PRESERVED FORTIFIED FULVIC ACID ENRICHED REAGENT WATER[b] ON THE PRIMARY DB-1 COLUMN

ANALYTE	Fortified Conc., µg/L	Mean Meas. Conc., µg/L	%RSD	Percent Recovery
Alachlor	2.18	2.38	1.57	109
Atrazine	12.6	11.6	2.31	92
Bromacil	1.88	1.89	3.33	101
Bromochloroacetonitrile	1.00	1.11	1.51	111
Bromodichloromethane	1.00	0.87	1.93	87
Bromoform	1.00	0.97	1.50	97
Carbon Tetrachloride	1.00	0.88	3.91	88
Chloropicrin	1.00	1.13	2.49	113
Chloroform	1.00	1.03	2.47	103
Cyanazine	3.77	4.02	3.99	107
Dibromoacetonitrile	1.00	1.14	1.61	114
Dibromochloromethane	1.00	0.89	1.78	89
1,2-Dibromo-3-chloropropane	1.00	0.93	1.37	93
1,2-Dibromoethane	1.00	0.96	1.58	96
Dichloroacetonitrile	1.00	1.05	0.98	105
1,1-Dichloro-2-propanone	1.00	1.03	0.90	103
Endrin	0.311	0.325	3.50	104
Endrin Aldehyde	0.437	0.505	1.99	116
Endrin Ketone	0.310	0.319	2.62	103
Heptachlor	0.313	0.358	5.45	114
Heptachlor Epoxide	0.875	0.978	1.28	112
Hexachlorobenzene	0.124	0.139	1.82	112
Hexachlorocyclopentadiene	0.374	0.363	3.55	97
Lindane (g-BHC)	0.188	0.206	1.79	110
Methoxychlor	1.26	1.41	4.78	112
Metolachlor	4.39	4.84	1.27	110
Metribuzin	1.24	1.30	2.08	105
Simazine	12.5	12.0	1.09	96
Tetrachloroethylene	1.00	0.90	4.02	90

TABLE 5.A. PRECISION AND ACCURACY RESULTS USING MTBE [a] (cont'd)
NH_4Cl PRESERVED FORTIFIED FULVIC ACID ENRICHED REAGENT WATER[b] ON THE PRIMARY DB-1 COLUMN

ANALYTE	Fortified Conc., µg/L	Mean Meas. Conc., µg/L	%RSD	Percent Recovery
Trichloroacetonitrile	1.00	1.11	2.41	111
1,1,1-Trichloroethane	1.00	0.96	3.89	96
1,1,2-Trichloroethane	2.80	2.81	2.89	100
Trichloroethylene	1.00	0.93	3.55	93
1,2,3-Trichloropropane	3.12	2.92	0.82	93
1,1,1-Trichloro-2-propanone	1.00	1.10	2.05	110
Trifluralin	0.439	0.517	1.27	118
Surrogate ===> Decafluorobyphenyl	10.0	10.4	1.84	104

(a) Based upon the analysis of eight replicate MTBE sample extracts.
(b) Reagent water fortified at 1.0 mg/L with fulvic acid extracted from Ohio River water. Sample simulated high TOC matrix.

TABLE 5.B. PRECISION AND ACCURACY RESULTS USING MTBE [a]
Na_2SO_3 PRESERVED FORTIFIED FULVIC ACID ENRICHED REAGENT WATER ON THE PRIMARY DB-1 COLUMN

ANALYTE	Fortified Conc., µg/L	Mean Meas. Conc., µg/L	%RSD	Percent Recovery
Bromodichloromethane	1.00	0.87	1.13	87
Bromoform	1.00	0.97	1.28	97
Carbon Tetrachloride	1.00	0.88	1.71	88
Chloral Hydrate	1.00	0.90	0.95	90
Chloroform	1.00	0.96	1.51	96
Dibromochloromethane	1.00	0.88	1.25	88
1,2-Dibromo-3-chloropropane	1.00	0.92	0.98	92
1,2-Dibromoethane	1.00	0.93	1.01	93
Tetrachloroethylene	1.00	0.90	2.07	90
1,1,1-Trichloroethane	1.00	0.97	1.57	97
Trichloroethylene	1.00	0.94	1.62	94
Surrogate ===> Decafluorobyphenyl	10.0	10.6	2.56	106

(a) Based upon the analysis of eight replicate MTBE sample extracts.
(b) Reagent water fortified at 1.0 mg/L with fulvic acid extracted from Ohio River water. Sample simulated high TOC matrix.

TABLE 6.A. PRECISION AND ACCURACY RESULTS USING MTBE[a]
NH_4Cl PRESERVED FORTIFIED GROUND WATER[b] ON THE PRIMARY
DB-1 COLUMN

ANALYTE	Unfort. matrix conc., µg/L	Fort. Conc., µg/L	Mean Meas. Conc., µg/L	%RSD	Percent Recovery
Alachlor	ND [c]	8.72	9.01	2.93	103
Atrazine	ND	50.4	46.7	3.30	93
Bromacil	ND	7.52	6.53	7.81	87
Bromochloroacetonitrile	ND	5.00	5.74	1.38	115
Bromodichloromethane	1.70	5.00	6.68	2.59	100
Bromoform	20.1	5.00	24.8	1.61	95
Carbon Tetrachloride	ND	5.00	4.99	6.65	100
Chloropicrin	ND	5.00	5.29	3.59	106
Chloroform	0.571	5.00	5.73	3.68	103
Cyanazine	ND	15.1	15.4	6.07	102
Dibromoacetonitrile	ND	5.00	5.84	1.59	117
Dibromochloromethane	6.00	5.00	11.1	1.89	102
1,2-Dibromo-3-chloropropane	ND	5.00	5.04	1.64	101
1,2-Dibromoethane	ND	5.00	4.87	1.90	97
Dichloroacetonitrile	ND	5.00	5.29	1.52	106
1,1-Dichloro-2-propanone	ND	5.00	5.01	1.30	100
Endrin	ND	1.24	1.32	4.81	106
Endrin Aldehyde	ND	1.75	1.91	2.36	109
Endrin Ketone	ND	1.24	1.22	3.77	98
Heptachlor	ND	1.25	1.33	4.46	106
Heptachlor Epoxide	ND	3.50	3.67	2.92	105
Hexachlorobenzene	ND	0.50	0.509	3.42	103
Hexachlorocyclopentadiene	ND	1.50	1.41	3.70	94
Lindane (g-BHC)	ND	0.75	0.773	1.91	103
Methoxychlor	ND	5.04	5.60	5.86	111
Metolachlor	ND	17.6	18.2	3.06	103
Metribuzin	ND	4.96	4.85	6.15	98
Simazine	ND	50.0	48.3	3.30	97
Tetrachloroethylene	ND	5.00	4.97	6.29	99

TABLE 6.A. PRECISION AND ACCURACY RESULTS USING MTBE[a] (cont'd)
NH_4Cl PRESERVED FORTIFIED GROUND WATER[b] ON THE PRIMARY DB-1 COLUMN

ANALYTE	Unfort. matrix conc., µg/L	Fort. Conc., µg/L	Mean Meas. Conc., µg/L	%RSD	Percent Recovery
Trichloroacetonitrile	ND	5.00	5.59	4.89	112
1,1,1-Trichloroethane	1.77	5.00	6.62	4.60	97
1,1,2-Trichloroethane	ND	11.2	10.4	2.98	93
Trichloroethylene	ND	5.00	4.74	5.78	95
1,2,3-Trichloropropane	0.340	12.5	12.5	3.92	97
1,1,1-Trichloro-2-propanone	ND	5.00	5.21	1.58	104
Trifluralin	ND	1.76	1.94	3.38	110
Surrogate ===> Decafluorobyphenyl		10.0	10.4	2.25	104

(a) Based upon the analysis of eight replicate MTBE sample extracts.
(b) Chlorinated ground water from a water source displaying a hardness of 460 mg/L as $CaCO_3$.
(c) ND indicates not detected above the EDL.

TABLE 6.B. PRECISION AND ACCURACY RESULTS USING MTBE[a]
Na_2SO_3 PRESERVED FORTIFIED GROUND WATER[b] ON THE PRIMARY DB-1 COLUMN

ANALYTE	Unfort. matrix conc., µg/L	Fort. Conc., µg/L	Mean Meas. Conc., µg/L	%RSD	Percent Recovery
Bromodichloromethane	1.77	5.00	6.64	1.70	97
Bromoform	20.5	5.00	24.6	1.63	82
Carbon Tetrachloride	ND [c]	5.00	4.99	2.72	100
Chloral Hydrate	ND	2.00	1.84	1.38	92
Chloroform	0.600	5.00	5.22	1.89	92
Dibromochloromethane	6.16	5.00	11.0	1.53	98
1,2-Dibromo-3-chloropropane	ND	5.00	5.01	1.19	100
1,2-Dibromoethane	ND	5.00	4.79	1.86	96
Tetrachloroethylene	ND	5.00	4.95	2.49	99
1,1,1-Trichloroethane	1.91	5.00	6.73	3.18	96
Trichloroethylene	ND	5.00	4.69	2.38	94
Surrogate ===> Decafluorobyphenyl		10.0	10.1	8.71	101

(a) Based upon the analysis of eight replicate MTBE sample extracts.
(b) Chlorinated ground water from a water source displaying a hardness of 460 mg/L as $CaCO_3$.
(c) ND indicates Not Detected above the detection limit.

TABLE 7. LABORATORY PERFORMANCE CHECK SOLUTION

Parameter	Analyte	Conc., µg/mL in MTBE or pentane	Acceptance Criteria
Instrument Sensitivity	Lindane (gamma-BHC)	0.000200	Detection of Analyte; Signal to Noise > 3
Chromatographic Performance	Hexachlorocyclopentadiene	0.0200	PGF between 0.80 and 1.15[a]
Column Performance	Bromodichloromethane Trichloroethylene	0.0300 0.0300	Resolution > 0.50[b]
	Bromacil Alachlor	0.0830 0.0830	Resolution > 0.50
Analyte Breakdown	Endrin	0.0300	%BD[c] < 20 %

[a] PGF = Peak Gaussian Factor. Calculated using the equation:

$$PGF = \frac{1.83 \times W(1/2)}{W(1/10)}$$

where W(1/2) is the peak width at half height and W(1/10) is the peak width at tenth height.

[b] Resolution between the two peaks as defined by the equation:

$$R = \frac{t}{W}$$

where t is the difference in elution times between the two peaks and W is the average peak width, at the baseline, of the two peaks.

[c] %BD = Percent Breakdown. Endrin breakdown calculated using the equation.

$$\%BD = \frac{(\text{AREA Endrin Ketone} + \text{AREA Endrin Aldehyde})}{(\text{AREA Endrin Ketone} + \text{AREA Endrin Aldehyde} + \text{AREA Endrin})} \times 100$$

Note: If laboratory EDL's differ from those listed in this method, concentrations of the LPC standard must be adjusted to be compatible with the laboratory EDL's.

TABLE 8. METHOD DETECTION LIMIT USING PENTANE
NH_4Cl PRESERVED REAGENT WATER ON PRIMARY DB-1 COLUMN

ANALYTE	Fort. Conc. µg/L	Observ.[b] Conc. µg/L	Avg. %Rec.	%RSD	MDL[c] µg/L	EDL[d] µg/L
Alachlor	0.109	0.095[a]	87	5.37	0.015	0.050
Atrazine	0.633	0.663	105	5.00	0.099	0.390
Bromacil	0.094	0.058	62	21.44	0.037	0.330
Bromochloroacetonitrile	0.040	0.047	118	3.61	0.005	0.026
Bromodichloromethane	0.040	0.054	135	42.05	0.068	0.068
Bromoform	0.040	0.033	83	20.60	0.020	0.035
Carbon Tetrachloride	0.040	0.060	150	27.76	0.050	0.050
Chloropicrin	0.040	0.045	113	4.25	0.006	0.023
Chloroform	0.040	0.110	275	24.36	0.080	0.080
Cyanazine	0.189	0.170[a]	90	13.37	0.068	0.200
Dibromoacetonitrile	0.040	0.046	115	3.84	0.005	0.030
Dibromochloromethane	0.040	0.050	125	5.48	0.008	0.026
1,2-Dibromo-3-chloropropane	0.040	0.053	133	5.39	0.009	0.017
1,2-Dibromomethane	0.040	0.053	133	19.85	0.032	0.032
Dichloroacetonitrile	0.040	0.037	93	20.09	0.022	0.042
1,1-Dichloro-2-propanone	0.040	0.042	105	4.86	0.006	0.022
Endrin	0.016	0.019	119	4.69	0.003	0.016
Endrin Aldehyde	0.022	0.023	105	5.52	0.004	0.022
Endrin Ketone	0.016	0.014	88	9.50	0.004	0.020
Heptachlor	0.016	0.011[a]	69	18.14	0.006	0.009
Heptachlor Epoxide	0.044	0.045	102	5.02	0.007	0.016
Hexachlorobenzene	0.0062	0.008	129	9.56	0.002	0.002
Hexachloropentadiene	0.040	0.022	55	24.42	0.016	0.016
Lindane (g-BHC)	0.0094	0.006	64	91.20	0.017	0.017
Methoxychlor	0.063	0.069	110	12.76	0.026	0.066
Metolachlor	0.219	0.267	122	10.35	0.083	0.172
Metribuzin	0.062	0.076	123	18.15	0.041	0.041
Simazine	0.625	0.662	106	9.42	0.187	0.420
Tetrachloroethylene	0.040	0.052	130	5.33	0.008	0.016

TABLE 8. METHOD DETECTION LIMIT USING PENTANE (cont'd)
NH_4Cl PRESERVED REAGENT WATER ON PRIMARY DB-1 COLUMN

ANALYTE	Fort. Conc. µg/L	Observ.[b] Conc. µg/L	Avg. %Rec.	%RSD	MDL[c] µg/L	EDL[d] µg/L
Trichloroacetonitrile	0.040	0.048	120	2.79	0.004	0.014
1,1,1-Trichloroethane	0.040	0.058	145	4.26	0.007	0.017
1,1,2-Trichloroethane	0.140	0.141	101	4.01	0.017	0.052
Trichloroethylene	0.040	0.064	160	21.80	0.042	0.042
1,2,3-Trichloropropane	0.156	0.151	97	3.54	0.016	0.116
1,1,1-Trichloro-2-propanone	0.040	0.045	113	3.65	0.005	0.024
Trifluralin	0.040	0.021	53	19.28	0.012	0.012
Surrogate ===> Decafluorobyphenyl	10.0	11.2	112	3.98		

(a) Quantitated from confirmation column due to baseline interference on primary column.
(b) Based upon the analysis of eight replicate pentane sample extracts.
(c) MDL designates the statistically derived MDL and is calculated by multiplying the standard deviation of the eight replicates by the student's t-value (2.998) appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.
(d) Estimated Detection Limit (EDL) -- Defined as either the MDL or a level of compound in a sample yielding a peak in the final extract with a signal to noise (S/N) ratio of approximately 5, whichever is greater.

TABLE 9. PRECISION AND ACCURACY RESULTS[a]
USING PENTANE
NH_4Cl PRESERVED FORTIFIED REAGENT WATER ON THE PRIMARY DB-1 COLUMN

ANALYTE	Fortified Conc., µg/L	Mean Meas. Conc., µg/L	%RSD	Percent Recovery
Alachlor	2.18	1.98 [b]	5.09	91
Atrazine	12.6	12.0	3.09	95
Bromacil	1.88	1.74	2.95	93
Bromochloroacetonitrile	5.00	4.63	3.18	93
Bromodichloromethane	5.00	4.46	4.07	89
Bromoform	5.00	4.81	2.76	96
Carbon Tetrachloride	5.00	4.61	4.14	92
Chloropicrin	5.00	4.51	2.46	90
Chloroform	5.00	4.95	2.90	99
Cyanazine	3.77	4.00 [b]	2.59	106
Dibromoacetonitrile	5.00	4.80	2.87	96
Dibromochloromethane	5.00	4.23	3.38	85
1,2-Dibromo-3-chloropropane	5.00	4.73	3.00	95
1,2-Dibromoethane	5.00	4.69	2.54	94
Dichloroacetonitrile	5.00	4.73	3.39	95
1,1-Dichloro-2-propanone	5.00	4.78	3.04	96
Endrin	0.311	0.312	2.61	100
Endrin Aldehyde	0.437	0.443	2.29	101
Endrin Ketone	0.310	0.311	2.10	100
Heptachlor Epoxide	0.875	0.866	2.11	99
Heptachlor	0.313[b]	0.30	3.47	97
Hexachlorobenzene	0.124	0.123	2.51	99
Hexachlorocyclopentadiene	0.374	0.384	3.30	103
Lindane (g-BHC)	0.188	0.176	10.23	94
Methoxychlor	1.26	1.28	3.03	102
Metolachlor	4.39	4.42	2.36	101
Metribuzin	1.24	1.34	2.13	108
Simazine	12.5	12.5	2.20	100
Tetrachloroethylene	5.00	4.46	3.67	89

TABLE 9. PRECISION AND ACCURACY RESULTS[a] (cont'd)
USING PENTANE
NH_4Cl PRESERVED FORTIFIED REAGENT WATER ON THE PRIMARY DB-1 COLUMN

ANALYTE	Fortified Conc., µg/L	Mean Meas. Conc., µg/L	%RSD	Percent Recovery
Trichloroacetonitrile	5.00	5.07	4.02	101
1,1,1-Trichloroethane	5.00	4.70	3.39	94
1,1,2-Trichloroethane	2.80	2.62	2.03	93
Trichloroethylene	5.00	4.84	2.98	97
1,2,3-Trichloropropane	3.12	3.13	1.76	100
1,1,1-Trichloro-2-propanone	5.00	4.88	2.80	98
Trifluralin	0.439	0.446	2.74	102
Surrogate===> Decafluorobyphenyl	10.0	10.7	1.88	107

(a) Based upon the analysis of eight replicate pentane sample extracts.

(b) Quantitated from confirmation column due to baseline interference on primary column.

TABLE 10. ANALYTE PEAK IDENTIFICATION, RETENTION TIMES, CONCENTRATIONS AND CONDITIONS USING MTBE FOR FIGURE 1
NH_4Cl PRESERVED FORTIFIED REAGENT WATER ON THE
PRIMARY DB-1 COLUMN

PEAK #	ANALYTE	Retention Time[a] minutes	Conc. µg/L
1	Chloroform	7.04	5.00
2	1,1,1-Trichloroethane	8.64	5.00
3	Carbon Tetrachloride	9.94	5.00
4	Trichloroacetonitrile	10.39	5.00
5	Dichloroacetonitrile	12.01	5.00
6	Bromodichloromethane	12.42	5.00
7	Trichloroethylene	12.61	5.00
8	Chloral Hydrate	13.41	5.00
9	1,1-Dichloro-2-Propanone	14.96	5.00
10	1,1,2-Trichloroethane	19.91	44.8
11	Chloropicrin	23.10	5.00
12	Dibromochloromethane	23.69	5.00
13	Bromochloroacetonitrile	24.03	5.00
14	1,2-Dibromoethane (EDB)	24.56	5.00
15	Tetrachloroethylene	26.24	5.00
16	1,1,1-Trichloropropanone	27.55	5.00
17	Bromoform	29.17	5.00
18	Dibromoacetonitrile	29.42	5.00
19	1,2,3-Trichloropropane	30.40	50.0
20	1,2-Dibromo-3-chloropropane (DBCP)	35.28	5.00
21	Surrogate: Decafluorobiphenyl	36.35	10.0
22	Hexachlorocyclopentadiene	40.33	28.0
23	Trifluralin	45.17	7.04
24	Simazine	46.27	200
25	Atrazine	46.55	200
26	Hexachlorobenzene	47.39	1.98
27	Lindane (gamma-BHC)	47.95	30.1
28	Metribuzin	50.25	19.9

TABLE 10. ANALYTE PEAK IDENTIFICATION, RETENTION TIMES, CONCENTRATIONS AND CONDITIONS USING MTBE FOR FIGURE 1 (cont'd)
NH_4Cl PRESERVED FORTIFIED REAGENT WATER ON THE
PRIMARY DB-1 COLUMN

PEAK #	ANALYTE	Retention Time[a] minutes	Conc. µg/L
29	Bromacil	52.09	30.1
30	Alachlor	52.25	34.9
31	Cyanazine	53.43	60.4
32	Heptachlor	53.72	5.00
33	Metolachlor	55.44	70.0
34	Heptachlor Epoxide	58.42	14.0
35	Endrin	64.15	5.00
36	Endrin Aldehyde	65.46	7.00
37	Endrin Ketone	72.33	4.96
38	Methoxychlor	73.53	20.1

NOTE: Bromofluorobenzene (ret. time 31.00 min.) as the internal standard was not included in this chromatogram.

(a) **Column A** - 0.25 mm ID x 30 m fused silica capillary with chemically bonded methyl polysiloxane phase (J&W, **DB-1**, 1.0 µm film thickness or equivalent). The linear velocity of the helium carrier is established at 25 cm/sec at 35°C.

The column oven is temperature programmed as follows:

[1] HOLD at 35°C for 22 min
[2] INCREASE to 145°C at 10°C/min and hold at 145°C for 2 min.
[3] INCREASE to 225°C at 20°C/min and hold at 225°C for 15 min.
[4] INCREASE to 260°C at 10°C/min and hold at 260°C for 30 min. or until all expected compounds have eluted.

Injector temperature: 200°C
Detector temperature: 290°C

FIGURE 1. FORTIFIED REAGENT WATER EXTRACT USING MTBE ON PRIMARY DB-1 COLUMN

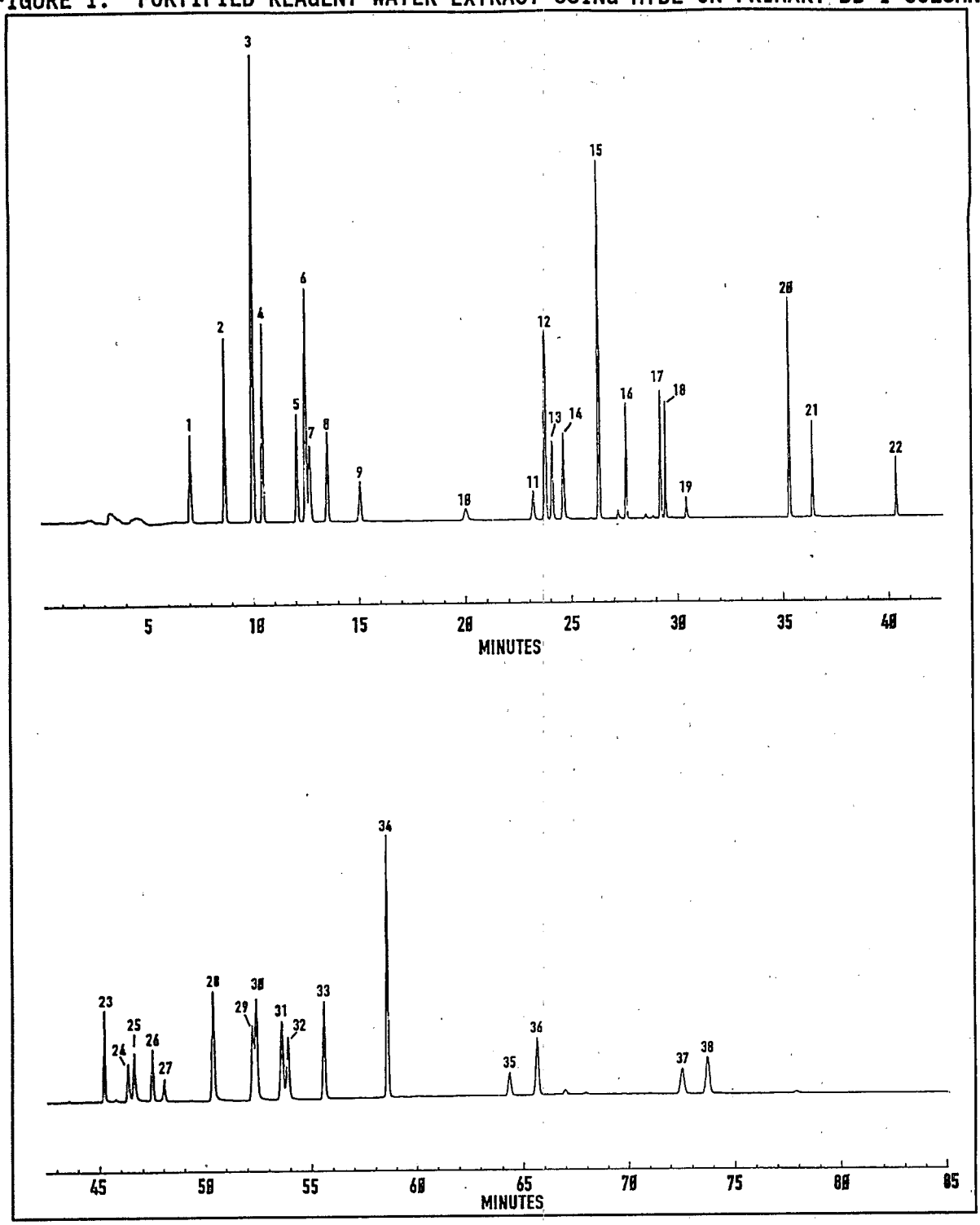


TABLE 11. ANALYTE PEAK IDENTIFICATION, RETENTION TIMES, CONCENTRATIONS AND CONDITIONS USING MTBE FOR FIGURE 2
NH_4Cl PRESERVED FORTIFIED REAGENT WATER ON THE
CONFIRMATION Rtx-1301

PEAK #	ANALYTE	Retention Time[a] minutes	Conc. µg/L
1	Chloroform	7.73	5.00
2	1,1,1-Trichloroethane	7.99	5.00
3	Carbon Tetrachloride	8.36	5.00
4	Trichloroacetonitrile	10.35	5.00
5	Trichloroethylene	11.96	5.00
6	Bromodichloromethane	15.28	5.00
7	1,1-Dichloro-2-Propanone	20.50	5.00
8	Chloropicrin	23.69	5.00
9	Tetrachloroethylene	24.77	5.00
10	1,1,2-Trichloroethane	25.01	44.8
11	Dichloroacetonitrile	25.21	5.00
12	Dibromochloromethane	26.32	5.00
13	1,2-Dibromoethane (EDB)	26.46	5.00
14	1,1,1-Trichloropropanone	28.47	5.00
15	Bromochloroacetonitrile	29.86	5.00
16	Bromoform	30.36	5.00
17	1,2,3-Trichloropropane	31.73	50.0
18	Dibromoacetonitrile	32.77	5.00
19	1,2-Dibromo-3-chloropropane (DBCP)	36.11	5.00
20	Surrogate: Decafluorobiphenyl	36.28	10.0
21	Hexachlorocyclopentadiene	39.53	28.0
22	Trifluralin	45.43	7.04
23	Hexachlorobenzene	46.47	1.98
24	Atrazine/Simazine	48.56	400
25	Lindane (gamma-BHC)	49.68	30.1
26	Heptachlor	53.15	5.00
27	Metribuzin	53.92	19.9

TABLE 11. ANALYTE PEAK IDENTIFICATION, RETENTION TIMES, CONCENTRATIONS AND CONDITIONS USING MTBE FOR FIGURE 2 (cont'd)
NH_4Cl PRESERVED FORTIFIED REAGENT WATER ON THE
CONFIRMATION Rtx-1301

PEAK #	ANALYTE	Retention Time[a] minutes	Conc. µg/L
28	Alachlor	54.38	34.9
29	Metolachlor	57.07	70.0
30	Heptachlor Epoxide	59.05	14.0
31	Bromacil	59.60	30.1
32	Cyanazine	59.89	60.4
33	Endrin	65.24	5.00
34	Endrin Aldehyde	71.56	7.00
35	Methoxychlor	76.73	20.1
36	Endrin Ketone	81.28	4.96

NOTE: Bromofluorobenzene (ret. time 31.30 min.) as the internal standard was not included in this chromatogram.

(a) **Column B -** 0.25 mm ID x 30 m with chemically bonded 6 % cyanopropylphenyl / 94 % dimethyl polysiloxane phase (Restek, **Rtx-1301**, 1.0 µm film thickness or equivalent). The linear velocity of the helium carrier gas is established at 25 cm/sec at 35°C.

The column oven is temperature programmed as follows:
The column oven is temperature programmed as follows:
[1] HOLD at 35°C for 22 min
[2] INCREASE to 145°C at 10°C/min and hold at 145°C for 2 min
[3] INCREASE to 225°C at 20°C/min and hold at 225°C for 15 min
[4] INCREASE to 260°C at 10°C/min and hold at 260°C for 30 min. or until all expected compounds have eluted.

Injector temperature: 200°C
Detector temperature: 290°C

FIGURE 2. FORTIFIED REAGENT WATER EXTRACT USING MTBE ON CONFIRMATION Rtx-1301 COLUMN

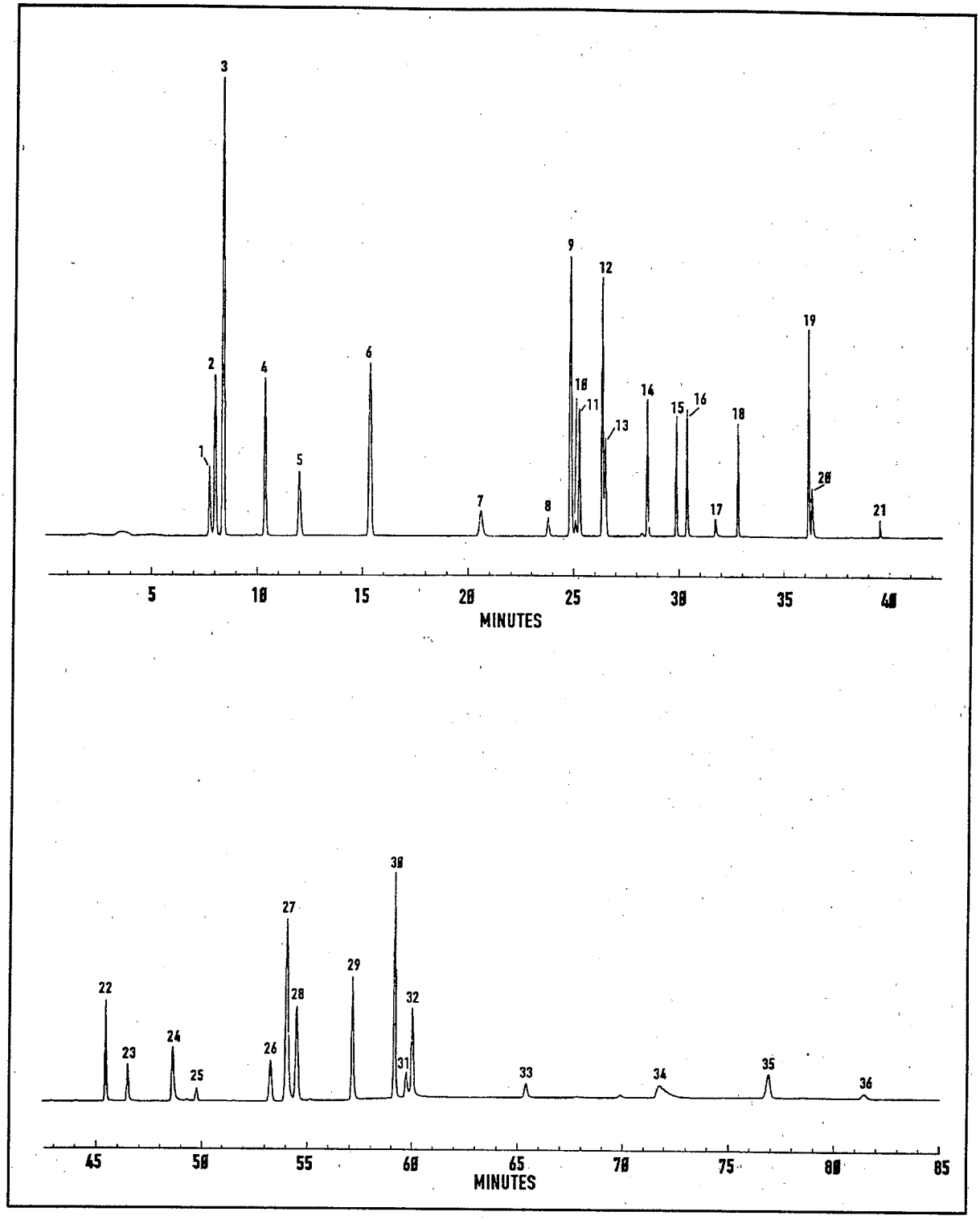


TABLE 12. ANALYTE PEAK IDENTIFICATION, RETENTION TIMES, CONCENTRATIONS AND CONDITIONS USING PENTANE FOR FIGURE 3
NH_4Cl PRESERVED FORTIFIED REAGENT WATER ON THE
PRIMARY DB-1 COLUMN

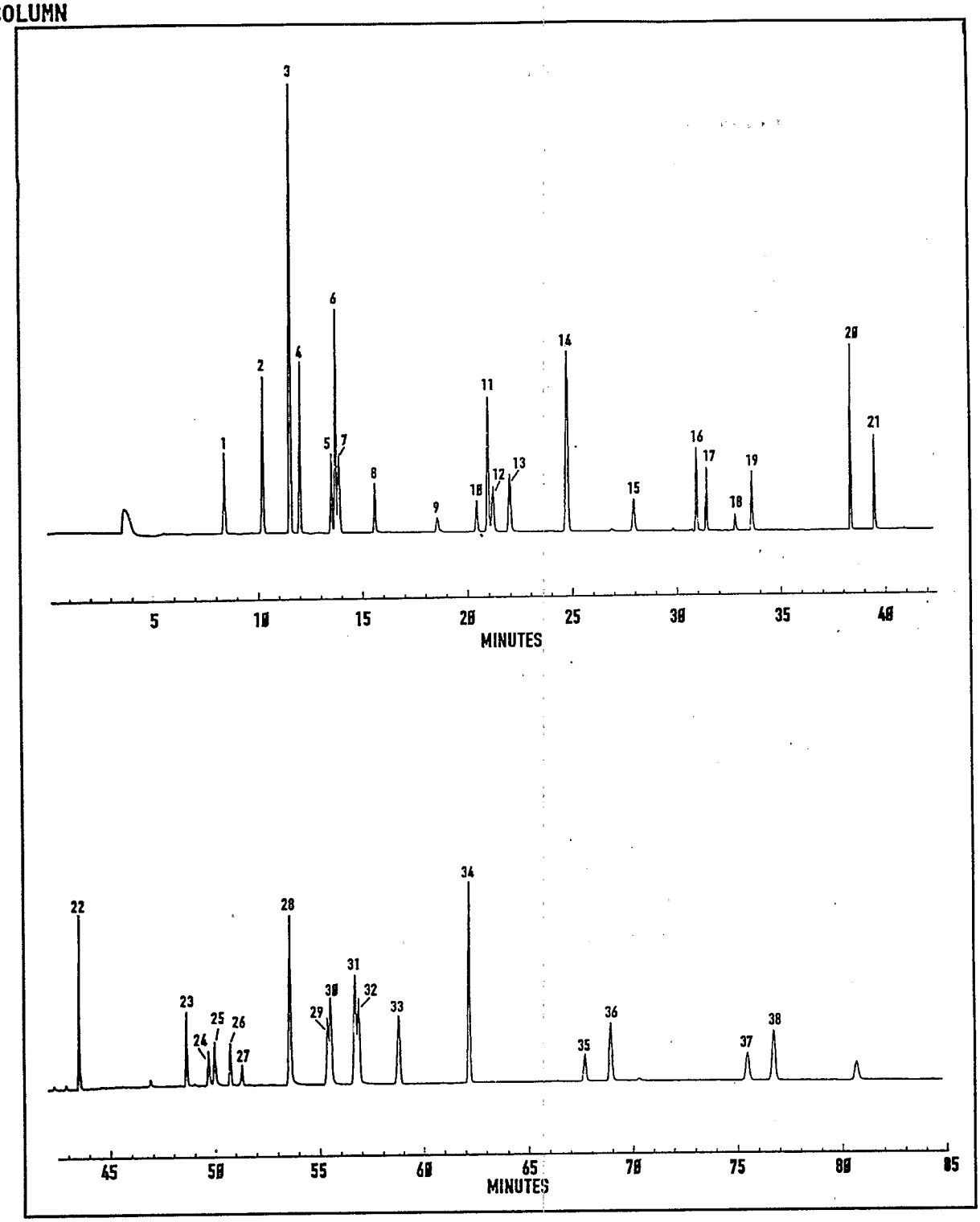
PEAK #	ANALYTE	Retention Time[a] minutes	Conc. µg/L
1	Chloroform	8.41	5.00
2	1,1,1-Trichloroethane	10.26	5.00
3	Carbon Tetrachloride	11.56	5.00
4	Trichloroacetonitrile	12.03	5.00
5	Dichloroacetonitrile	13.53	5.00
6	Bromodichloromethane	13.73	5.00
7	Trichloroethylene	13.89	5.00
8	1,1-Dichloro-2-Propanone	15.60	5.00
9	1,1,2-Trichloroethane	18.57	44.8
10	Chloropicrin	20.49	5.00
11	Dibromochloromethane	21.03	5.00
12	Bromochloroacetonitrile	21.25	5.00
13	1,2-Dibromoethane (EDB)	22.03	5.00
14	Tetrachloroethylene	24.75	5.00
15	1,1,1-Trichloropropanone	27.94	5.00
16	Bromoform	30.97	5.00
17	Dibromoacetonitrile	31.45	5.00
18	1,2,3-Trichloropropane	32.82	50.0
19	Internal Standard: Bromofluorobenzene	33.60	1.00 µg/mL in pentane extract
20	1,2-Dibromo-3-chloropropane (DBCP)	38.34	5.00
21	Surrogate: Decafluorobiphenyl	39.48	10.0
22	Hexachlorocyclopentadiene	43.92	28.0
23	Trifluralin	49.04	7.04
24	Simazine	50.08	200
25	Atrazine	50.37	200
26	Hexachlorobenzene	51.11	1.98
27	Lindane (gamma-BHC)	51.66	30.1

TABLE 12. ANALYTE PEAK IDENTIFICATION, RETENTION TIMES, CONCENTRATIONS AND CONDITIONS USING PENTANE FOR FIGURE 3 (cont'd)
NH_4Cl PRESERVED FORTIFIED REAGENT WATER ON THE
PRIMARY DB-1 COLUMN

PEAK #	ANALYTE	Retention Time[a] minutes	Conc. µg/L
28	Metribuzin	53.95	19.9
29	Bromacil	55.72	30.1
30	Alachlor	55.87	34.9
31	Cyanazine	57.04	60.4
32	Heptachlor	57.21	5.00
33	Metolachlor	59.13	70.0
34	Heptachlor Epoxide	62.50	14.0
35	Endrin	68.00	5.00
36	Endrin Aldehyde	69.25	7.00
37	Endrin Ketone	75.74	4.96
38	Methoxychlor	76.98	20.1

(a) **Column A** - 0.25 mm ID x 30 m fused silica capillary with chemically bonded methyl polysiloxane phase (J&W, **DB-1**, 1.0 µm film thickness or equivalent). The linear velocity of the helium carrier is established at 25 cm/sec at 35°C.
The column oven is temperature programmed as follows:
[1] HOLD at 15°C for 0 min
[2] INCREASE to 50°C at 2°C/min and hold at 50°C for 10 min
[3] INCREASE to 225°C at 10°C/min and hold at 225°C for 15 min
[4] INCREASE to 260°C at 10°C/min and hold at 260°C for 30 min. or until all expected compounds have eluted.
Injector temperature: 200°C
Detector temperature: 290°C

FIGURE 3. FORTIFIED REAGENT WATER EXTRACT USING PENTANE ON PRIMARY DB-1 COLUMN



METHOD 552.2 DETERMINATION OF HALOACETIC ACIDS AND DALAPON IN DRINKING WATER BY LIQUID-LIQUID EXTRACTION, DERIVATIZATION AND GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTION.

Revision 1.0

J.W. Hodgeson (USEPA), J. Collins and R.E. Barth (Technology Applications Inc.) - Method 552.0, (1990)

J.W. Hodgeson (USEPA), D. Becker (Technology Applications Inc.) - Method 552.1, (1992)

D.J. Munch, J.W. Munch (USEPA) and A.M. Pawlecki (International Consultants, Inc.), Method 552.2, Rev. 1.0, (1995)

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METHOD 552.2 DETERMINATION OF HALOACETIC ACIDS AND DALAPON IN DRINKING WATER BY LIQUID-LIQUID EXTRACTION, DERIVATIZATION AND GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTION

1. SCOPE AND APPLICATION

1.1 This is a gas chromatographic (GC) method (1-8) applicable to the determination of the listed halogenated acetic acids in drinking water, ground water, raw source water and water at any intermediate treatment stage. In addition, the chlorinated herbicide, Dalapon, may be determined using this method.

Analyte	Chemical Abstract Services Registry Number
Bromochloroacetic Acid (BCAA)	5589-96-3
Bromodichloroacetic Acid (BDCAA)	7113-314-7
Chlorodibromoacetic Acid (CDBAA)	5278-95-5
Dalapon	75-99-0
Dibromoacetic Acid (DBAA)	631-64-1
Dichloroacetic Acid (DCAA)	79-43-6
Monobromoacetic Acid (MBAA)	79-08-3
Monochloroacetic Acid (MCAA)	79-11-8
Tribromoacetic Acid (TBAA)	75-96-7
Trichloroacetic Acid (TCAA)	76-03-9

1.2 This method is applicable to the determination of the target analytes over the concentration ranges typically found in drinking water (1,2,4). Experimentally determined method detection limits (MDLs) for the above listed analytes are provided in Table 2. Actual MDLs may vary according to the particular matrix analyzed and the specific instrumentation employed. The haloacetic acids are observed ubiquitously in chlorinated drinking water supplies at concentrations ranging from <1 to >50 µg/L.

1.3 This method is designed for analysts skilled in liquid-liquid extractions, derivatization procedures and the use of GC and interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 9.3.

1.4 When this method is used for the analyses of waters from unfamiliar sources, it is strongly recommended that analyte identifications be confirmed by GC using a dissimilar column or by GC/MS if concentrations are sufficient.

2. SUMMARY OF METHOD

2.1 A 40-mL volume of sample is adjusted to pH <0.5 and extracted with 4-mL of methyl-tert-butyl-ether (MTBE). The haloacetic acids that have been partitioned into the organic phase are then converted to

their methyl esters by the addition of acidic methanol followed by slight heating. The acidic extract is neutralized by a back-extraction with a saturated solution of sodium bicarbonate and the target analytes are identified and measured by capillary column gas chromatography using an electron capture detector (GC/ECD). Analytes are quantitated using procedural standard calibration.

3. DEFINITIONS

3.1 INTERNAL STANDARD (IS) -- A pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component.

3.2 SURROGATE ANALYTE (SA) -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction or other processing and is measured with the same procedures used to measure other sample components. The purpose of the SA is to monitor method performance with each sample.

3.3 LABORATORY DUPLICATES (LD1 AND LD2) -- Two aliquots of the same sample designated as such in the laboratory. Each aliquot is extracted, derivatized and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.4 FIELD DUPLICATES (FD1 AND FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.5 LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water or other blank matrix that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.6 FIELD REAGENT BLANK (FRB) -- An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.7 LABORATORY FORTIFIED BLANK (LFB) -- An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.8 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.9 STOCK STANDARD SOLUTION (SSS) -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

3.10 PRIMARY DILUTION STANDARD SOLUTION (PDS) -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.11 CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution and stock standard solutions of the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.12 QUALITY CONTROL SAMPLE (QCS) -- A solution of method analytes of known concentration which is used to fortify an aliquot of reagent water or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.13 LABORATORY PERFORMANCE CHECK SOLUTION (LPC) -- A solution of selected method analytes used to evaluate the performance of the instrumental system with respect to a defined set of method criteria.

3.14 METHOD DETECTION LIMIT (MDL) -- The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

3.15 MATERIAL SAFETY DATA SHEET (MSDS) -- Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire and reactivity data including storage, spill, and handling precautions.

3.16 ESTIMATED DETECTION LIMIT (EDL) -- Defined as either the MDL or a level of a compound in a sample yielding a peak in the final extract with a signal to noise (S/N) ratio of approximately 5, whichever is greater.

3.17 PROCEDURAL STANDARD CALIBRATION -- A calibration method where aqueous calibration standards are prepared and processed (e.g. purged, extracted and/or derivatized) in exactly the same manner as a sample. All steps in the process from addition of sampling preservatives through instrumental analyses are included in the calibration. Using procedural standard calibration compensates for any inefficiencies in the processing procedure.

3.18 CONTINUING CALIBRATION CHECK (CCC) -- A calibration standard containing one or more method analytes, which is analyzed periodically to verify the accuracy of the existing calibration curves or response factors for those analytes.

4. INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or elevated baselines in chromatograms. All reagents and apparatus must be routinely demonstrated to be free from interferences under the conditions of the analysis by analyzing laboratory reagent blanks as described in Section 9.5. Subtracting blank values from sample results is not permitted.

4.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot water and detergent and thorough rinsing with tap water and reagent water. Drain and heat in an oven or muffle furnace at 400°C for 1 hr. Do not heat volumetric ware but instead rinse three times with HPLC grade or better acetone. Thorough rinsing with reagent grade acetone may be substituted for the heating provided method blank analysis confirms no background interferant contamination is present. Thermally stable materials such as PCBs may not be eliminated by these treatments. After drying and cooling, store glassware in a clean environment free of all potential contamination. To prevent any accumulation of dust or other contaminants, store glassware inverted or capped with aluminum foil.

4.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Each new bottle of solvent should be analyzed before use. An interference free solvent is a solvent containing no peaks yielding data at $\geq$ MDL (Table 2) and at the retention times of the analytes of interest. Purification of solvents by distillation in all-glass systems may be required.

4.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. Routine between-sample rinsing of the sample syringe and associated equipment with MTBE can minimize sample cross-contamination. After analysis of a sample containing high concentrations of analytes, one or more injections of MTBE should be made to ensure that accurate values are obtained for the next sample.

4.3 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 water sampled. Analyte identifications should be confirmed using the confirmation column specified in Table 1 or by GC/MS if the concentrations are sufficient.

4.4 Bromochloroacetic acid coelutes with an interferant on the DB-1701 confirmation column. The interferant has been tentatively identified as dimethyl sulfide. However, because of the difference in peak shapes, the peak for the ester of BCAA tends to "ride on" the interferant peak and quantitative confirmation can be performed by manual integration that includes only the peak area of the target ester.

4.5 Methylation using acidic methanol results in a partial decarboxylation of tribromoacetic acid (8). Therefore a substantial peak for bromoform will be observed in the chromatograms. Its elution does not, however, interfere with any other analytes. Furthermore, this demonstrates the need for procedural standards to establish the calibration curve by which unknown samples are quantitated.

5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound must be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be minimized. 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 also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified (9-11) for the information of the analyst.

5.2 The toxicity of the extraction solvent, MTBE, has not been well defined. Susceptible individuals may experience adverse affects upon skin contact or inhalation of vapors. Therefore protective clothing and gloves should be used and MTBE should be used only in a chemical fume hood or glove box. The same precaution applies to pure standard materials.

6. APPARATUS AND EQUIPMENT

6.1 SAMPLE CONTAINERS -- Amber glass bottles, approximately 50 mL, fitted with Teflon-lined screw caps.

6.2 EXTRACTION VIALS -- 60 mL clear glass vials with teflon-lined screw caps.

6.3 VIALS -- Autosampler, 2.0 mL vials with screw or crimp cap and a teflon-faced seal.

6.4 STANDARD SOLUTION STORAGE CONTAINERS -- 10-20 ml amber glass vials with teflon lined-screw caps.

6.5 GRADUATED CONICAL CENTRIFUGE TUBES WITH TEFLON-LINED SCREW CAPS -- 15-mL with graduated 1 mL markings.

6.6 BLOCK HEATER (or SAND BATH) -- Capable of holding screw cap conical centrifuge tubes in Section 6.4.

6.7 PASTEUR PIPETS -- Glass, disposable.

6.8 PIPETS -- 2.0 mL and 4.0 mL, type A, TD, glass.

6.9 VOLUMETRIC FLASKS -- 5 ml, 10 mL.

6.10 MICRO SYRINGES -- 10 µL, 25 µL, 50 µL, 100 µL, 250 µL, 500 µL and 1000 µL.

6.11 BALANCE -- analytical, capable of weighing to 0.0001 g.

6.12 GAS CHROMATOGRAPH -- Analytical system complete with gas chromatograph equipped for electron capture detection, split/splitless capillary or direct injection, temperature programming, differential flow control, and with all required accessories including syringes, analytical columns, gases and strip-chart recorder. A data system is recommended for measuring peak areas. An autoinjector is recommended for improved precision of analyses. The gases flowing through the electron capture detector should be vented through the laboratory fume hood system.

6.13 PRIMARY GC COLUMN -- DB-5.625 [fused silica capillary with chemically bonded (5% phenyl)-methylpolysiloxane)] or equivalent bonded, fused silica column, 30m x 0.25mm ID, 0.25 µm film thickness.

6.14 CONFIRMATION GC COLUMN -- DB-1701 [fused silica capillary with chemically bonded (14% cyanopropylphenyl)-methylpolysiloxane)] or equivalent bonded, fused silica column, 30 m x 0.25 mm ID, 0.25 µm film thickness.

7. REAGENTS AND STANDARDS

7.1 REAGENT WATER -- Reagent water is defined as a water in which an interference is not observed ≥ to the MDL of each analyte of interest.

7.1.1 A Millipore Super-Q water system or its equivalent may be used to generate deionized reagent water. Distilled water that has been passed through granular charcoal may also be suitable.

7.1.2 Reagent water is monitored through analysis of the laboratory reagent blank (Section 9.5).

7.2 SOLVENTS

7.2.1 METHYL-TERT-BUTYL ETHER -- High purity, demonstrated to be free of analytes and interferences, redistilled in glass if necessary.

7.2.2 METHANOL -- High purity, demonstrated to be free of analytes and interferences.

7.2.3 ACETONE -- High purity, demonstrated to be free of analytes and interferences.

7.3 REAGENTS

7.3.1 SODIUM SULFATE, Na_2SO_4 -- (ACS) granular, anhydrous. If interferences are observed, it may be necessary to heat the sodium sulfate in a shallow tray at 400°C for up to 4 hr. to remove phthalates and other interfering organic substances. Alternatively, it can be extracted with methylene chloride in a Soxhlet apparatus for 48 hr. Store in a capped glass bottle rather than a plastic container.

7.3.2 COPPER II SULFATE PENTAHYDRATE, $CuSO_4 \cdot 5H_2O$ -- ACS reagent grade.

7.3.3 SODIUM BICARBONATE, $NaHCO_3$ -- ACS reagent grade.

7.3.4 AMMONIUM CHLORIDE, NH_4Cl -- ACS reagent grade, used to convert free chlorine to monochloramine. Although this is not the traditional dechlorination mechanism, ammonium chloride is categorized as a dechlorinating agent in this method.

7.4 SOLUTIONS

7.4.1 10% H_2SO_4/METHANOL SOLUTION -- Use caution when preparing sulfuric acid solutions. To prepare a 10% solution, add 5 mL sulfuric acid dropwise (due to heat evolution)

to 20-30 mL methanol contained in a 50.0 mL volumetric flask that has been placed in a cooling bath. Then dilute to the 50.0 mL mark with methanol.

7.4.2 SATURATED SODIUM BICARBONATE SOLUTION -- Add sodium bicarbonate to a volume of water, mixing periodically until the solution has reached saturation.

7.5 STANDARDS

7.5.1 1,2,3-TRICHLOROPROPANE, 99+% -- For use as the internal standard. Prepare an internal standard stock standard solution of 1,2,3-trichloropropane in MTBE at a concentration of approximately 1 mg/mL. From this stock standard solution, prepare a primary dilution standard in MTBE at a concentration of 25 µg/mL.

7.5.2 2,3-DIBROMOPROPIONIC ACID, 99+% -- For use as a surrogate compound. Prepare a surrogate stock standard solution of 2,3-dibromopropionic acid in MTBE at a concentration of approximately 1 mg/mL. From this stock standard solution, prepare a primary dilution standard in MTBE at a concentration of 10 µg/mL.

7.5.3 STOCK STANDARD SOLUTION (SSS)

Prepare separate stock standard solutions for each analyte of interest at a concentration of 1-5 mg/mL in MTBE. Method analytes may be obtained as neat materials or ampulized solutions (> 99% purity) from a number of commercial suppliers. These stock standard solutions should be stored at -10°C and protected from light. They are stable for at least one month but should be checked frequently for signs of evaporation.

7.5.3.1. For analytes which are solids in their pure form, prepare stock standard solutions by accurately weighing approximately 0.01 to 0.05 grams of pure material in a 10.0 mL volumetric flask. Dilute to volume with MTBE. When a compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard.

7.5.3.2. Stock standard solutions for analytes which are liquid in their pure form at room temperature can be accurately prepared in the following manner.

7.5.3.3. Place about 9.8 mL of MTBE into a 10.0 mL volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes to allow solvent film to evaporate

from the inner walls of the volumetric, and weigh to the nearest 0.1 mg.

7.5.3.4. Use a 10 µL syringe and immediately add 10.0 µL of standard material to the flask by keeping the syringe needle just above the surface of the MTBE. Be sure that the standard material falls dropwise directly into the MTBE without contacting the inner wall of the volumetric.

7.5.3.5. Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in milligrams per milliliter from the net gain in weight.

7.5.4 PRIMARY DILUTION STANDARD (PDS) -- Prepare the primary dilution standard solution by combining and diluting stock standard solutions with MTBE (the surrogate stock standard solution was prepared in Section 7.5.2). This primary dilution standard solution should be stored at -10°C and protected from light. It is stable for at least one month but should be checked before use for signs of evaporation. As a guideline to the analyst, the primary dilution standard solution used in the validation of this method is described below.

	Concentration, µg/mL
Monochloroacetic acid	60
Monobromoacetic acid	40
Dalapon	40
Dichloroacetic acid	60
Trichloroacetic acid	20
Bromochloroacetic acid	40
Dibromoacetic acid	20
Bromodichloroacetic acid	40
Chlorodibromoacetic acid	100
Tribromoacetic acid	200
2,3-Dibromopropionic acid (surr.)	100

This primary dilution standard is used to prepare calibration standards, which comprise five concentration levels of each analyte with the lowest standard being at or near the MDL of each analyte. The concentrations of the other standards should define a range containing the expected sample concentrations or the working range of the detector.

NOTE: When purchasing commercially prepared standards, solutions prepared in methanol <u>must not be used</u> because it has been found that the haloacetic acids are subject to spontaneous methylation when stored in this solvent (12).

Furthermore, tribromoacetic acid has been found to be unstable in methanol because it undergoes decarboxylation when stored in this solvent.

7.5.4.1. Include the surrogate analyte, 2,3-dibromopropionic acid, within the primary dilution standard prepared in Section 7.5.4. By incorporating the surrogate into the primary dilution standard, it is diluted alongside the target analytes in the standard calibration curve. This is done so that the peaks for the surrogate and the ester of chlorodibromoacetic acid, which elute fairly closely, are relatively close in size and adequate resolution is therefore insured. Furthermore, if a sample should have a very large concentration of chlorodibromoacetic acid, it may be impossible to obtain an accurate measurement of surrogate recovery. If this happens, reextraction with a higher surrogate concentration would be an option.

7.5.6 LABORATORY PERFORMANCE CHECK STANDARD (LPC) -- A low level calibration standard can serve as the LPC standard.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 SAMPLE VIAL PREPARATION

8.1.1 Grab samples must be collected in accordance with conventional sampling practices (13) using amber glass containers with TFE-lined screw-caps and capacities of at least 50 ml.

8.1.2 Prior to shipment to the field, add crystalline or granular ammonium chloride (NH_4Cl) to the sample container in an amount to produce a concentration of 100 mg/L in the sample. For a typical 50 mL sample, 5 mg of ammonium chloride is added.

NOTE: Enough ammonium chloride must be added to the sample to convert the free chlorine residual in the sample matrix to combined chlorine. Typically, the ammonium chloride concentration here will accomplish that. If high doses of chlorine are used, additional ammonium chloride may be required.

8.2 SAMPLE COLLECTION

8.2.1 Fill sample bottles to just overflowing but take care not to flush out the ammonium chloride.

8.2.2 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 3-5 minutes). Remove the aerator so that no

air bubbles can be visibly detected and collect samples from the flowing system.

8.2.3 When sampling from an open body of water, fill a 1-quart wide-mouth bottle or 1-liter beaker with sample from a representative area, and carefully fill sample vials from the container.

8.2.4 After collecting the sample in the bottle containing the ammonium chloride, seal the bottle and agitate by hand for 1 min.

8.3 SAMPLE STORAGE/HOLDING TIMES

8.3.1 Samples must be iced or refrigerated at 4°C and maintained at these conditions away from light until extraction. Synthetic ice (i.e., blue ice) is not recommended. Holding studies performed to date have suggested that, in samples preserved with NH_4Cl, the analytes are stable for up to 14 days. Since stability may be matrix dependent, the analyst should verify that the prescribed preservation technique is suitable for the samples under study.

8.3.2 Extracts (Section 11.2.7) must be stored at 4°C or less away from light in glass vials with Teflon-lined caps. Extracts must be analyzed within 7 days from extraction if stored at 4°C or within 14 days if stored at -10°C or less.

9. QUALITY CONTROL

9.1 Each laboratory that uses this method is required to operate a formal quality control (QC) program. Minimum quality control requirements are monitoring the laboratory performance check standard, initial demonstration of laboratory capability, performance of the method detection limit study, analysis of laboratory reagent blanks and laboratory fortified sample matrices, determination of surrogate compound recoveries in each sample and blank, monitoring internal standard peak area or height in each sample, blank and CCC, and analysis of QC samples. Additional QC practices may be added.

9.2 LABORATORY PERFORMANCE CHECK STANDARD (LPC)

At the beginning of an analysis set, prior to any calibration standard or sample analysis and after an initial solvent analysis, a laboratory performance check standard must be analyzed. This check standard insures proper performance of the GC by evaluation of the instrument parameters of detector sensitivity, peak symmetry, and peak resolution. It furthermore serves as a check on the continuity of the instrument's performance. In regards to sensitivity, it allows the analyst to ascertain that this parameter has not changed drastically since the analysis of the MDL study. Inability to demonstrate acceptable instrument performance indicates the need for

re-evaluation of the instrument system. Criteria are listed in Table 8.

9.2.1 The sensitivity requirement is based on the EDLs published in this method. If laboratory EDLs differ from those listed in Table 2, concentrations of the LPC standard may be adjusted to be compatible with the laboratory EDLs.

9.2.2 If column or chromatographic performance cannot be met, one or more of the following remedial actions should be taken. Break off approximately 1 meter of the injector end of the column and re-install, install a new column, adjust column flows or modify the oven temperature program.

9.3 INITIAL DEMONSTRATION OF CAPABILITY (IDC)

9.3.1 Calibrate for each analyte of interest as specified in Section 10. Select a representative fortification concentration for each of the target analytes. Concentrations near those in Table 4 are recommended. Prepare 4-7 replicates laboratory fortified blanks by adding an appropriate aliquot of the primary dilution standard or quality control sample to reagent water. (This reagent water should contain ammonium chloride at the same concentration as that specified for samples as per Section 8.1.2.) Analyze the LFBs according to the method beginning in Section 11.

9.3.2 Calculate the mean percent recovery and the standard deviation of the recoveries. For each analyte, the mean recovery value, expressed as a percentage of the true value, must fall in the range of 80-120% and the relative standard deviation should be less than 20%. For those compounds that meet these criteria, performance is considered acceptable and sample analysis may begin. For those compounds that fail these criteria, this procedure must be repeated using 4-7 fresh samples until satisfactory performance has been demonstrated. Maintain these data on file to demonstrate initial capabilities.

9.3.3 Furthermore, before processing any samples, the analyst must analyze at least one laboratory reagent blank to demonstrate that all glassware and reagent interferences are under control.

9.3.4 The initial demonstration of capability is used primarily to preclude a laboratory from analyzing unknown samples via a new, unfamiliar method prior to obtaining some experience with it. As laboratory personnel gain experience with this method, the quality of data should improve beyond those required here.

9.3.5 The analyst is permitted to modify GC columns, GC conditions, internal standard or surrogate compounds. Each time such method modifications are made, the analyst must repeat the procedures in Section 9.3.1 through Section 9.3.4 and Sect. 9.4.

9.4 METHOD DETECTION LIMIT STUDY (MDL)

9.4.1. Prior to the analysis of any field samples, the method detection limits must be determined. Initially, estimate the concentration of an analyte which would yield a peak equal to 5 times the baseline noise and drift. Prepare seven replicate laboratory fortified blanks at this estimated concentration with reagent water that contains ammonium chloride at the same concentration as that specified for samples as per Section 8.1.2. Analyze the LFB's according to the method beginning in Section 11.

9.4.2. Calculate the mean recovery and the standard deviation for each analyte. Multiply the student's t value at 99% confidence and n-1 degrees of freedom (3.143 for seven replicates) by this standard deviation to yield a statistical estimate of the detection limit. This calculated value is the MDL.

9.4.3. Since the statistical estimate is based on the preci- sion of the analysis, an additional estimate of detection can be determined based upon the noise and drift of the baseline as well as precision. This estimate is the EDL (Table 2).

9.5 LABORATORY REAGENT BLANKS (LRB) -- Each time a set of samples is extracted or reagents are changed, a LRB must be analyzed. If the LRB produces an interferant peak within the retention time window (Section 12.3) of any analyte that would prevent the determination of that analyte or a peak of concentration greater than the MDL for that analyte, the analyst must determine the source of contamination and eliminate the interference before processing samples. Field samples of an extraction set associated with an LRB that has failed the specified criteria are considered suspect.

NOTE: Reagent water containing ammonium chloride at the same concentrations as in the samples (Section 8.1.2) is used to prepare the LRB.

9.6 LABORATORY FORTIFIED BLANK (LFB) -- Since this method utilizes procedural calibration standards, which are fortified reagent water, there is no difference between the LFB and the continuing calibration check standard. Consequently, the analysis of an LFB is not required (Section 10.2).

9.7 LABORATORY FORTIFIED SAMPLE MATRIX (LFM)

9.7.1 Chlorinated water supplies will usually contain significant background concentrations of several method analytes, especially dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA). The concentrations of these acids may be equal to or greater than the fortified concentrations. Relatively poor accuracy and precision may be anticipated when a large background must be subtracted. For many samples, the concentrations may be so high that fortification may lead to a final extract with instrumental responses exceeding the linear range of the electron capture detector. If this occurs, the extract must be diluted. In spite of these problems, sample sources should be fortified and analyzed as described below. By fortifying sample matrices and calculating analyte recoveries, any matrix induced analyte bias is evaluated.

9.7.2. The laboratory must add known concentrations of analytes to one sample per extraction set or a minimum of 10% of the samples, whichever is greater. The concentrations should be equal to or greater than the background concentrations in the sample selected for fortification. If the fortification level is less than the background concentration, recoveries are not reported. Over time, samples from all routine sample sources should be fortified.

9.7.3 Calculate the mean percent recovery, R, of the concentration for each analyte, after correcting the total mean measured concentration, A, from the fortified sample for the background concentration, B, measured in the unfortified sample, i.e.:

$$R = 100\ (A - B)\ /\ C,$$

where C is the fortifying concentration. In order for the recoveries to be considered acceptable, they must fall between 70% and 130% for all the target analytes.

9.7.4 If a recovery falls outside of this acceptance range, a matrix induced bias can be assumed for the respective analyte and the data for that analyte must be reported to the data user as suspect due to matrix effects.

9.8 ASSESSING SURROGATE RECOVERY

The surrogate analyte is fortified into the aqueous portion of all continuing calibration standards, samples and laboratory reagent blanks. The surrogate is a means of assessing method performance in every analysis from extraction to final chromatographic performance.

9.8.1 When surrogate recovery from a sample, blank or CCC is < 70% or > 130%, check (1) calculations to locate possible errors, (2) standard solutions for degradation, (3) contamination, and (4) instrument performance. If those steps do not reveal the cause of the problem, reanalyze the extract.

9.8.2 If the extract reanalysis meets the surrogate recovery criterion, report only data for the reanalyzed extract.

9.8.3 If the extract reanalysis fails the 70-130% recovery criterion, the analyst should check the calibration by analyzing the most recently acceptable continuing calibration check standard. If the CCC fails the criteria of Section 10.2.1, recalibration is in order per Section 10.1. If the CCC is acceptable, it may be necessary to extract another aliquot of sample. If the sample re-extract also fails the recovery criterion, report all data for that sample as suspect.

9.9 ASSESSING THE INTERNAL STANDARD

9.9.1. The analyst must to monitor the IS response (peak area or peak height) of all injections during each analysis day. A mean IS response should be determined from the five point calibration curve. The IS response for any run should not deviate from this mean IS response by more than 30%. It is also acceptable if the IS response of a injection is within 15% of the daily continuing calibration standard IS response.

9.9.2 If a deviation greater than this occurs with an individual extract, optimize instrument performance and inject a second aliquot of that extract.

9.9.2.1 If the reinjected aliquot produces an acceptable internal standard response, report results for that aliquot.

9.9.2.2 If a deviation of greater than 30% is obtained for the reinjected extract, the analyst should check the calibration by analyzing the most recently acceptable CCC. If the CCC fails the criteria of Section 10.2.1, recalibration is in order per Section 10.1. If the CCC is acceptable, analysis of the sample should be repeated beginning with Section 11, provided the sample is still available. Otherwise, report results obtained from the reinjected extract, but annotate as suspect.

9.10 QUALITY CONTROL SAMPLE (QCS) -- At least quarterly, analyze a QCS from an external source. If measured analyte concentrations are not of acceptable accuracy, check the entire analytical procedure to locate and correct the problem source.

9.11 The laboratory may adapt additional QC 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. For example, field or laboratory duplicates may be analyzed to assess the precision of the environmental measurements or field reagent blanks may be used to assess contamination of samples under site conditions, transportation and storage.

10. CALIBRATION AND STANDARDIZATION

10.1 INITIAL CALIBRATION CURVE

10.1.1 Calibration is performed by extracting procedural standards, i.e.; fortified reagent water, by the procedure set forth in Section 11. A five-point calibration curve is to be prepared by diluting the primary dilution standard into MTBE at the appropriate levels. The desired amount of each MTBE calibration standard is added to separate 40 mL aliquots of reagent water to produce a calibration curve ranging from the detection limit to approximately 50 times the detection limit. (These MTBE calibration standards should be prepared so that 20 μL or less of the solution is added the water aliquots.) Also, the reagent water used for the procedural standards contains ammonium chloride at the same concentration as that in the samples as per Section 8.1.2.

10.1.2 Establish GC operating parameters equivalent to the suggested specifications in Table 1. The GC system must be calibrated using the internal standard (IS) technique. Other columns or conditions may be used if equivalent or better performance can be demonstrated.

10.1.2 Five calibration standards are required. The lowest should contain the analytes at a concentration near to but greater than the MDL (Table 2) for each compound. The others should be evenly distributed throughout the concentration range expected in the samples.

10.1.3 Inject 2 μL of each calibration standard extract and tabulate peak height or area response and concentration for each analyte and the internal standard.

10.1.4 Generate a calibration curve by plotting the area ratios (A_a/A_{is}) against the concentration C_a of the five calibration standards where

A_a is the peak area of the analyte.
A_{is} is the peak area of the internal standard.
C_a is the concentration of the analyte.

This curve can be defined as either first or second order. Also, the working calibration curve must be verified daily by measurement of one or more calibration standards (Section 10.2). If the response for any analyte falls outside the predicted response by more than 30%, the calibration check must be repeated using a freshly prepared calibration standard. Should the retest fail, a new calibration curve must be generated.

10.1.5 Alternately, an average relative response factor can be calculated and used for quantitation. Relative response factors are calculated for each analyte at the five concentration levels using the equation below:

$$RRF = \frac{(A_a)(C_{is})}{(A_{is})(C_a)}$$

If the RRF value over the working range is constant (<20% RSD), the RRF can be assumed to be invariant and the average RRF used for calculations. Also, the average RRF must be verified daily by measurement of one or more calibration standards (Section 10.2). If the RRF for the continuing calibration standard deviates from the average RRF by more than 30%, the calibration check must be repeated using a freshly prepared calibration standard. Should the retest fail, a new calibration curve must be generated.

10.1.6 A data system may be used to collect the chromatographic data, calculate relative response factors, or calculate linear or second order calibration curves.

10.2 CONTINUING CALIBRATION CHECK (CCC)

10.2.1 At least one CCC must be extracted with each set of samples. A CCC must be analyzed at the beginning of each analysis set, after every tenth sample analysis and after the final sample analysis, to ensure that the instrument is still within calibration. These checks should be at two different concentration levels. Calculate analyte recoveries for all target analytes. In order for the calibration check to be considered valid and subsequently for the preceding ten samples to be considered acceptable with respect to calibration, recoveries must fall between 70% and 130% for all the target analytes.

NOTE: Continuing calibration check standards need not necessarily be different extracts but can be injections from the same extract as long as the holding time requirements (Sect. 8.3.2) are met.

10.2.2 If this criteria cannot be met, the continuing calibration check standard extract is re-injected in order to determine if the response deviations observed from the initial analysis are repeated. If this criteria still cannot be met, a second CCC should be extracted and analyzed or a CCC that has already been analyzed and has been found to be acceptable should be run. If this second CCC fails, then the instrument is considered out of calibration and needs to be recalibrated.

11. PROCEDURE

11.1 SAMPLE EXTRACTION

11.1.1 Remove the samples from storage (Sect. 8.3.1) and allow them to equilibrate to room temperature.

11.1.2 Place 40 mL of the water sample into a precleaned 60 mL glass vial with a teflon-lined screw cap using a graduated cylinder.

11.1.3 Add 20 µL of surrogate standard (10.0 µg/mL 2,3-dibromopropionic acid in MTBE per Section 7.5.2).

NOTE: When fortifying an aqueous sample with either surrogate or target analytes contained in MTBE, be sure that the needle of the syringe is well below the level of the water. After injection, cap the sample and invert once. This insures that the standard solution is mixed well with the water.

11.1.4 Adjust the pH to less than 0.5 by adding at least 2 mL of concentrated sulfuric acid. Cap, shake and then check the pH with a pH meter or narrow range pH paper.

11.1.5 Quickly add approximately 2 g of copper II sulfate pentahydrate and shake until dissolved. This colors the aqueous phase blue and therefore allows for the analyst to better distinguish between the aqueous phase and the organic phase in this micro extraction.

11.1.6 Quickly add 16 g of muffled sodium sulfate and shake for 3 to 5 minutes until almost all is dissolved. Sodium sulfate is added to increase the ionic strength of the aqueous phase and thus further drive the haloacetic acids into the organic phase. The addition of this salt and the copper II sulfate should be done quickly so that the heat generated from the addition of the acid (Section 11.1.4) will help dissolve the salts.

11.1.7 Add 4.0 mL MTBE and place on the mechanical shaker for 30 minutes. (If hand-shaken, two minutes is sufficient if performed vigorously).

11.1.8 Allow the phases to separate for approximately 5 minutes.

11.2 METHYLATION

11.2.1 Using a pasteur pipet, transfer approximately 3 mL of the upper MTBE layer to a 15 mL graduated conical centrifuge tube.

11.2.2 Add 1 mL 10% sulfuric acid in methanol to each centrifuge tube.

11.2.3 Cap the centrifuge tubes and place in the heating block (or sand bath) at 50°C and maintain for 2 hr. The vials must fit snugly into the heating block to ensure proper heat transfer. At this stage, methylation of the method analytes is attained.

11.2.4 Remove the centrifuge tubes from the heating block (or sand bath) and allow them to cool before removing the caps.

11.2.5 Add 4 mL saturated sodium bicarbonate solution to each centrifuge tube in 1 mL increments. Exercise caution when adding the solution because the evolution of CO_2 in this neutralization reaction is rather rapid.

11.2.6 Shake each centrifuge tube for 2 minutes. As the neutralization reaction moves to completion, it is important to continue to exercise caution by venting frequently to release the evolved CO_2.

11.2.7 Transfer exactly 1.0 ml of the upper MTBE layer to an autosampler vial. A duplicate vial should be filled using the excess extract.

11.2.8 Add 10 µL of internal standard to the vial to be analyzed. (25 µg/mL 1,2,3-trichloropropane in MTBE per Section 7.5.1).

11.2.9 Analyze the samples as soon as possible. The sample extract may be stored up to 7 days if kept at 4°C or less or up to 14 days if kept at -10°C or less. Keep the extracts away from light in amber glass vials with Teflon-lined caps.

11.3 GAS CHROMATOGRAPHY

11.3.1 Table 1 summarizes recommended GC operating conditions and retention times observed using this method. Figure 1 illustrates the performance of the recommended primary column with the method analytes. Figure 2 illustrates the performance of

the recommended confirmation column with the method analytes. Concentrations of the analytes of these chromatograms are those listed in Table 4 for the fortified reagent water samples. Other GC columns or chromatographic conditions may be used if the requirements of Section 9 are met.

11.3.2 Calibrate the system (Section 10.1) or verify the existing calibration by analysis of a CCC daily as described in Section 10.2.

11.3.3 Inject 2 μL of the sample extract. Record the resulting peak sizes in area or height units.

11.3.4 If the response for the peak exceeds the working range of the system, dilute the extract, add an appropriate additional amount of internal standard and reanalyze. The analyst must not extrapolate beyond the calibration range established.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Identify sample components by comparison of retention times to retention data from the calibration standard analysis. If the retention time of an unknown peak corresponds, within limits (Section 12.2), to the retention time of a standard compound, then the identification is considered positive. Calculate analyte concentrations in the samples and reagent blanks from the calibration curves generated in Section 10.1.

12.2 If an average relative response factor has been calculated (Sect 10.1.5), analyte concentrations in the samples and reagent blanks are calculated using the following equation:

$$C_a = \frac{(A_a)(C_{is})}{(A_{is})(RRF)}$$

12.3 The width of the retention time window used to make identifications should be based upon 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 chromatogram.

13. METHOD PERFORMANCE

13.1 In a single laboratory, recovery and precision data were obtained at three concentrations in reagent water (Tables 3 and 4). The MDL and EDL data are given in Table 2. In addition, recovery and precision data were obtained at a medium concentration for dechlorinated tap water (Table 5), high ionic strength reagent water (Table 6) and high humectant ground water (Table 7).

14. POLLUTION PREVENTION

14.1 This method utilizes a micro-extraction procedure which requires the use of very small quantities of organic solvents. This feature reduces the hazards involved with the use of large volumes of potentially harmful organic solvents needed for conventional liquid-liquid extractions. This method also uses acidic methanol as the derivatizing reagent.

14.2 For information about pollution prevention that may be applicable to laboratory operations consult "Less is Better: Laboratory Chemical Management for Waste Reduction" available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

15. WASTE MANAGEMENT

15.1 Due to the nature of this method there is little need for waste management. No large volumes of solvents or hazardous chemicals are used. The matrices of concern are finished drinking water or source water. However, the Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations, and that laboratories protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Also compliance is required with any sewage discharge permits and regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel" also available from the American Chemical Society at the address in Sect. 14.2.

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17. TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

FIGURE 1. ELUTION OF METHOD ANALYTES ON THE PRIMARY COLUMN (DB-5.625)

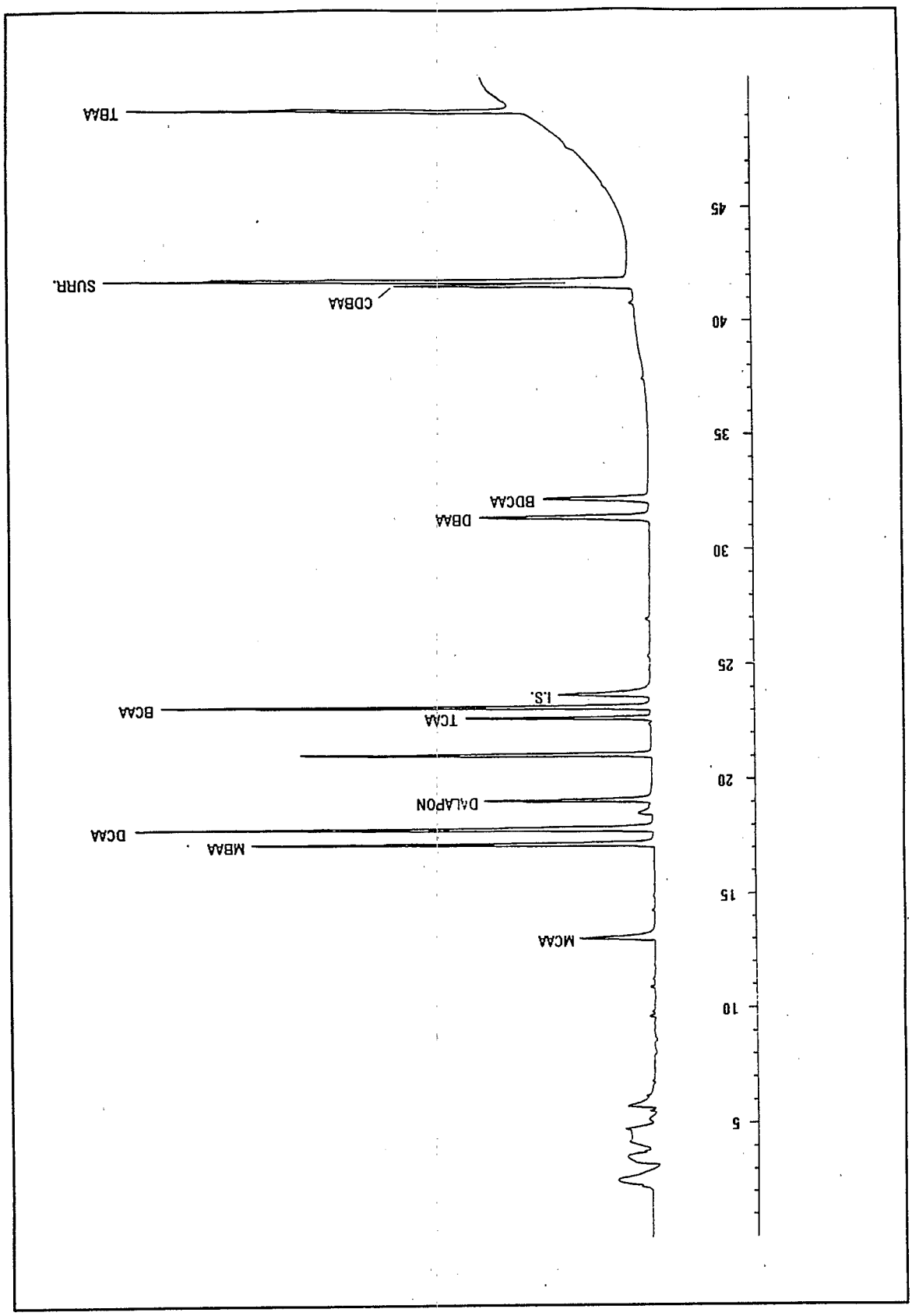

FIGURE 2. ELUTION OF METHOD ANALYTES ON THE CONFIRMATION COLUMN (DB-1701)

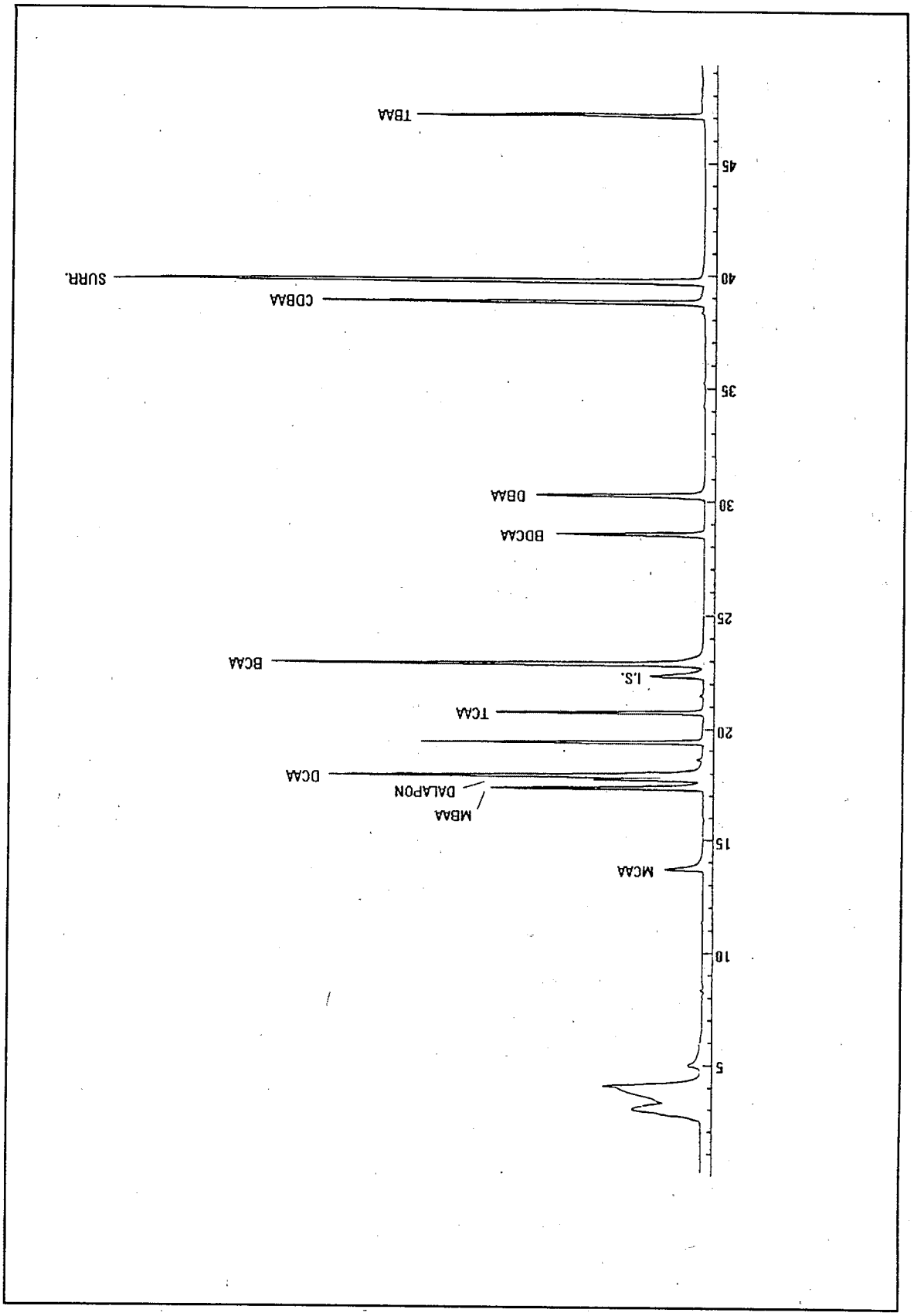

TABLE 1. RETENTION DATA AND CHROMATOGRAPHIC CONDITIONS

Analyte	Retention Time, min. Column A	Column B
Monochloroacetic Acid (MCAA)	13.03	13.70
Monobromoacetic Acid (MBAA)	17.15	17.33
Dichloroacetic Acid (DCAA)	17.80	17.88
Dalapon	19.08	17.73
Trichloroacetic Acid (TCAA)	22.67	20.73
Bromochloroacetic Acid (BCAA)	23.15	22.87
1,2,3-Trichloropropane (I.S.)	23.70	22.35
Dibromoacetic Acid (DBAA)	31.38	30.27
Bromodichloroacetic acid (BDCAA)	32.18	28.55
Chlorodibromoacetic acid (CDBAA)	41.57	38.78
2,3-Dibromopropionic acid (SURR)	41.77	39.72
Tribromoacetic Acid (TBAA)	49.22	47.08

Column A: DB-5.625, 30 m x 0.25 mm i.d., 0.25 µm film thickness, Injector Temp. = 200°C, Detector Temp. = 260°C, Helium Linear Velocity = 24 cm/sec at 35°C, Splitless injection with 30 s delay

Program: Hold at 35°C for 10 min, ramp to 75°C at 5C°/min. and hold 15 min., ramp to 100°C at 5C°/min. and hold 5 min, ramp to 135°C at 5C°/min. and hold 2 min.

Column B: DB-1701, 30 m x 0.25 mm i.d., 0.25 µm film thickness, Injector Temp. = 200°C, Detector Temp. = 260°C, Linear Helium Velocity = 25 cm/sec at 35°C, splitless injection with 30 s delay.

Program: Hold at 35°C for 10 min, ramp to 75°C at 5C°/min. and hold 15 min., ramp to 100°C at 5C°/min. and hold 5 min, ramp to 135°C at 5C°/min. and hold 0 min.

TABLE 2. ANALYTE ACCURACY AND PRECISION DATA AND METHOD DETECTION LIMITS[a]

LEVEL 1 IN REAGENT WATER

Analyte	Fortified Conc. µg/L	Mean Meas. Conc. µg/L	Std. Dev. µg/L	Rel. Std. Dev., %	Method Detection Limit[b] µg/L	Estimated Detection Limit[c] µg/L
MCAA	0.600	0.516	0.087	17	0.273	0.60
MBAA	0.400	0.527	0.065	12	0.204	0.20
DCAA	0.600	0.494	0.077	16	0.242	0.24
Dalapon	0.400	0.455	0.038	8.4	0.119	0.40
TCAA	0.200	0.219	0.025	11	0.079	0.20
BCAA	0.400	0.498	0.080	16	0.251	0.25
DBAA	0.200	0.238	0.021	8.8	0.066	0.20
BDCAA	0.400	0.357	0.029	8.1	0.091	0.40
CDBAA	1.00	1.19	0.149	12	0.468	0.75
TBAA	2.00	1.91	0.261	14	0.820	1.5

[a] Produced by analysis of seven aliquots of fortified reagent water.

[b] The MDL is a statistical estimate of the detection limit. To determine the MDL for each analyte, the standard deviation of the mean concentration of the seven replicates is calculated. This standard deviation is then multiplied by the student's t-value at 99% confidence and n-1 degrees of freedom (3.143 for seven replicates). The result is the MDL.

[c] The EDL is defined as either the MDL or a level of a compound in a sample yielding a peak in the final extract with a signal to noise (S/N) ratio of approximately 5, whichever is greater.

TABLE 3. ANALYTE ACCURACY AND PRECISION DATA[a]

LEVEL 2 IN REAGENT WATER

Analyte	Fortified Conc. µg/L	Mean Meas. Conc. µg/L	Std. Dev. µg/L	Rel. Std. Dev., %	Mean Recovery %
Monochloroacetic Acid	1.50	1.42	0.103	7.3	94.7
Monobromoacetic Acid	1.00	1.02	0.051	5.0	102
Dichloroacetic Acid	1.50	1.27	0.122	9.6	84.7
Dalapon	1.00	0.935	0.087	9.3	93.5
Trichloroacetic Acid	0.500	0.465	0.048	10	93.0
Bromochloroacetic Acid	1.00	0.869	0.049	5.6	86.9
Dibromoacetic Acid	0.500	0.477	0.044	9.2	95.4
Bromodichloroacetic Acid	1.00	1.07	0.098	9.2	107
Chlorodibromoacetic Acid	2.50	2.62	0.150	5.7	105
Tribromoacetic Acid	5.00	5.19	0.587	11	104

[a] Produced by the analysis of seven aliquots of fortified reagent water.

TABLE 4. ANALYTE ACCURACY AND PRECISION DATA[a]

LEVEL 4 IN REAGENT WATER

Analyte	Fortified Conc. µg/L	Mean Meas. Conc. µg/L	Std. Dev. µg/L	Rel. Std. Dev., %	Mean Recovery %
Monochloroacetic Acid	6.00	5.24	0.664	13	87.3
Monobromoacetic Acid	4.00	4.36	0.475	11	109
Dichloroacetic Acid	6.00	6.89	0.782	11	115
Dalapon	4.00	3.87	0.147	3.8	96.8
Trichloroacetic Acid	2.00	1.74	0.144	8.3	87.0
Bromochloroacetic Acid	4.00	4.33	0.402	9.3	108
Dibromoacetic Acid	2.00	1.87	0.113	6.0	93.5
Bromodichloroacetic Acid	4.00	3.93	0.377	9.6	98.2
Chlorodibromoacetic Acid	10.0	11.4	0.866	7.6	114
Tribromoacetic Acid	20.0	24.0	1.82	7.6	120

[a] Produced by the analysis of seven aliquots of fortified reagent water.

TABLE 5. ANALYTE ACCURACY AND PRECISION DATA[a,b]

LEVEL 3 IN DECHLORINATED TAP WATER[c]

Analyte	Background Conc. µg/L	Forti-fied Conc. µg/L	Mean Meas. Conc. µg/L	Std. Dev. µg/L	Rel. Std. Dev. %	Mean Rec. %
Monochloroacetic Acid	<0.6	3.00	2.53	0.090	3.6	84.3
Monobromoacetic Acid	0.420	2.00	2.20	0.034	1.5	89.0
Dichloroacetic Acid	0.625	3.00	3.77	0.096	2.5	105
Dalapon	<0.4	2.00	1.96	0.157	8.0	98.0
Trichloroacetic Acid	0.300	1.00	1.12	0.167	15	82.0
Bromochloroacetic Acid	1.23	2.00	2.91	0.062	2.1	84.0
Dibromoacetic Acid	1.27	1.00	2.35	0.110	4.7	108
Bromodichloroacetic Acid	0.588	2.00	2.52	0.388	15	96.6
Chlorodibromoacetic Acid	1.23	5.00	6.36	0.502	7.9	103
Tribromoacetic Acid	<2.0	10.0	11.8	1.65	14	118

[a] Produced by analysis of seven aliquots of fortified dechlorinated tap water.

[b] Background level subtracted.

[c] Chlorinated surface water from a local utility to which ammonium chloride was added as the dechlorinating agent.

TABLE 6. ANALYTE ACCURACY AND PRECISION DATA[a,b]

LEVEL 3 IN HIGH IONIC STRENGTH WATER[c]

Analyte	Background Conc. µg/L	Forti-fied Conc. µg/L	Mean Meas. Conc. µg/L	Std. Dev. µg/L	Rel. Std. Dev. %	Mean Rec %
Monochloroacetic Acid	0.761	3.00	3.32	0.429	13	85.3
Monobromoacetic Acid	1.47	2.00	3.19	0.099	3.1	86.0
Dichloroacetic Acid	1.50	3.00	4.44	0.264	5.9	98.0
Dalapon	0.675	2.00	2.39	0.259	11	85.8
Trichloroacetic Acid	1.01	1.00	1.75	0.110	6.3	74.0
Bromochloroacetic Acid	2.06	2.00	3.71	0.269	7.3	82.5
Dibromoacetic Acid	4.36	1.00	5.48	0.255	4.7	112
Bromodichloroacetic Acid	1.07	2.00	3.37	0.308	9.1	115
Chlorodibromoacetic Acid	2.48	5.00	7.94	1.00	13	109
Tribromoacetic Acid	4.63	10.0	17.2	1.55	9.0	126

[a] Produced by analysis of seven aliquots of fortified high ionic strength water.

[b] Background level subtracted.

[c] Chlorinated ground water from a water source displaying a hardness of 460 mg/L as $CaCO_3$

TABLE 7. ANALYTE ACCURACY AND PRECISION DATA[a]

LEVEL 3 IN HIGH HUMIC CONTENT GROUND WATER[b]

Analyte	Background Conc. µg/L	Forti-fied Conc. µg/L	Mean Meas. Conc. µg/L	Std. Dev. µg/L	Rel. Std. Dev. %	Mean Rec. %
Monochloroacetic Acid	<0.6	3.00	2.91	0.082	2.8	97.0
Monobromoacetic Acid	<0.4	2.00	1.99	0.105	5.3	99.5
Dichloroacetic Acid	<0.6	3.00	2.88	0.104	3.6	96.0
Dalapon	<0.4	2.00	2.00	0.227	11	100
Trichloroacetic Acid	<0.2	1.00	0.618	0.053	8.6	61.8
Bromochloroacetic Acid	<0.4	2.00	1.82	0.059	3.2	91.0
Dibromoacetic Acid	<0.2	1.00	0.715	0.020	2.8	71.5
Bromodichloroacetic Acid	<0.4	2.00	1.99	0.164	8.2	99.5
Chlorodibromoacetic Acid	<1.0	5.00	5.50	0.218	4.0	110
Tribromoacetic Acid	<2.0	10.0	9.67	1.13	12	96.7

[a] Produced by analysis of seven aliquots of fortified simulated high humic content ground water.

[b] Reagent water fortified at 1.0 mg/L with fulvic acid extracted from Ohio River water. Sample simulates high TOC matrix.

TABLE 8. LABORATORY PERFORMANCE CHECK SOLUTION

PARAMETER	ANALYTE	CONC., µg/mL IN MTBE	ACCEPTANCE CRITERIA
INSTRUMENT SENSITIVITY	MCAA	0.006	DETECTION OF ANALYTE; S/N[a] > 3
CHROMATOGRAPHIC PERFORMANCE	BCAA	0.004	PGF[b] BETWEEN 0.80 AND 1.15
COLUMN PERFORMANCE	CDBAA SURROGATE. (2,3-DBPA)	0.010 0.010	RESOLUTION[c] > 0.50

[a] S/N, a ratio of peak signal to baseline noise.

peak signal - measured as height of peak.
baseline noise - measured as maximum deviation in baseline (in units of height) over a width equal to the width of the base of the peak.

[b] PGF = Peak Gaussian Factor

$$PGF = \frac{1.83 \times W_{1/2}}{W_{1/10}}$$

where $W_{1/2}$ = the peak width at half height (in secs).
$W_{1/10}$ = the peak width at one-tenth height (in secs).

This is a measure of the symmetry of the peak.

[c] Resolution between two peaks is defined by the equation:

$$R = \frac{t}{W_{ave}}$$

where t = the difference in elution times between the two peaks.
W_{ave} = the average peak width of the two peaks (measurements taken at baseline).

This a measure of the degree of separation of two peaks under specific chromatographic conditions.

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