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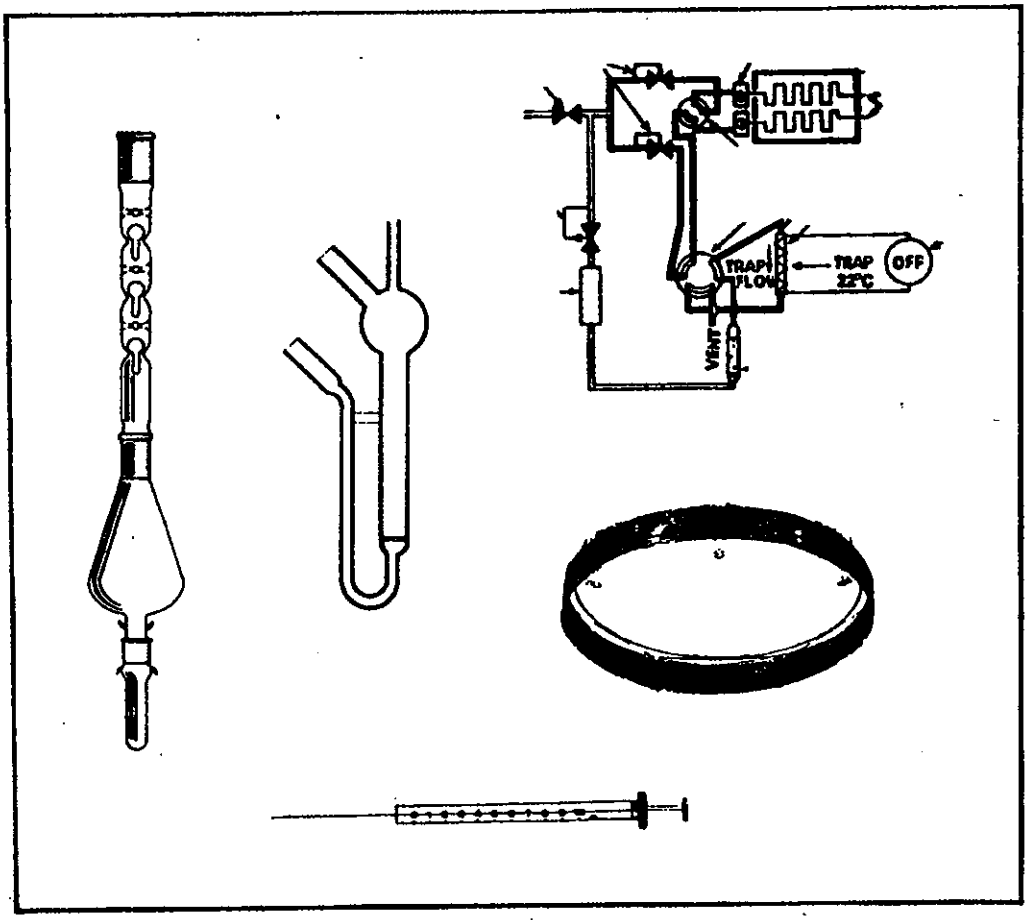
Methods for the Determination of Organic Compounds in Drinking Water



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METHODS FOR THE DETERMINATION OF ORGANIC COMPOUNDS IN DRINKING WATER

Environmental Monitoring Systems Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

DISCLAIMER

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring Systems Laboratory - Cincinnati (EMSL-Cincinnati) conducts research to:

- Develop and evaluate analytical methods to identify and measure the concentration of chemical pollutants in drinking water, surface waters, groundwater, wastewater, sediments, sludge, and solid waste.

- 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.

This publication of the Environmental Monitoring Systems Laboratory - Cincinnati titled, "Determination of Organic Compounds in Drinking Water" was prepared to gather together under a single cover a set of 13 laboratory analytical methods for organic compounds in drinking water. We are 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.

Thomas Clark, Director
Environmental Monitoring Systems
Laboratory - Cincinnati

ABSTRACT

Thirteen analytical methods for the identification and measurement of organic compounds in drinking water are described in detail. Six of the methods are for volatile organic compounds (VOCs) and certain disinfection by-products, and these methods were cited in the Federal Register of July 8, 1987, under the National Primary Drinking Water Regulations. The other seven methods are designed for the determination of a variety of synthetic organic compounds and pesticides, and these methods were cited in proposed drinking water regulations in the Federal Register of May 22, 1989. Five of the methods utilize the inert gas purge-and-trap extraction procedure for VOCs, six methods employ a classical liquid-liquid extraction, one method uses a new liquid-solid extraction technique, and one method is for direct aqueous analysis. Of the 13 methods, 12 use either packed or capillary gas chromatography column separations followed by detection with mass spectrometry or a selective gas chromatography detector. One method is based on a high performance liquid chromatography separation.

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INTRODUCTION

William L. Budde

Many of the nearly 200 organic analytes included in this manual may be identified and measured in drinking water using two or more of the documented analytical methods. For example, nearly 50 compounds are listed as analytes in four different methods. This approach of multiple methods for many analytes was selected to provide the maximum flexibility to method users from small and large laboratories. Some methods require relatively modest equipment, and others require sophisticated instrumentation. This flexible approach should meet the needs and requirements of nearly all laboratories.

GENERAL METHOD FEATURES

Each of the methods in the manual was written to stand-alone, that is, each method may be removed from the manual, photocopied, inserted into another binder, and used without loss of information. Revisions of these methods will be made available in a similar stand-alone format to facilitate the replacement of existing methods as new technical developments occur. This flexibility comes at the cost of some duplication of material, for example, the definitions of terms section of each method is nearly identical. The authors believe that the added bulk of the manual is a small price to pay for the flexibility of the format.

An important feature of the methods in this manual is the consistent use of terminology, and this feature is especially helpful in the quality control sections where standardized terminology is not yet available. The terms were carefully selected to be meaningful without extensive definition, and therefore should be easy to understand and use. The names of authors of the methods are provided to assist users in obtaining direct telephone support when required.

SAMPLE MATRICES

All methods were developed for relatively clean water matrices, that is, drinking water and some ground and surface waters. Some methods have been tested only in reagent water and/or drinking water. While some of these methods may provide reliable results with more complex water matrices, for example, industrial wastewaters and beverages, techniques for dealing with more complex matrices have not been included in the methods in order to keep them as simple and brief as possible. Therefore caution is needed when applying these methods to matrices other than relatively clean water.

Methods developed for drinking water include provisions for removal of free chlorine (dechlorination) which is assumed to be present in all samples. Dechlorination is necessary to stop the formation of trichloromethanes and other disinfection by-products, or to prevent the formation of method interferences and analytes generated from chlorination of impurities in reagents and solvents.

Similarly, pH adjustments are included in some of the methods for several reasons: (a) to retard growth in dechlorinated water of bacteria that can decompose some analytes; (b) to prevent acid or base catalyzed decomposition of analytes; and (c) to improve the extraction efficiency of certain analytes.

DETECTION LIMITS

Most methods include either a method detection limit (MDL) or an estimated detection limit (EDL) for each analyte. These limits are intended to provide an indication of the capability of the method, but they may not be of regulatory significance.

The MDL is calculated from the standard deviation of replicate measurements, and is defined as the minimum concentration of a substance that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero. The EDL is either the MDL, or a concentration of compound in a clean water matrix that gives a peak in the final extract with a signal-to-noise ratio of about 5.

If the replicate measurements needed to calculate an MDL are obtained under ideal conditions, for example, during a short period of time within a work shift, the resulting standard deviation may be small and give an unrealistically low MDL. The data acquired for measurement of an MDL should be obtained over a period of time (several days or more). Obtained in this way, the standard deviation includes normal day-to-day variations, and the MDL will be more realistic.

CALIBRATION STANDARDS AND QUALITY CONTROL SAMPLES

The methods contain separate calibration and quality control sections, and accurate calibration standards and quality control samples are needed to implement the methods. Calibration standards and quality control samples should be obtained from different sources so that the quality control sample can provide an independent check on the calibration and the other method variables.

Calibration standards and quality control samples may be available commercially, or may be available on a limited basis from the Quality Assurance Research Division, Environmental Monitoring Systems Laboratory - Cincinnati, 26 W. Martin Luther King Drive, Cincinnati, OH, 45268.

METHODS FOR VOLATILE ORGANIC COMPOUNDS (VOCS)

Six of the methods in the manual are for the determination of VOCs and certain disinfection by-products. These methods were cited in the Federal Register of July 8, 1987 under the National Primary Drinking Water Regulations. These are Methods 502.1, 502.2, 503.1, 504, 524.1 and 524.2.

The six VOC methods have been distributed in the form of photocopied documents by EMSL-Cincinnati to several hundred laboratories in the last two

years. Five of these methods utilize the same basic purge-and-trap extraction technique, but, depending on the specific method selected, the user has a choice of a packed or capillary column gas chromatography (GC) separation and a mass spectrometer (MS) or conventional GC detector. The other method (Method 504) is a microextraction procedure for two compounds of special interest, ethylene dibromide (EDB) and 1,2-dibromo-3-chloropropane (DBCP).

Solicited and unsolicited written and telephoned comments have been received from some of the laboratories using the VOC methods, and some of these users suggested certain technical and editorial changes. In addition, the staff of the Chemistry Research Division recognized that some changes were needed to make the methods easier to understand and use, and bring them up-to-date. The revisions of the six VOC methods contained in the manual incorporate a few technical and many editorial changes which are summarized below.

Few technical changes were made to the six VOC methods. The use of ascorbic acid as a dechlorinating agent is described. Ascorbic acid has been extensively tested as a dechlorinating agent, and has been found to be as effective as sodium thiosulfate, but without the undesirable generation of sulfur dioxide at low pH.

The open split interface between the GC and the MS was incorporated into Method 524.2, but the interfaces previously mentioned were retained. Data is presented in the method to show that the open split interface can provide acceptable precision, accuracy, and detection limits. The previous revision of Method 524.2 allowed any interface that could meet the precision and accuracy requirements of the method. Many laboratories will find the open split interface to be the most economical for this method.

Changes were made in the recommended chromatographic conditions and internal standards in Method 502.2. These changes allow the measurement of all 60 VOCs in a single calibration solution.

Extensive editorial changes were made in all six VOC methods. These editorial changes were necessary to provide an organized, consistent, and much more complete presentation of the myriad details needed by laboratories to successfully implement the methods. The addition of these details, the consistent use of terminology, and the uniform organization of all the methods should substantially reduce the number of questions received and provide the user community with the information needed to obtain high quality results.

METHODS FOR SYNTHETIC ORGANIC COMPOUNDS (SOCS)

Four of the SOC methods were developed for a national pesticides survey conducted by EPA during 1987-1989, and these are designated Methods 507, 508, 515.1, and 531.1. One screening method (Method 508A) for polychlorinated biphenyls (PCBs) was developed as a result of a specific request from the Office of Drinking Water (ODW). Method 505, a relatively simple microextraction procedure patterned after Method 504, was developed to provide a rapid method for the determination of chlorinated hydrocarbon pesticides and

commercial PCB mixtures (Aroclors) in drinking water. Method 525.1 is a broad spectrum GC/MS method for a variety of compounds under consideration for regulation, and it was developed specifically to utilize the new liquid-solid extraction technology and minimize use of the solvent methylene chloride.

Three of the methods used in the national pesticides survey utilize a liquid-liquid extraction of the SOCs from water followed by a high resolution capillary column GC separation and detection with an electron capture or other selective detector (Methods 507, 508, and 515.1). One of the methods (531.1) employs the direct analysis of a water sample with a high performance liquid chromatography (HPLC) separation and post-column derivatization to a compound detected with a fluorescence detector.

Method 508A was designed as a screening procedure for polychlorinated biphenyls (PCBs). The method uses the powerful chlorinating agent antimony pentachloride to convert all the PCB congeners in a sample extract to decachlorobiphenyl which is separated with either packed or capillary column gas chromatography, and detected with an electron capture detector.

Method 505 provides a rapid procedure for chlorinated hydrocarbon pesticides and commercial PCB mixtures (Aroclors). This method uses a high resolution capillary column GC separation and detection with an electron capture detector.

The broad spectrum GC/MS method (Method 525.1) uses a liquid-solid extraction (LSE) procedure based on commercial LSE cartridges or disks. The cartridges are small (about 0.5 in. x 3 in.) plastic or glass tubes packed with reverse phase liquid chromatography packing materials. The disks are made of Teflon containing silica which is coated with a chemically bonded C-18 organic phase. Water samples are passed through the cartridges or disks and some organic compounds are sorbed on the solid phase. After air drying, the organic compounds are eluted using a very small volume of an organic solvent. Cartridges from six suppliers were used in the methods research, and a quality control procedure was developed to permit selection of cartridges with acceptable performance characteristics. The disks are manufactured by a single company, so only one type was evaluated.

The LSE procedure is attractive because it greatly reduces the use and worker exposure to methylene chloride and similar solvents. The compounds in the cartridge extract are separated, identified, and measured with a high resolution capillary column GC/MS procedure. This allows the simultaneous determination of 42 SOCs including chlorinated hydrocarbon pesticides, polycyclic aromatic hydrocarbons, phthalate and adipate esters, individual PCB congeners, several triazine pesticides, and pentachlorophenol. Laboratories will find this method attractive because of its potential economy of operation when a wide variety of analytes are to be determined.

METHOD 502.1. VOLATILE HALOGENATED ORGANIC COMPOUNDS IN WATER BY PURGE AND TRAP GAS CHROMATOGRAPHY

Revision 2.0

T. A. Bellar - Method 502.1, Revision 1.0 (1986)

T. A. Bellar - Method 502.1, Revision 2.0 (1989)

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

METHOD 502.1

VOLATILE HALOGENATED ORGANIC COMPOUNDS IN WATER BY PURGE AND TRAP GAS CHROMATOGRAPHY

1. SCOPE AND APPLICATION

1.1 This method is applicable for the determination of various halogenated volatile compounds in finished drinking water, raw source water, or drinking water in any treatment stage.(1) The following compounds can be determined by this method:

Analyte	Chemical Abstract Service Registry Number
Bromobenzene	108-86-1
Bromochloromethane	74-97-5
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Bromomethane	74-83-9
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-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
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Trichloroethene	79-01-6
Trichlorofluoromethane	75-69-4
1,2,3-Trichloropropane	96-18-4
Vinyl chloride	75-01-4

1.2 This method is applicable to the determination of Total Trihalomethanes and other volatile synthetic organic compounds as required by drinking water regulations of 40 Code of Federal Regulations Part 141.

1.3 Single laboratory accuracy and precision data show that this procedure is useful for the detection and measurement of multi-component mixtures added to carbon filtered finished water and raw source water at concentrations between 0.20 and 0.40 µg/L with method detection limits (MDL)(2) generally less than 0.01 µg/L. The upper concentration limit of the method is about 1000 µ/L for most compounds. Determination of complex mixtures containing partially resolved compounds may be hampered by concentration differences larger than a factor of 10. This problem commonly occurs when finished drinking waters are analyzed because of the relatively high trihalomethane content. When such samples are analyzed, chloroform will affect the method detection limit for 1,2-dichloroethane.

1.4 Accuracy and precision data are not yet available for Bromomethane, 2,2-dichloropropane, cis- and trans-1,3,-dichloropropene.

1.5 This method is recommended for use only by analysts experienced in the measurement of purgeable organics at the low µg/L level or by experienced technicians under the close supervision of a qualified analyst. It is also recommended for use only with a purge and trap system devoted to the analysis of low level samples.

2. SUMMARY OF METHOD

2.1 Organohalides and other highly volatile organic compounds 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 an inert gas to desorb trapped sample components onto a gas chromatography (GC) column. The gas chromatograph is temperature programmed to separate the method analytes which are then detected with a halogen specific detector.

2.2 A second chromatographic column is described that can be used to help confirm GC identifications or resolve coeluting compounds. Confirmatory analyses may be performed by gas chromatography/mass spectrometry (GC/MS) according to Method 524.1 or Method 524.2.

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 that are components of the same solution. The internal standard must be an analyte that is not a sample component.

3.2 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.

3.3 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.

3.4 Laboratory reagent blank (LRB) -- An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents and internal standards 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.

3.5 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.

3.6 Laboratory performance check solution (LPC) -- A solution of one or more compounds used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.7 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.

3.8 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 -- 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.

3.10 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.

3.11 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 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 generated from a source of reagents different than those used to prepare the primary dilution standards and the calibration standard and is used to check laboratory performance.

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. 10.4) or field reagent blanks (Sect. 10.6) provide information about the presence of contaminants. When potential interfering peaks are noted in laboratory reagent blanks, the analyst must eliminate the problem before analyzing samples. 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, laboratory reagent blanks must be analyzed until system memory is reduced to an acceptable level.

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 (3-5) for the information of the analyst.

5.2 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: carbon tetrachloride, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloro-ethene, 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. APPARATUS AND EQUIPMENT

6.1 SAMPLE CONTAINERS - 40-mL to 120-mL screw cap vials (Pierce #13075 or equivalent) each equipped with a PTFE-faced silicone septum (Pierce #12722 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 in a 105°C oven for one hour, then remove and allow to cool in an area known to be free of organic solvent vapors.

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 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.

6.2.3 The desorber (Figure 2) must be capable of rapidly heating the trap to 180°C. 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 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 <30°C (Sect. 11.3); therefore, a subambient oven controller may be required.

6.3.2 Two gas chromatography columns are recommended. Column 1 (Sect. 6.3.3) is a highly efficient column that provides outstanding separations for a wide variety of organic compounds. Column 1 should be used as the primary analytical column unless routinely occurring analytes are not adequately resolved. Column 2 (Sect. 6.3.4) is recommended for use as an alternate column. Retention times for the listed analytes on the two columns are presented in Table 1.

6.3.3 Column 1 - 1.5 to 2.5 m x 0.1 in ID stainless steel or glass, packed with 1% SP-1000 on Carbopack-B (60/80 mesh) or equivalent. The flow rate of the helium carrier gas is established at 40 mL/min. The column temperature is programmed to hold at 45°C for three min, increased to 220°C at 8°C/min, and held at 220°C for 15 min or until all expected compounds have eluted. During handling, packing, and programming, active sites can be exposed on the Carbopack-B packing which can result in tailing peak geometry and poor resolution of many constituents. To protect the analytical column, pack the first 5 cm of the column with 3% SP-1000 on Chromosorb-W (60/80 mesh) followed by the Carbopack-B packing. Condition the precolumn and the Carbopack columns with carrier gas flow at 220°C overnight. Pneumatic shocks and rough treatment of packed columns will cause excessive fracturing of the Carbopack. If pressure in excess of 60 psi is required to obtain 40 mL/min carrier flow, the column should be repacked. A sample chromatogram obtained with Column 1 is presented in Figure 3.

6.3.4 Column 2 - 1.5 to 2.5 m long x 0.1 in ID stainless steel or glass, packed with n-octane chemically bonded on Porasil-C (100/120 mesh) or equivalent. The flow rate of the helium carrier gas is established at 40 mL/min. The column temperature is programmed to hold at 50°C for three min, increased to 170°C at 6°C/min, and held at 170°C for four min or until all expected compounds have eluted. NOTE: This material was not commercially available at time of publication. Check with suppliers for a suitable substitute if this material cannot be located.

6.3.5 An electrolytic conductivity or microcoulometric detector is required. These halogen-specific systems eliminate misidentifications due to non-organohalides which are coextracted during the purge step. A Tracor Hall Model 700-A detector was used to develop the single laboratory method performance data described in Sect. 13. The operating conditions used to collect these data are as follow:

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:	Helium at 40 mL/min

6.3.6 It is acceptable to insert a photoionization detector between the analytical column and the halide detector to simultaneously analyze for the regulated volatile organic compounds (VOC) that are aromatic or unsaturated (6). Some of the analytes listed in the Scope of Method 503.1 can be determined in this manner. See Method 502.2.

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 CONSUMABLE MATERIALS

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 - 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 by crushing through 26 mesh screen.

7.2 COLUMN PACKING MATERIALS

7.2.1 1% SP-1000 on 60/80 mesh Carbopack-B or equivalent.

7.2.2 n-Octane chemically bonded on Porasil-C, 100/120 mesh (Durapak or equivalent).

7.2.3 3% SP-1000 on 60/80 mesh Chromosorb-W or equivalent.

7.3 REAGENTS

7.3.1 Methanol - demonstrated to be free of analytes.

7.3.2 Reagent water demonstrated to be free of analytes - 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.

7.3.3 Ascorbic acid or sodium thiosulfate - ACS Reagent grade, granular.

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

7.3.5 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 are available from several sources.

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

7.4.1 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.

7.4.2 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.

7.4.3 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.

7.4.4 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 times may be extended only if the analyst proves their validity by analyzing quality control samples.

7.5 PRIMARY DILUTION STANDARDS - Use standard stock 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 solutions (Sect. 9.1) 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 solutions for them. Storage times described for stock standard solutions in Sect. 7.4.4 also apply to primary dilution standard solutions.

7.6 QUALITY CONTROL SAMPLE - Prepare or obtain from a certified source a methyl alcohol solution at a concentration of 1.00 µg/mL for the regulated volatile organic contaminants and the unregulated contaminants of interest. It will be necessary to prepare more than one solution and to increase the concentration of some of the contaminants proportional to the instrument detection limits if all of the analytes in Sect. 1.1 are being measured by this method. The concentrate should be prepared from a source of stock standards different than those used for Sect. 7.5

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 SAMPLE COLLECTION, DECHLORINATION, AND PRESERVATION

8.1.1 Collect all samples in duplicate. If samples contain residual chlorine, and measurements of the concentrations of disinfection by-products (trihalomethanes, etc.) at the time of sample collection are desired, add about 25 mg of ascorbic acid (or 3 mg sodium thiosulfate) to the sample bottle before filling. Fill sample bottles to overflowing, but take care not to flush out the rapidly dissolving ascorbic acid (or sodium thiosulfate). No air bubbles should pass through the sample as the bottle is filled, or be trapped in the sample when the bottle is sealed. Adjust the pH of the duplicate samples to <2 by carefully

adding one drop of 1:1 HCl for each 20 mL of sample volume. Seal the sample bottles, PFTE-face down, and shake vigorously for 1 min.

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 from the flowing stream.

8.1.3 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 duplicate sample bottles from the 1-quart container.

8.1.4 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 that they will be at 4°C on arrival at the laboratory.

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.

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

8.3.1 Duplicate field reagent blanks 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, 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.

8.3.2 Use the same procedures used for samples to add ascorbic acid (or sodium thiosulfate) and HCl to blanks (Sect. 8.1.1).

9. CALIBRATION AND STANDARDIZATION

9.1 PREPARATION OF CALIBRATION STANDARDS

9.1.1 Calibration standards containing mixtures of analytes that are at least 80 percent resolved are prepared as needed. The number of calibration solutions (CALs) needed depends on the resolution requirement and 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. The lowest level calibration standard should contain analytes at a concentration two to ten times the MDL (Table 2) for that compound. The other CAL standards should contain each analyte of concern at concentrations that define the range of the sample analyte concentrations.

9.1.2 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. Use a microsyringe and rapidly inject the alcoholic standard into the water. Remove the needle as quickly as possible after injection. Accurate calibration standards are prepared by adding 20 µL of the primary dilution standard to 25 mL or more of reagent water using the syringe described in Sect. 6.4.3. Aqueous standards are not stable and should be discarded after one hour unless sealed and stored as described in Sect. 8.2 and 8.4.

9.2 CALIBRATION WITH AQUEOUS STANDARDS

9.2.1 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.

9.2.2 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. 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 that analyte or use a single point calibration standard as described in Sect. 9.2.3.

9.2.3 Single point calibration is a viable alternative to a calibration curve. Prepare single point standards from the primary dilution standards in methanol. The single

point standards should be prepared at a concentration that produces a response close (±20%) to that of the unknowns.

9.2.4 As a second alternative to a calibration curve, internal standard calibration techniques may be used. The following organohalides are recommended for this purpose: 2-bromo-1-chloropropane or 1,4-dichlorobutane. The internal standard is added to the sample just before purging. Check the validity of the internal standard calibration factors daily by analyzing a calibration standard. Since the calculated concentrations can be strongly biased by inaccurate detector response measurements for the internal standard or by coelution of an unknown, it is required that the area measurement of the internal standard for each sample be within ±3 standard deviations of those obtained from calibration standards. If they do not then internal standards can not be used.

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

9.3.1 Fill the purging device with 5.0 mL of reagent water or aqueous calibration standard.

9.3.2 Start to purge the aqueous mixture. Inject a known volume (between 100 and 2000 µL at room temperature) of the calibration gas (at room temperature) directly into the purging device with a gas tight syringe. Slowly inject the gaseous sample through an 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.

9.3.3 Determine the aqueous equivalent concentration of vinyl chloride standard injected with 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); and
V = Volume of standard injected in milliliters.

9.4 INSTRUMENT PERFORMANCE - Check the performance of the entire analytical system daily using data gathered from analyses of field blanks, standards, duplicate samples, and the quality control sample.

9.4.1 All of the peaks contained in the standard chromatograms must be sharp and symmetrical. Peak tailing significantly in excess of that shown in the method chromatogram (Figure 3) must be corrected. Tailing problems are generally traceable to active sites on the GC column or the detector operation. If only the compounds eluting before chloroform give random responses or unusually wide peak widths, are poorly resolved, or are missing, the problem is usually traceable to the trap/desorber. If only brominated compounds show poor peak geometry or do not properly respond at low concentrations, repack the trap. Excessive detector reactor temperatures can also cause low bromoform response. If negative peaks appear in the chromatogram, replace the ion exchange column and replace the electrolyte in the detector.

9.4.2 Check the precision between replicate analyses. A properly operating system should perform with an average relative standard deviation of less than 10%. Poor precision is generally traceable to pneumatic leaks, especially around the sample purger and detector reactor inlet and exit, electronic problems, or sampling and storage problems. Monitor the retention times for each organohalide using data generated from calibration standards. If individual retention times vary by more than 10% over an 8-h period or do not fall within 10% of an established norm, the source of retention data variance must be corrected before acceptable data can be generated.

10. QUALITY CONTROL

10.1 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. The laboratory must maintain records to document the quality of the data generated. Additional quality control practices are recommended.

10.2 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, sorbants, 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.

10.3 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 0.1-5 ug/L (see regulations and maximum contaminant levels for guidance on appropriate concentrations).

10.3.1 Prepare each replicate by adding an appropriate aliquot of a quality control sample to reagent water. If a quality control sample containing the method analytes is not available, a primary dilution standard made from a source of reagents different than those used to prepare the calibration standards may be used. Also add the appropriate amounts of internal standard and surrogates if they are being used. Analyze each replicate according to the procedures described in Section 11, and on a schedule that results in the analyses of all replicates over a period of several days.

10.3.2 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. Calculate the MDL of each analyte using the procedures described in (2).

10.3.3 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. The method detection limits must be sufficient to detect analytes at the regulatory levels. 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.

10.3.4 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.

10.4 Laboratory reagent blanks. With each batch of samples processed as a group within a work shift, analyze a laboratory reagent blank to determine the background system contamination.

10.5 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 10.3. If more than 20 samples are included in a batch, analyze one LFB for every 20 samples. Use the procedures described in 10.3.3 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. Add

these results to the on-going control charts to document data quality.

10.6 With each set of field samples a field reagent blank (FRB) should be analyzed. The results of these analyses will help define contamination resulting from field sampling and transportation activities. An acceptable FRB may replace the LRB.

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

10.8 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.

10.9 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. It is recommended that sample matrix effects be evaluated at least quarterly using the QCS described in 10.8.

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

11. PROCEDURE

11.1 INITIAL CONDITIONS

11.1.1 Recommended chromatographic conditions are summarized in Sect. 6.3.3. Other packed or capillary (open tubular) columns may be used if the requirements of Sect. 10.3 are met.

11.1.2 Calibrate the system daily as described in Sect. 9.2.

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. Warm the sample 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. If applicable, add 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.

11.3 SAMPLE DESORPTION - After the 11-min purge, attach the trap to the chromatograph, adjust the purge and trap system to the desorb mode and initiate the temperature program sequence of the gas chromatograph. Introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while backflushing the trap with an inert gas between 20 and 60 mL/min for 4.0 ± 0.1 min. If rapid heating cannot be achieved, the GC column must be used as a secondary trap by cooling it to 30°C (subambient temperature if poor peak geometry and random retention problems persist) instead of the initial operating temperature for analysis. 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. After the purging device has been emptied, leave the syringe valve open to allow the purge gas to vent through the sample introduction needle.

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. Wait 15 s, then close the syringe valve on the purging device to begin gas flow through the trap. 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. 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 those generated by knowns, then the identification may be considered as positive. If the suspect peak falls outside this range or coelutes with other compounds (Table 1) then the sample should be reanalyzed according to Sect. 2.2.

12.2 Determine the concentration of the unknowns 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.

$$\text{Concentration of unknown } (\mu g/L) = \frac{\text{Peak height sample}}{\text{Peak height standard}} \times \text{Concentration of standard } (\mu g/L)$$

12.3 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.

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

13. ACCURACY AND PRECISION

13.1 Single laboratory (EMSL-Cincinnati) accuracy and precision for the organohalides added to Ohio River water and carbon-filtered tap water are presented in Table 2.(1) Method detection limits for several of the listed analytes are also presented in Table 2.(1) Some laboratories may not be able to achieve these detection limits since results are dependent upon instrument sensitivity and matrix effects.

13.2 This method was tested by 20 laboratories using drinking water fortified with various organohalides at six concentrations between 8 and 505 µg/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte. Linear equations to describe these relationships are presented in Table 3 (9).

14. REFERENCES

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7. Slater, R.W., Graves, R.L. and G.D. McKee, "A Comparison of Preservation Techniques for Volatile Organic Compounds in Chlorinated Tap Waters," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

8. Bellar, T.A. and J.J. Lichtenberg, "The Determination of Synthetic Organic Compounds in Water by Purge and Sequential Trapping Capillary Column Gas Chromatography," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

9. EPA Method Validation Study 23, Method 601 (Purgeable Halocarbons), U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

TABLE 1. RETENTION TIMES FOR ORGANOHALIDES

Analyte	Retention Time (min)[a] Column 1	Column 2
Chloromethane	1.50	5.28
Bromomethane	2.17	7.05
Dichlorodifluoromethane	2.62	(b)
Vinyl chloride	2.67	5.28
Chloroethane	3.33	8.68
Methylene chloride	5.25	10.1
Trichlorofluoromethane	7.18	(b)
1,1-Dichloroethene	7.93	7.72
Bromochloromethane	8.48	12.7
1,1-Dichloroethane	9.30	12.6
trans-1,2-Dichloroethene	10.1	9.38
cis-1,2-Dichloroethene	10.1	12.1
Chloroform	10.7	12.1
1,2-Dichloroethane	11.4	15.4
Dibromomethane	11.6	14.9
1,1,1-Trichloroethane	12.6	13.1
Carbon tetrachloride	13.0	11.1
Bromodichloromethane	13.7	14.6
Dichloroacetonitrile[c]	14.7	(b)
1,2-Dichloropropane	14.9	16.6
1,1-Dichloropropene	15.1	(b)
Trichloroethene	15.8	13.1
1,3-Dichloropropane	16.2	(b)
Dibromochloromethane	16.5	16.6
1,1,2-Trichloroethane	16.5	18.1
1,2-Dibromoethane	17.4	18.9
2-Chloroethylethyl ether[c]	17.6	(b)
2-Chloroethylvinyl ether[c]	18.0	(b)
Bromoform	19.2	19.2
1,1,1,2-Tetrachloroethane	19.4	21.8
1,2,3-Trichloropropane	21.3	(b)
Chlorocyclohexane[c]	21.4	(b)
1,1,2,2-Tetrachloroethane	21.6	(b)
Tetrachloroethene	21.7	15.0
Pentachloroethane[d]	21.7	(b)
1-Chlorocyclohexene[c]	22.4	19.9
Chlorobenzene	24.2	18.8
1,2-Dibromo-3-chloropropane	26.0	(b)
Bromobenzene	27.1	(b)
2-Chlorotoluene	32.1	22.0
bis-2-Chloroisopropyl ether	32.2	(b)
1,3-Dichlorobenzene	34.0	22.4
1,2-Dichlorobenzene	34.9	23.9
1,4-Dichlorobenzene	35.45	22.3

(a) = Columns and conditions are described in Sect. 6.3.3 and 6.3.4.
(b) = Not determined.
(c) = Compound not a method analyte.
(d) = Pentachloroethane apparently decomposes to tetrachloroethene in the analytical system.

TABLE 2. SINGLE LABORATORY ACCURACY, PRECISION, AND METHOD DETECTION LIMITS FOR VOLATILE HALOGENATED ORGANIC COMPOUNDS IN WATER

Analyte	Concentration (µg/L)	Average Recovery (%)	Number of Samples	Relative Standard Deviation (%)	Method Detection Limit (µg/L)
Bromobenzene	0.40	93	20	12	(a)
Bromochloromethane	0.40	90	19	9.5	(a)
Bromodichloromethane	0.20	100	17	6.5	0.003
Bromoform	0.20	95	17	15.0	0.05
Carbon tetrachloride	0.20	90	17	7.0	0.003
Chlorobenzene	0.40	88	18	9.3	0.005
Chlorocyclohexane	0.40	93	21	8.3	(a)
1-Chlorocyclohexene	0.40	93	21	12.8	(a)
Chloroethane	0.40	93	20	18	0.008
2-Chloroethylethyl ether	0.40	95	18	7.5	0.02
Chloromethane	0.40	93	16	8.5	0.01
2-Chlorotoluene	0.40	85	20	9.3	(a)
Dibromochloromethane	0.20	95	17	7.0	0.008
1,2-Dibromoethane	0.40	93	18	12.5	0.04
Dibromomethane	0.40	100	5	8.0	(a)
1,2-Dichlorobenzene	0.40	95	21	13	(a)
1,3-Dichlorobenzene	0.40	95	21	8.3	(a)
1,4-Dichlorobenzene	0.40	90	20	13	(a)
Dichlorodifluoromethane	0.40	103	12	20	(a)
1,1-Dichloroethane	0.20	95	17	6.0	0.003
1,2-Dichloroethane	0.20	110	17	7.0	0.002
1,1-Dichloroethene	0.40	88	18	9.3	0.003
1,2-Dichloroethene(b)	0.40	88	20	7.0	0.002
1,2-Dichloropropane	0.40	95	20	3.5	(a)
1,3-Dichloropropane	0.40	98	21	6.5	(a)
1,1-Dichloropropene	0.40	88	18	9.3	(a)
Methylene chloride	0.20	85	17	12.0	(a)
1,1,1,2-Tetrachloroethane	0.40	93	20	8.0	(a)
1,1,2,2-Tetrachloroethane	0.40	95	18	9.0	0.01
Tetrachloroethene	0.20	90	17	9.5	0.001
1,1,1-Trichloroethane	0.40	93	20	8.0	0.003
1,1,2-Trichloroethane	0.40	95	15	6.0	0.007
Trichloroethene	0.20	94	17	6.0	0.001
Trichlorofluoromethane	0.40	90	21	9.3	(a)
1,2,3-Trichloropropane	0.40	100	20	9.5	(a)
Vinyl Chloride	0.20	110	12	15	0.01

(a) = Not determined.
(b) = Includes cis- and trans- isomers.

TABLE 3. SINGLE ANALYST PRECISION, MULTI-LABORATORY PRECISION, AND ACCURACY FOR VOLATILE HALOGENATED ORGANIC COMPOUNDS IN DRINKING WATER

Analyte	Single Analyst	Multi-Laboratory Precision	Accuracy As Mean Recovery ($\bar{X}$)
Bromodichloromethane	$0.13\bar{X} + 1.41$	$0.18\bar{X} + 3.06$	$1.00C + 0.96$
Bromoform	$0.10\bar{X} + 0.20$	$0.24\bar{X} + 1.25$	$1.02C - 1.81$
Carbon Tetrachloride	$0.10\bar{X} + 1.57$	$0.20\bar{X} + 1.09$	$1.00C - 2.20$
Chlorobenzene	$0.07\bar{X} + 1.71$	$0.16\bar{X} + 1.43$	$1.00C - 1.39$
Chloroethane	$0.07\bar{X} + 0.65$	$0.19\bar{X} + 0.39$	$1.08C - 1.97$
Chloroform	$0.05\bar{X} + 5.58$	$0.09\bar{X} + 6.21$	$0.90C + 3.44$
Chloromethane	$0.28\bar{X} + 0.27$	$0.49\bar{X} + 1.51$	$0.91C - 0.99$
Dibromochloromethane	$0.10\bar{X} + 1.55$	$0.23\bar{X} + 0.91$	$0.98C + 2.89$
1,2-Dichlorobenzene	$0.12\bar{X} + 2.02$	$0.17\bar{X} + 2.26$	$0.91C + 1.12$
1,3-Dichlorobenzene	$0.15\bar{X} + 0.64$	$0.24\bar{X} + 1.48$	$0.91C - 0.13$
1,4-Dichlorobenzene	$0.09\bar{X} + 0.39$	$0.15\bar{X} + 0.39$	$0.91C + 0.26$
1,1-Dichloroethane	$0.09\bar{X} + 0.47$	$0.18\bar{X} + 1.13$	$0.93C - 2.04$
1,2-Dichloroethane	$0.06\bar{X} + 1.69$	$0.18\bar{X} + 1.21$	$1.03C - 0.41$
1,1-Dichloroethene	$0.12\bar{X} + 0.13$	$0.31\bar{X} - 0.71$	$1.03C - 1.16$
trans-1,2-Dichloroethene	$0.16\bar{X} + 0.29$	$0.24\bar{X} + 0.95$	$0.98C - 1.02$
1,2-Dichloropropane	$0.19\bar{X} - 0.61$	$0.27\bar{X} - 0.10$	$0.98C + 1.19$
Methylene Chloride	$0.08\bar{X} + 1.04$	$0.17\bar{X} + 2.43$	$0.97C - 1.50$
1,1,2,2-Tetrachloroethane	$0.09\bar{X} - 1.42$	$0.20\bar{X} + 1.65$	$0.92C - 0.82$
Tetrachloroethene	$0.17\bar{X} + 0.96$	$0.25\bar{X} + 0.58$	$0.96C + 0.35$
1,1,1-Trichloroethane	$0.14\bar{X} - 0.33$	$0.27\bar{X} - 0.76$	$0.92C + 0.02$
1,1,2-Trichloroethane	$0.06\bar{X} + 0.99$	$0.19\bar{X} + 0.69$	$0.84C + 0.83$
Trichloroethene	$0.13\bar{X} + 0.23$	$0.32\bar{X} - 0.57$	$0.92C - 0.10$
Trichlorofluoromethane	$0.22\bar{X} + 0.03$	$0.30\bar{X} + 0.64$	$0.92C + 1.21$
Vinyl Chloride	$0.14\bar{X} - 0.17$	$0.32\bar{X} + 0.07$	$1.06C - 1.86$

$\bar{X}$ = Mean recovery, in µg/L
C = True value for the concentration, in µg/L

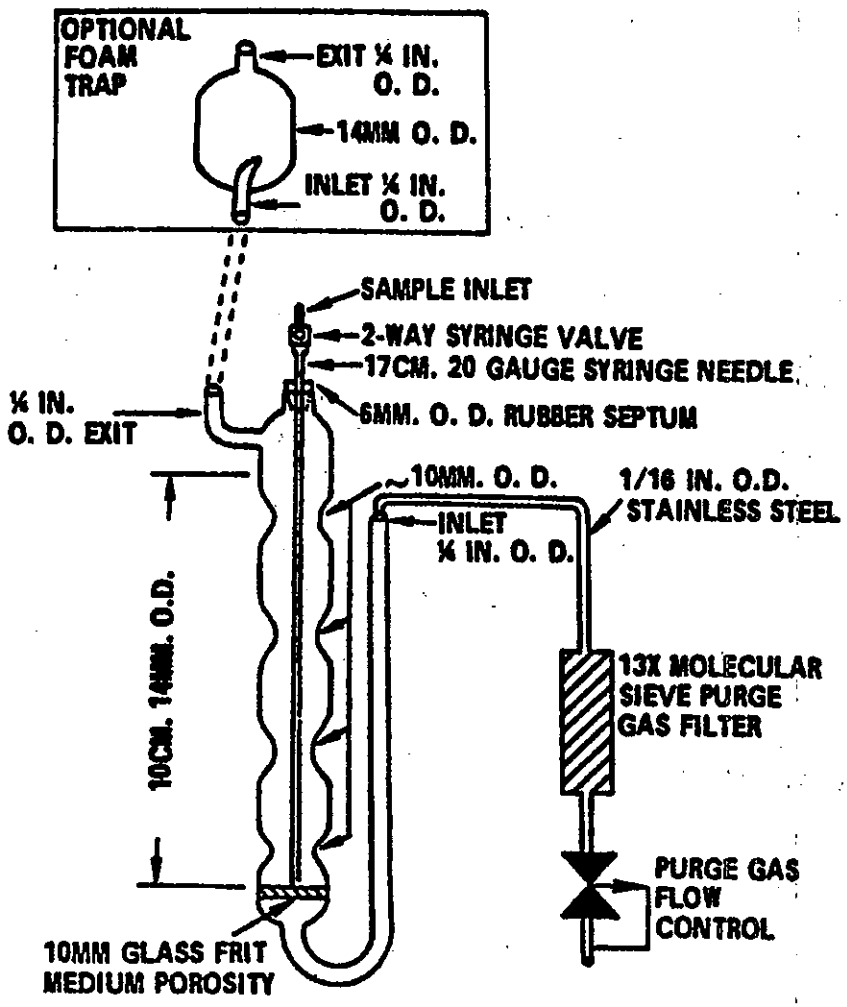

FIGURE 1. PURGING DEVICE

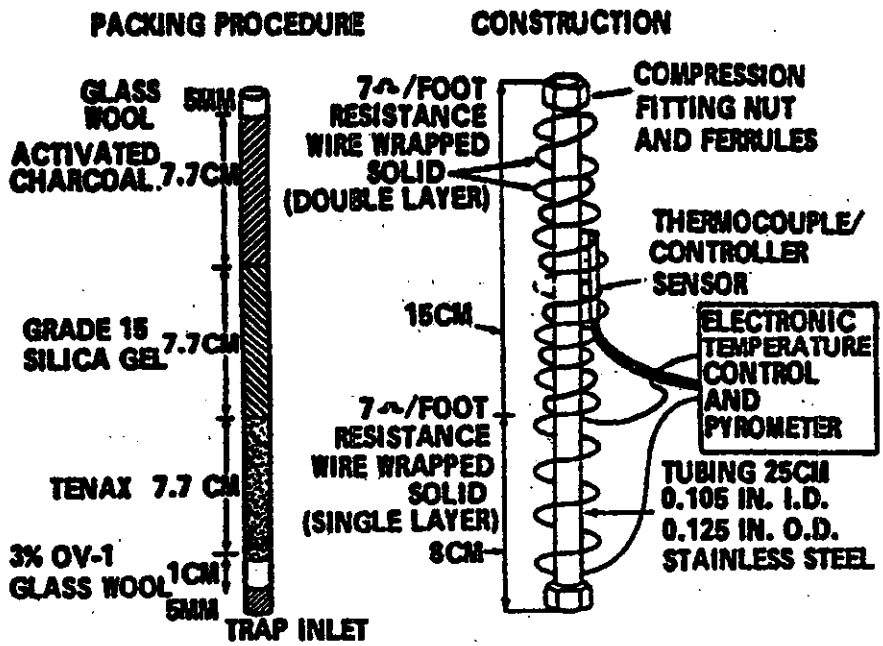

FIGURE 2. TRAP PACKINGS AND CONSTRUCTION TO INCLUDE DESORB CAPABILITY

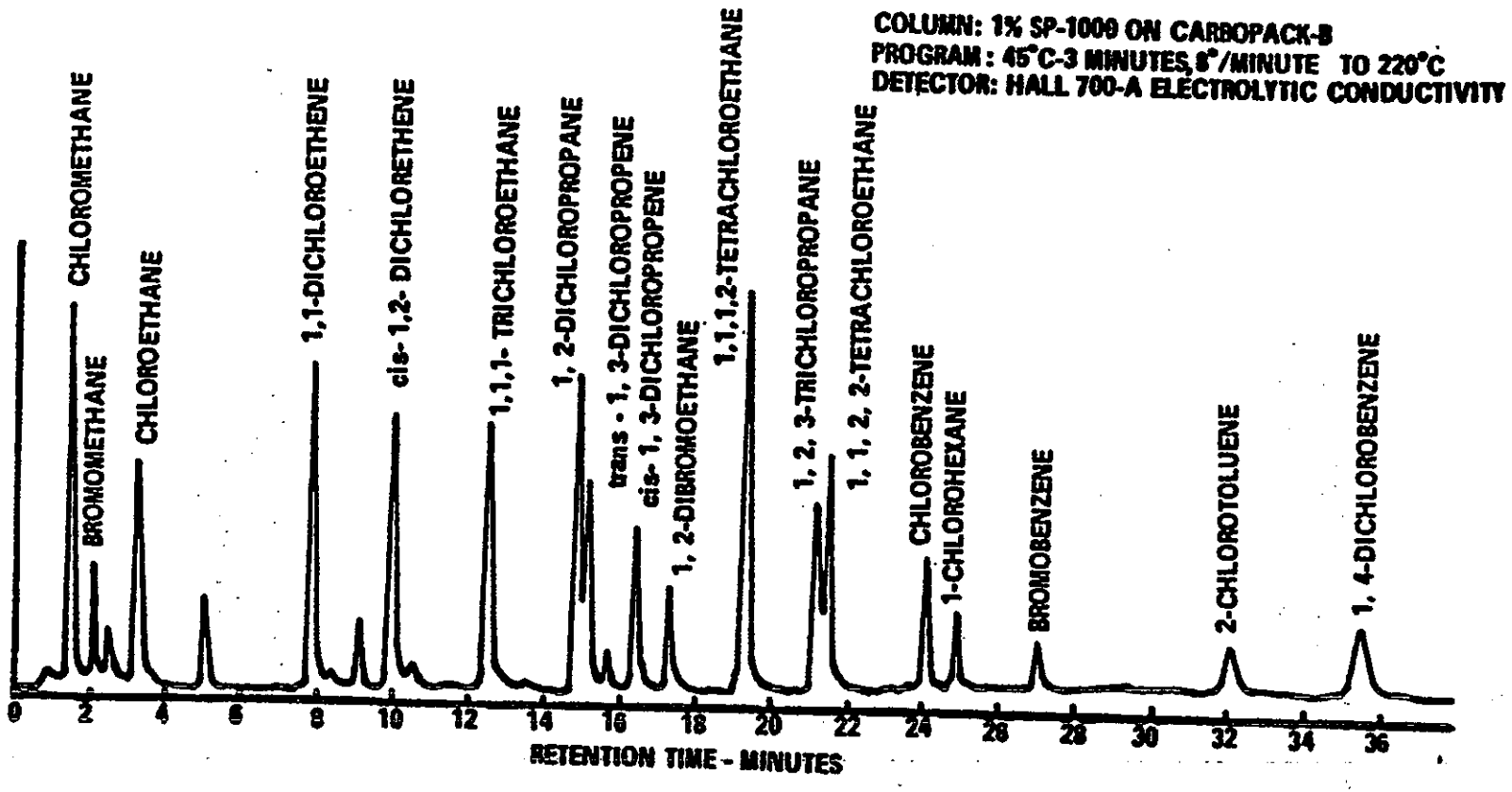

FIGURE 3. GAS CHROMATOGRAM OF PURGEABLE HALOCARBONS

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 2.0

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)

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
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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 synthetic compounds as required by drinking water regulations of 40 Code of Federal Regulations Part 141. 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

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 a halogen specific detector placed in series.

2.2 Tentative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing resultant GC retention times. Additional confirmatory information can be gained by comparing the relative response from the two detectors. Each identified component is measured by relating the response produced for that compound to the response produced by a compound that is used as an internal standard. For absolute confirmation, a gas chromatography/mass spectrometry(GC/MS) determination according to method 524.1 or method 524.2 is recommended.

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 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. 10.3) 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. APPARATUS AND EQUIPMENT

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.

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 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), 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. 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 demonstrated satisfactory for 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. It was used to develop the method performance statements in Sect. 13.

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. It was used to develop the method performance statements in Sect. 13.

6.3.5 Column 3 - 30 m long x 0.53 mm ID DB-62 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 10.0 eV (nominal) lamp and electroconductivity detector(ELCD) is required. This allows to simultaneously analyze volatile organic compounds (VOC) 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 CONSUMABLE MATERIALS

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 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 analytes. 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. 9.1) 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 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, DECHLORINATION, AND PRESERVATION

8.1.1 Collect all samples in duplicate. If samples contain residual chlorine, and measurements of the concentrations of disinfection by-products (trihalomethanes, etc.) at the time of sample collection are desired, add about 25 mg of ascorbic acid (or 3 mg of sodium thiosulfate) to the sample bottle before filling. Fill sample bottles to overflowing, but take care not to flush out the rapidly dissolving ascorbic acid (or sodium thiosulfate). No air bubbles should pass through the sample as the bottle is filled, or be trapped in the sample when the bottle is sealed. Adjust the pH of the duplicate samples to <2 by carefully adding one drop of 1:1 HCl for each 20 mL of sample volume. Seal the sample bottles, PFTE-face down, and shake vigorously for 1 min.

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 from the flowing stream.

8.1.3 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 duplicate sample bottles from the 1-quart container.

8.1.4 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 that they will be at 4°C on arrival at the laboratory.

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.

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

8.3.1 Duplicate field reagent blanks 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, 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.

8.3.2 Use the same procedures used for samples to add ascorbic acid (or sodium thiosulfate) and HCl to blanks (Sect. 8.1.1).

9. CALIBRATION AND STANDARDIZATION

9.1 PREPARATION OF CALIBRATION STANDARDS

9.1.1 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. Every CAL solution contains the internal standard at same concentration (10 µg/L).

9.1.2 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. 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.

9.2 CALIBRATION

9.2.1 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.

9.2.2 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. 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 or use a single point calibration standard as described in Sect. 9.2.3.

9.2.3 Single point calibration is a viable alternative to a calibration curve. Prepare single point standards from the primary dilution standards in methanol. The single point standards should be prepared at a concentration that produces a response close (± 20%) to that of the unknowns.

9.2.4 As a second alternative to a calibration curve, internal standard calibration techniques may be used. The organohalides recommended for this purpose 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 calibration factors daily by analyzing a calibration standard. Since the calculated concentrations can be strongly biased by inaccurate detector response measurements for the internal standard or by coelution of an unknown, 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. If they do not, then internal standards can not be used.

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

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

9.3.2 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.

9.3.3 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

10. QUALITY CONTROL

10.1 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. The laboratory must maintain records to document the quality of the data generated. Additional quality control practices are recommended.

10.2 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.

10.3 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 0.1-5 µg/L (see regulations and maximum contaminant levels for guidance on appropriate concentrations).

10.3.1 Prepare each replicate by adding an appropriate aliquot of a quality control sample to reagent water. If a quality control sample containing the method analytes is not available, a primary dilution standard made from a source of reagents different than those used to prepare the calibration standards may be used. Also add the appropriate amounts of internal standard and surrogates if they are being used. Analyze each replicate according to the procedures described

in Section 11, and on a schedule that results in the analyses of all replicates over a period of several days.

10.3.2 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. Calculate the MDL of each analyte using the procedures described in (4).

10.3.3 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. The method detection limits must be sufficient to detect analytes at the regulatory levels. 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.

10.3.4 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.

10.4 Laboratory reagent blanks. With each batch of samples processed as a group within a work shift, analyze a laboratory reagent blank to determine the background system contamination.

10.5 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 10.3. If more than 20 samples are included in a batch, analyze one LFB for every 20 samples. Use the procedures described in 10.3.3 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. Add these results to the on-going control charts to document data quality.

10.6 With each set of field samples a field reagent blank (FRB) should be analyzed. The results of these analyses will help define contamination resulting from field sampling and transportation activities. An acceptable FRB may replace the LRB.

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

10.8 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.

10.9 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. It is recommended that sample matrix effects be evaluated at least quarterly using the QCS described in 10.8.

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

11. PROCEDURE

11.1 INITIAL CONDITIONS

11.1.1 Recommended chromatographic conditions are summarized in Sect. 6.3. Other columns or element specific detectors may be used if the requirements of Sect. 10.3 are met.

11.1.2 Calibrate the system daily as described in Sect. 9.2.

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. Warm the sample 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.

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. 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.

12.4 Determine the concentration of the unknowns 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 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.

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

13. ACCURACY AND PRECISION

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.

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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

	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
2,2-Dichloropropane	-	-	-	105	3.4	0.05

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)
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

		Retention Time (min)[a] and Rel. Std. Dev.			
	Analyte[b]	PID	RSD	ELCD	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
I3	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]	Retention Time (min)[a] and Rel. Std. Dev. PID	RSD	ELCD	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

	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	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	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)
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.

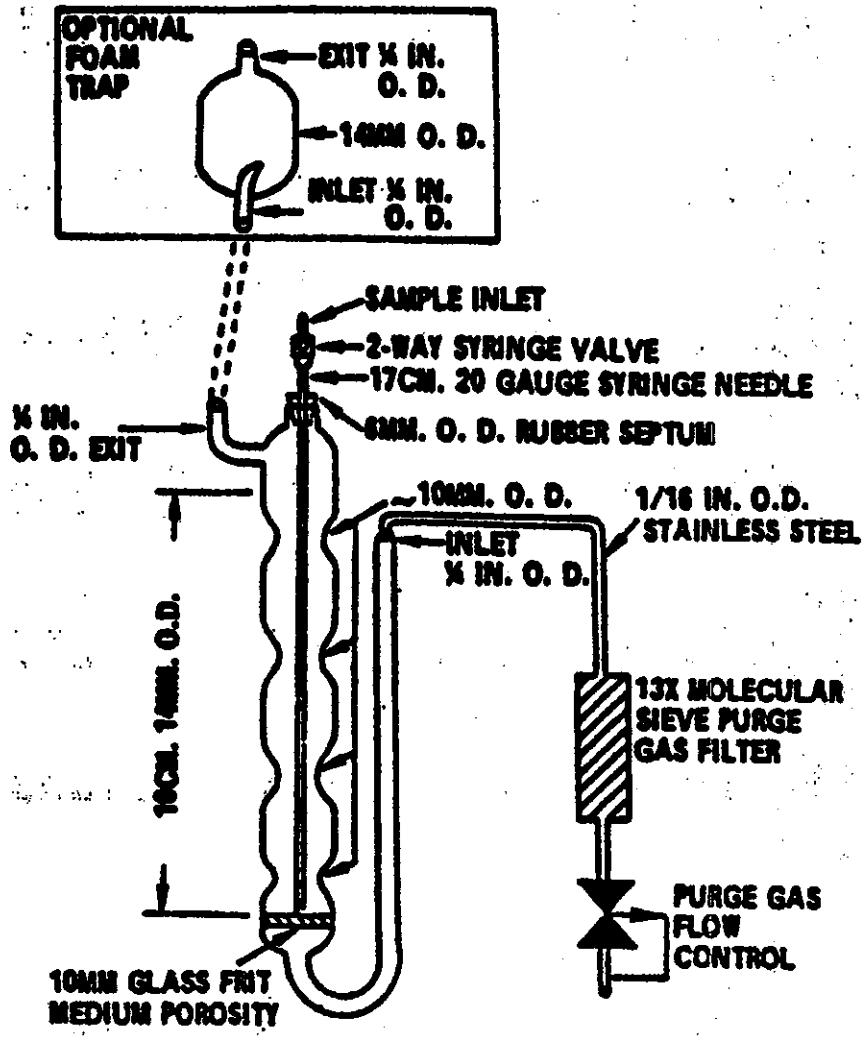

FIGURE 1. PURGING DEVICE

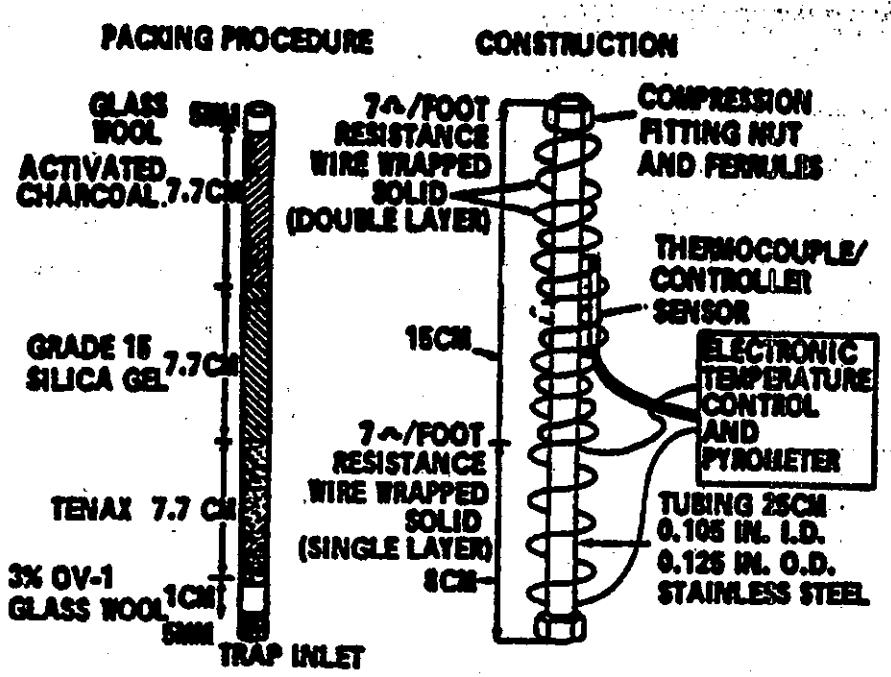

FIGURE 2. TRAP PACKINGS AND CONSTRUCTION TO INCLUDE DESORB CAPABILITY

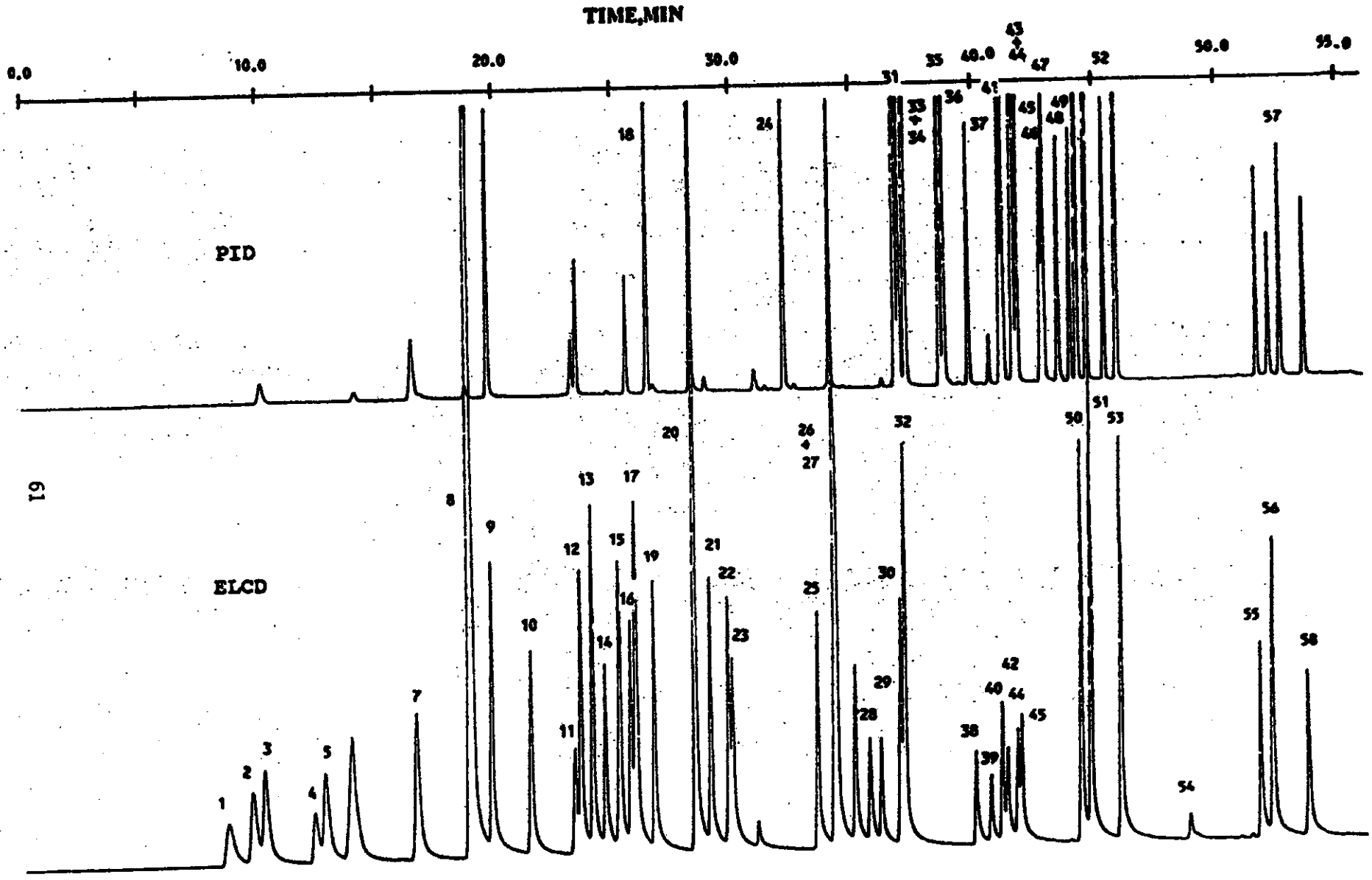

FIGURE 3. DUAL CHROMATOGRAM OF ORGANIC COMPOUNDS FOR COLUMN 1

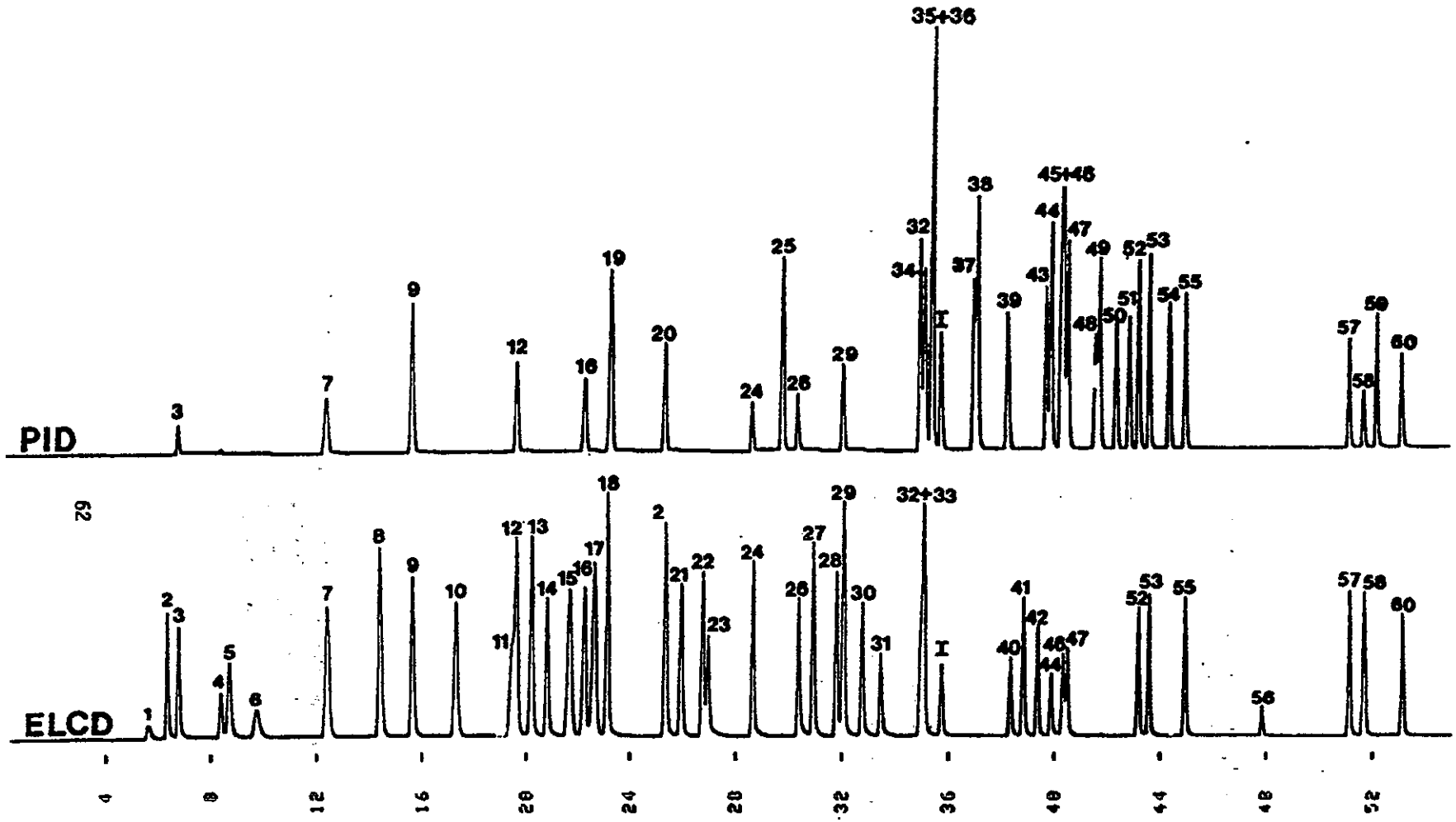

FIGURE 4. DUAL CHROMATOGRAM OF ORGANIC COMPOUNDS FOR COLUMN 2

METHOD 503.1. VOLATILE AROMATIC AND UNSATURATED ORGANIC COMPOUNDS IN WATER BY PURGE AND TRAP GAS CHROMATOGRAPHY

Revision 2.0

T. A. Bellar - Method 503.1, Revision 1.0 (1986)

T. A. Bellar - Method 503.1, Revision 2.0 (1989)

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
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METHOD 503.1

VOLATILE AROMATIC AND UNSATURATED ORGANIC COMPOUNDS IN WATER BY PURGE AND TRAP GAS CHROMATOGRAPHY

1. SCOPE AND APPLICATION

1.1 This method is applicable for the determination of various volatile aromatic and unsaturated compounds in finished drinking water, raw source water, or drinking water in any treatment stage (1,2). The following compounds can be determined by this method:

Analyte	Chemical Abstract Service Registry Number
Benzene	1-43-2
Bromobenzene	108-86-1
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
Chlorobenzene	108-90-7
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
Ethylbenzene	100-41-4
Hexachlorobutadiene	87-68-3
Isopropylbenzene	98-82-8
4-Isopropyltoluene	99-87-6
Naphthalene	91-20-3
n-Propylbenzene	103-65-1
Styrene	100-42-5
Tetrachloroethene	127-18-4
Toluene	108-88-3
1,2,3-Trichlorobenzene	87-61-6
1,2,4-Trichlorobenzene	120-82-1
Trichloroethene	79-01-6
1,2,4-Trimethylbenzene	95-63-6
1,3,5-Trimethylbenzene	108-67-8
o-Xylene	95-47-6
m-Xylene	108-38-3
p-Xylene	106-42-3

1.2 Single laboratory accuracy and precision data show that this procedure is useful for the detection and measurement of multi-component mixtures in finished water and raw source water at concentrations between 0.05 and 0.5 µg/L. Individual aromatic compounds can be measured at concentrations up to 1500 µg/L. Determination of complex mixtures containing partially resolved

compounds may be hampered by concentration differences larger than a factor of 10.

1.3 This method is recommended for use only by analysts experienced in the measurement of purgeable organics at the low µg/L level or by experienced technicians under the close supervision of a qualified analyst.

2. SUMMARY OF METHOD

2.1 Highly volatile organic compounds with low water solubility are extracted (purged) from a 5-mL sample by bubbling an inert gas through the aqueous sample. Purged sample components are trapped in a tube containing a suitable sorbent material. When purging is complete, the sorbent tube is heated and backflushed with an inert gas to desorb trapped sample components onto a gas chromatography (GC) column. The gas chromatograph is temperature programmed to separate the method analytes which are then detected with a photoionization detector.

2.2 A second chromatographic column is described that can be used to help confirm GC identifications or resolve coeluting compounds. Analyses may be performed by gas chromatography/mass spectrometry (GC/MS) according to Method 524.1 or Method 524.2.

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 that are components of the same solution. The internal standard must be an analyte that is not a sample component.

3.2 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.

3.3 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.

3.4 Laboratory reagent blank (LRB) -- An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents and internal standards 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.

3.5 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, preservationand all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.6 Laboratory performance check solution (LPC) -- A solution of one or more compounds used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.7 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.

3.8 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 -- 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.

3.10 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.

3.11 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 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 generated from a source of reagents different than those used to prepare the primary dilution standards and the calibration standard and is used to check laboratory performance.

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. 10.4) 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 Water will cause a broad negative baseline deflection in the retention area of Benzene. The method provides for a dry purge period to prevent this problem.

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 (3-5) 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, 1,4-dichlorobenzene, hexachlorobutadiene, tetrachloroethene, and trichloroethene. Pure standard materials and stock standard solutions of these compounds should be handled in a hood. A NIOSH/MESA approved respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6. APPARATUS AND EQUIPMENT

6.1 SAMPLE CONTAINERS - 40-mL to 120-mL screw cap vials (Pierce #13075 or equivalent) each equipped with a PTFE-faced silicone septum (Pierce #12722 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 in a 105°C oven for one hour, then remove and allow to cool in an area known to be free of organic solvent vapors.

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 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. It is recommended that 1.0 cm of methyl silicone coated packing be added at the inlet end to prolong the life of the trap. Add a sufficient amount of 2,6-diphenylene oxide polymer to fill 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 minutes at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

6.2.3 The desorber (Figure 2) must be capable of rapidly heating the trap to 180°C. 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 pounds per square inch across the trap during purging.

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 the temperature program.

6.3.2 Two gas chromatography columns are recommended. Column 1 (Sect. 6.3.3) is a highly efficient column that provides outstanding separations for a wide variety of organic compounds. Column 1 should be used as the primary analytical

column unless routinely occurring analytes are not adequately resolved. Column 2 (Sect. 6.3.4) is recommended for use as an alternate column. Retention times for the listed analytes on the two columns are presented in Table 1.

6.3.3 Column 1 - 1.5 to 2.5 m x 0.085 in ID #304 stainless steel or glass, packed with 5% SP-1200 and 1.75% Bentone 34 on Supelcoport (80/100 mesh) or equivalent. The flow rate of the helium carrier gas must be established at 30 mL/min. With this column, modification to the column ID and carrier gas flow rate will adversely affect resolution. The column temperature is held at 50°C for 2 min, then programmed at 3°C/min to 110°C and held at 110°C until all compounds have eluted. When not in use, maintain the column at 110°C. Condition new SP-1200/Bentone columns with carrier gas flow at 120°C for several days before connecting to the detector. A sample chromatogram obtained with Column 1 is presented in Figure 3.

6.3.4 Column 2 - 1.5 to 2.5 m long x 0.085 in ID #304 stainless steel or glass, packed with 5% 1,2,3-tris(2-cyanoethoxy) propane on Chromosorb W (60/80 mesh) or equivalent. The flow rate of the helium carrier gas must be established at 30 mL/min. The column temperature is programmed to hold at 40°C for 2 min, increase to 100°C at 2°C/min, and hold at 100°C until all expected compounds have eluted. A sample chromatogram obtained with Column 2 is presented in Figure 4.

6.3.5 A high temperature photoionization detector equipped with a 10.2 eV (nominal) lamp is required (HNU Systems, Inc., Model PI-51-02 or equivalent). Departures from the required flow rate of 30 mL/min will adversely effect method detection limits or precision.

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.

6.5 MISCELLANEOUS

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

7. REAGENT AND CONSUMABLE MATERIALS

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 - OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

7.2 COLUMN PACKING MATERIALS

7.2.1 5% SP-1200/1.75% Bentone 34 on 100/120 mesh Supelcoport or equivalent.

7.2.2 5% 1,2,3-tris(2-cyanoethoxy) propane on 60/80 mesh Chromosorb W or equivalent.

7.3 REAGENTS

7.3.1 Methanol - demonstrated to be free of analytes.

7.3.2 Reagent water demonstrated to be free of analytes - 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.

7.3.3 Ascorbic acid or sodium thiosulfate - ACS Reagent grade, granular.

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

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

7.4.1 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.

7.4.2 Using a 100-µL syringe, 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.

7.4.3 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.

7.4.4 Store stock standard solutions at 4°C in 15-mL bottles equipped with PTFE-lined screw caps. Methanol solutions are stable for at least four weeks when stored at 4°C. Storage times may be extended only if the analyst proves their validity by analyzing quality control samples.

7.5 PRIMARY DILUTION STANDARDS - Use standard stock 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 solutions (Sect. 9.1) 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 solutions from them. Storage times described for stock standards also apply to primary dilution standard solutions.

7.6 QUALITY CONTROL SAMPLE - Prepare or obtain from a certified source a methyl alcohol solution at a concentration of 1.00 µg/mL for the regulated volatile organic contaminants and the unregulated contaminants of interest. It will be necessary to prepare more than one solution and to increase the concentration of some of the contaminants proportional to the instrument detection limits if all of the analytes in Sect. 1.1 are being measured by this method. The concentrate should be prepared from a source of stock standards different than those used for Sect. 7.5.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 SAMPLE COLLECTION, DECHLORINATION, AND PRESERVATION

8.1.1 Collect all samples in duplicate. If samples contain residual chlorine, and measurements of the concentrations of disinfection by-products (trihalomethanes, etc.) at the time of sample collection are desired, add about 25 mg of ascorbic acid (or 3 mg sodium thiosulfate) to the sample bottle before filling. Fill sample bottles to overflowing, but take care not to flush out the rapidly dissolving ascorbic acid (or sodium thiosulfate). No air bubbles should pass through the sample as the bottle is filled, or be trapped in the sample when the bottle is sealed. Adjust the pH of the duplicate samples to <2 by carefully adding one drop of 1:1 HCl for each 20 mL of sample volume. Seal the sample bottles, PFTE-face down, and shake vigorously for 1 min.

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 from the flowing stream.

8.1.3 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 duplicate sample bottles from the 1-quart container.

8.1.4 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 that they will be at 4°C on arrival at the laboratory.

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.

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

8.3.1 Duplicate field reagent blanks 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, 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.

8.3.2 Use the same procedures used for samples to add ascorbic acid (or sodium thiosulfate) and HCl to blanks (Sect. 8.1.1).

9. CALIBRATION AND STANDARDIZATION

9.1 PREPARATION OF CALIBRATION STANDARDS

9.1.1 Calibration standards containing mixtures of analytes that are at least 80 percent resolved are prepared as needed. The number of calibration solutions (CALs) needed depends on the resolution requirement and 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. The lowest level calibration standard should contain analytes at a concentration two to ten times the MDL (Table 2) for that compound. The other CAL standards should

contain each analyte of concern at concentrations that define the range of the sample analyte concentrations.

9.1.2 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. Use a microsyringe and rapidly inject the alcoholic standard into the water. Remove the needle as quickly as possible after injection. Accurate calibration standards are prepared by adding 20 µL of the primary dilution standard to 25 mL or more of reagent water using the syringe described in Sect. 6.4.3. Aqueous standards are not stable and should be discarded after one hour unless preserved, sealed and stored as described in Sect. 8.2.

9.2 CALIBRATION

9.2.1 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.

9.2.2 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. 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 that analyte or use a single point calibration standard as described in Sect. 9.2.3.

9.2.3 Single point calibration is a viable alternative to a calibration curve. Prepare single point standards from the primary dilution standards in methanol. The single point standards should be prepared at a concentration that produces a response close (<±20%) to that of the unknowns. Do not use less than 20 µL of the primary dilution standard to produce a single point calibration standard in reagent water.

9.2.4 As a second alternative to a calibration curve, internal standard calibration techniques may be used. α,α,α-Trifluorotoluene is recommended as an internal standard for this method. The internal standard is added to the sample just before purging. Check the validity of the internal standard calibration factors daily by analyzing a calibration standard. Since the calculated concentrations

can be strongly biased by inaccurate detector response measurements for the internal standard or by coelution of an unknown, it is required that the area measurement of the internal standard for each sample be within ±3 standard deviations of those obtained from calibration standards. If they do not then internal standards can not be used.

9.3 INSTRUMENT PERFORMANCE - Check the performance of the entire analytical system daily using data gathered from analyses of field blanks, standards, duplicate samples, and the quality control sample.

9.3.1 All of the peaks contained in the standard chromatograms must be sharp and symmetrical. Peak tailing significantly in excess of that shown in the method chromatograms (Figures 6 and 7) must be corrected. If only the compounds eluting before ethylbenzene give random responses or unusually wide peak widths, are poorly resolved, or are missing, the problem is usually traceable to the trap/desorber. If negative peaks appear early in the chromatogram, increase the dry purge time to 5 min.

9.3.2 Check the precision between laboratory replicates. A properly operating system should perform with a relative standard deviation of less than 10%. Poor precision is generally traceable to pneumatic leaks, especially around the sample purger or to an improperly adjusted lamp intensity power. Monitor the retention times for each method analyte using data generated from calibration standards. If individual retention times vary by more than 10% over an 8-h period or do not fall within 10% of an established norm, the source of retention data variance must be corrected before acceptable data can be generated.

10. QUALITY CONTROL

10.1 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. The laboratory must maintain records to document the quality of the data generated. Additional quality control practices are recommended.

10.2 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, sorbants, 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.

10.3 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 0.1-5 ug/L (see regulations and maximum contaminant levels for guidance on appropriate concentrations).

10.3.1 Prepare each replicate by adding an appropriate aliquot of a quality control sample to reagent water. If a quality control sample containing the method analytes is not available, a primary dilution standard made from a source of reagents different than those used to prepare the calibration standards may be used. Also add the appropriate amounts of internal standard and surrogates if they are being used. Analyze each replicate according to the procedures described in Section 11, and on a schedule that results in the analyses of all replicates over a period of several days.

10.3.2 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. Calculate the MDL of each analyte using the procedures described in (8).

10.3.3 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. The method detection limits must be sufficient to detect analytes at the regulatory levels. 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.

10.3.4 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.

10.4 Laboratory reagent blanks. With each batch of samples processed as a group within a work shift, analyze a laboratory reagent blank to determine the background system contamination.

10.5 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 10.3. If more than 20 samples are included in a batch, analyze one LFB for every

20 samples. Use the procedures described in 10.3.3 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. Add these results to the on-going control charts to document data quality.

10.6 With each set of field samples a field reagent blank (FRB) should be analyzed. The results of these analyses will help define contamination resulting from field sampling and transportation activities. An acceptable FRB may replace the LRB.

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

10.8 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.

10.9 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. It is recommended that sample matrix effects be evaluated at least quarterly using the QCS described in 10.8.

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

11. PROCEDURE

11.1 INITIAL CONDITIONS

11.1.1 Recommended chromatographic conditions are summarized in Sect. 6.3. Other packed or capillary (open tubular) columns may be used if the requirements of Sect. 10.3 are met.

11.1.2 Calibrate the system daily as described in Sect. 9.2.

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 aqueous standards must be analyzed under identical conditions. Remove the plungers from two 5-mL syringes and attach a closed syringe valve to each. Warm the sample 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. If applicable, add 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. 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.

11.3 TRAP DRY AND SAMPLE DESORPTION - After the 11-min purge, completely dry the trap for at least 4 min by adjusting the purge and trap system to the dry purge position or by temporarily replacing the purge device with a clean, dry unit while maintaining purge gas flow. Empty the purging device using the sample syringe and wash the chamber with two 5-mL flushes of reagent water. After the 4-min dry purge, attach the trap to the chromatograph, adjust the purge and trap system to the desorb mode and initiate the temperature program sequence of the gas chromatograph. Introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while back-flushing the trap with an inert gas at 30 mL/min for 4.0 ± 0.1 min. The transfer is complete after approximately four min.

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. Wait 15 s, then close the syringe valve on the purging device to begin gas flow through the trap. 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 (< 30°C), the next sample can be analyzed.

12. 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 those generated by knowns then the identification may be considered as positive. If the suspect peak falls outside this range or coelutes with other compounds (Table 1), then the sample should be reanalyzed according to Sect. 2.2.

12.2 Determine the concentration of the unknowns 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:

Conc. of unknown (μg/L) = (Peak height sample/Peak height std.) x Conc. of standard. (<μg/L)

12.3 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. ACCURACY AND PRECISION

13.1 Single laboratory (EMSL-Cincinnati) accuracy and precision for most of the analytes added to Ohio River water and chlorinated drinking water are presented in Table 2 (2).

13.2 This method was tested by 20 laboratories using drinking water fortified with various method analytes at six concentrations between 2.2 and 600 µg/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte. Linear equations to describe these relationships are presented in Table 3 (9).

13.3 Multilaboratory studies have been conducted by the Quality Assurance Research Division of EMSL-Cincinnati to evaluate the performance of various laboratories. Accuracy and precision data applicable to this method for several purgeable aromatics in reagent water are presented in Table 4 (10).

14. REFERENCES

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TABLE 1. RETENTION TIMES FOR METHOD ANALYTES

Analyte	Retention Time (min) Col 1	Col 2
Benzene	3.32	2.75
Trichloroethene	3.85	2.37
α,α,α-Trifluorotoluene(a)	4.93	2.80
Toluene	5.40	4.25
Tetrachloroethene	6.71	2.80
Ethylbenzene	10.10	6.25
1-Chlorocyclohexene (b)	10.6	5.75
p-Xylene	10.8	6.72
Chlorobenzene	11.5	8.02
m-Xylene	11.5	6.27
o-Xylene	12.3	8.58
Isopropylbenzene	12.8	7.58
Styrene	13.9	11.5
1,4-Bromofluorobenzene(b)	14.2	12.3
n-Propylbenzene	14.7	8.63
tert-Butylbenzene	16.3	9.92
2-Chlorotoluene	16.4	11.4
4-Chlorotoluene	16.5	--
Bromobenzene	16.7	13.5
sec-Butylbenzene	17.1	9.92
1,3,5-Trimethylbenzene	17.4	10.2
4-Isopropyltoluene	18.2	11.4
1,2,4-Trimethylbenzene	18.2	12.5
1,4-Dichlorobenzene	19.2	16.3
1,3-Dichlorobenzene	20.2	15.0
n-Butylbenzene	20.2	12.8
Cyclopropylbenzene (b)	20.2	--
2,3-Benzofuran (b)	22.0	24.3
1,2-Dichlorobenzene	23.8	19.4
Hexachlorobutadiene	27.5	16.9
1,2,4-Trichlorobenzene	32.1	25.6
Naphthalene	42.4	38.3
1,2,3-Trichlorobenzene	43.9	30.3

(a) = Recommended internal standard (Sect. 8.1.6).

(b) = Not a method analyte.

TABLE 2. SINGLE LABORATORY ACCURACY, PRECISION, AND METHOD DETECTION LIMITS FOR VOLATILE AROMATIC AND UNSATURATED ORGANIC COMPOUNDS IN WATER

Analyte	Concentration Level (µg/L)	Number of Samples	Average Recovery (%)	Relative Standard Deviation (%)	Method Detection Limit (µg/L)
Benzene	0.40	13	100	2.8	0.02
Bromobenzene	0.50	19	93	6.2	0.002
n-Butylbenzene	0.40	7	78	15.7	0.02
sec-Butylbenzene	0.40	7	80	11.0	0.02
tert-Butylbenzene	0.40	7	88	8.7	0.006
Chlorobenzene	0.50	19	96	5.8	0.004
1-Chlorocyclohexene (b)	0.50	19	89	7.1	0.008
2-Chlorotoluene	-	-	-	-	0.008
4-Chlorotoluene	0.50	17	91	5.0	-
1,2-Dichlorobenzene	0.50	18	92	7.1	0.02
1,3-Dichlorobenzene	0.50	19	91	8.5	0.006
1,4-Dichlorobenzene	0.50	19	95	6.4	0.006
Ethylbenzene	0.40	7	93	8.5	0.002
Hexachlorobutadiene	0.50	10	74	16.8	0.02
Isopropylbenzene	0.40	7	88	8.7	0.005
4-Isopropyltoluene	-	-	-	-	0.009
Naphthalene	0.50	16	92	14.8	0.04
n-Propylbenzene	0.40	7	83	9.3	0.009
Styrene	-	-	-	-	0.008
Tetrachloroethene	0.50	19	97	7.8	0.01
Toluene	0.40	13	94	6.6	0.02
1,2,3-Trichlorobenzene	0.50	18	85	10.4	0.03
1,2,4-Trichlorobenzene	0.50	18	86	10.1	0.03
Trichloroethene	0.50	19	97	6.8	0.01
α,α,α-Trifluorotoluene(c)	0.50	18	88	9.7	0.02
1,2,4-Trimethylbenzene	0.40	7	75	8.7	0.006
1,3,5-Trimethylbenzene	0.50	10	92	8.7	0.003
m-Xylene	0.40	7	90	7.7	0.004
o-Xylene	0.40	7	90	7.2	0.004
p-Xylene	0.40	7	85	8.7	0.002

(a) = Matrices tested include drinking water and raw source water.
(b) = Not a method analyte.
(c) = Recommended internal standard (Sect. 9.2.4).

TABLE 3. SINGLE ANALYST PRECISION, OVERALL PRECISION, AND ACCURACY FOR VOLATILE AROMATIC ORGANIC COMPOUNDS IN DRINKING WATER

Analyte	Single Analyst Precision	Overall Precision	Accuracy as Mean Recovery(X)
Benzene	0.11X - 0.06	0.22X + 1.11	0.97C + 0.85
Chlorobenzene	0.10X + 0.12	0.16X + 0.36	0.94C + 0.12
1,2-Dichlorobenzene	0.10X + 0.42	0.18X + 0.28	0.91C + 0.44
1,3-Dichlorobenzene	0.08X + 0.33	0.15X + 0.33	0.93C + 0.21
1,4-Dichlorobenzene	0.09X + 0.39	0.15X + 0.39	0.91C + 0.26
Ethylbenzene	0.10X + 0.18	0.20X + 0.68	0.97C + 0.41
Toluene	0.10X + 0.18	0.21X + 0.16	0.94C + 0.17

X = mean recovery (µg/L)
C = true value for the concentration (µg/L)

TABLE 4. ACCURACY AND PRECISION DATA FOR PURGEABLE AROMATICS FROM MULTILABORATORY PERFORMANCE EVALUATION STUDIES

Analyte	Concentration Level (µg/L)	Number of Laboratories	Average Measured Concentrations (µg/L)	Relative Standard Deviation (%)	Average Recovery (%)
Benzene	94.1	9	91.9	18.6	98
	47.0	10	47.0	11.8	100
	18.8	8	18.7	16.4	100
	8.10	11	6.22	40.8	88
Chlorobenzene	41.4	5	39.8	6.20	96
	27.6	7	27.1	12.1	98
	13.8	6	14.3	6.73	104
	5.52	8	5.65	25.3	102
1,2-Dichlorobenzene	96.9	5	72.9	31.6	75
	19.4	4	16.5	18.8	85
1,4-Dichlorobenzene	68.6	5	62.5	22.8	91
	13.7	5	14.6	29.1	107
1,2,4-Trichlorobenzene	80.8	6	77.6	14.3	96
	6.7	6	8.46	30.7	126

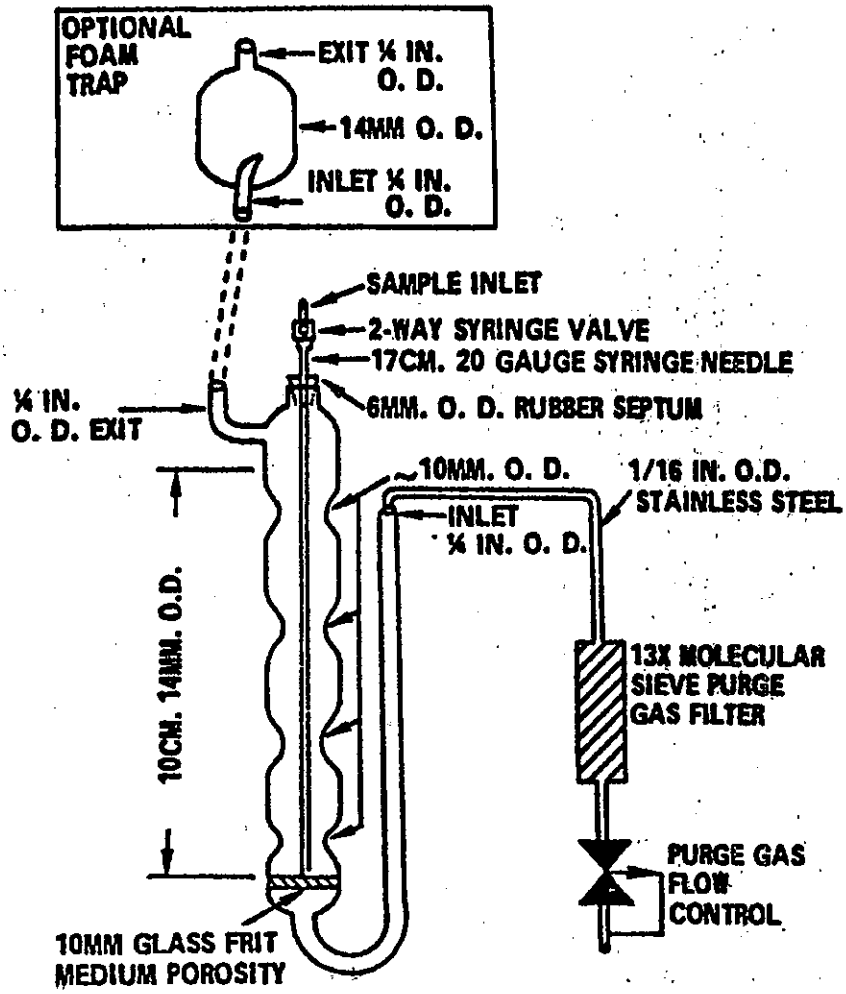

FIGURE 1. PURGING DEVICE

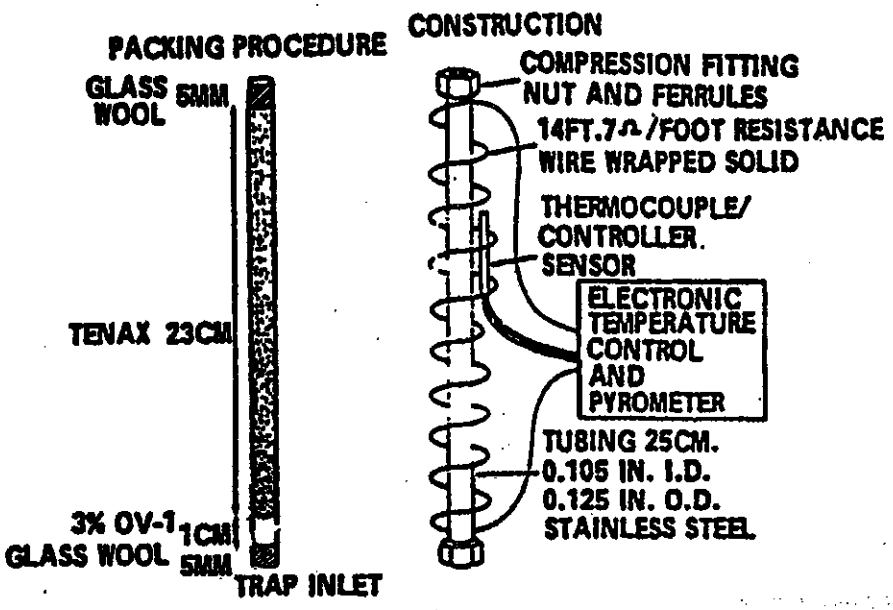

FIGURE 2. TRAP PACKINGS AND CONSTRUCTION TO INCLUDE DESORB CAPABILITY

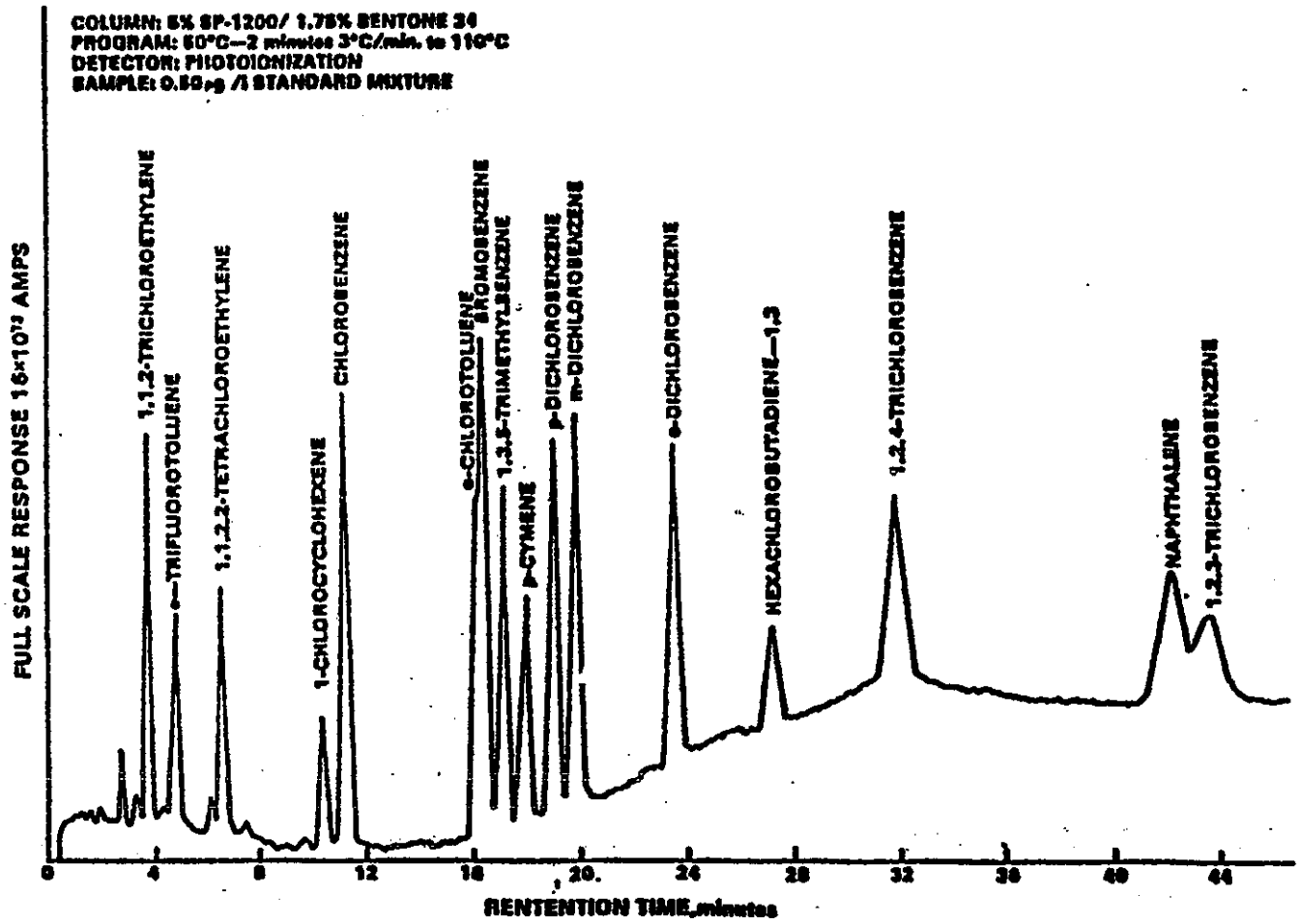

FIGURE 3. CHROMATOGRAM OF TEST MIXTURE

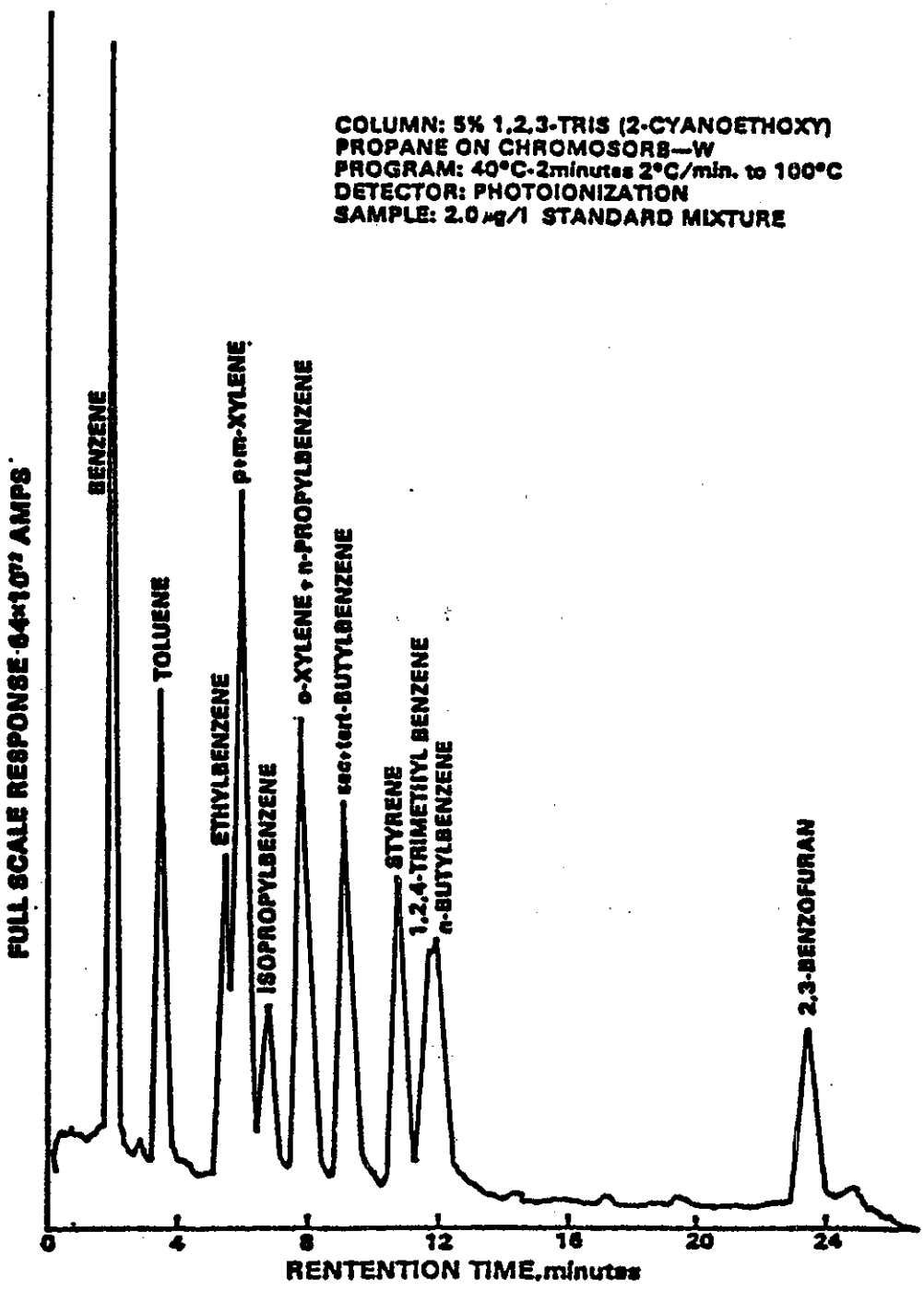

FIGURE 4. CHROMATOGRAM OF TEST MIXTURE

METHOD 504. 1,2-DIBROMOETHANE (EDB) AND 1,2-DIBROMO-3-CHLOROPROPANE (DBCP) IN WATER BY MICROEXTRACTION AND GAS CHROMATOGRAPHY

Revision 2.0

T. W. Winfield - Method 504, Revision 1.0 (1986)

T. W. Winfield - Method 504, Revision 2.0 (1989)

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
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METHOD 504

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

1. SCOPE AND APPLICATION

1.1 This method (1-4) 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 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 (5) and provide qualitative confirmation of results by gas chromatography/mass spectrometry (GC/MS) (6).

1.3 The experimentally determined method detection limits (MDL) (7) for EDB and DBCP were calculated to be 0.01 µg/L. The method has been shown to be 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 analysis. Aqueous calibration standards are extracted and analyzed in an identical manner as the samples in order to compensate for possible extraction losses.

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

2.3 Confirmatory evidence can be obtained using a dissimilar column. When component concentrations are sufficiently high, Method 524.1 or 524.2 may be employed for improved specificity.

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.

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. 7.3.4). 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 (4). 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. However, it is generally more economical to obtain a new source of solvent. Interference-free solvent is defined as a solvent containing less than 0.1 µg/L individual analyte interference. Protect interference-free solvents by storing in an area known to be 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 Current column technology suffers from the fact that EDB at low concentrations may be masked by very high levels of dibromochloromethane (DBCM), a common disinfection by-product of chlorinated drinking waters.

5. SAFETY

5.1 The toxicity and 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 (7-9) for the information of the analyst.

5.2 EDB and DBCP 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 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.

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. APPARATUS AND EQUIPMENT

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 PTFE-faced polyethelene film/foam extrusion (Fisher #02-883-3F or equivalent). 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 known to be free of organic solvent vapors.

6.2 VIALS, auto sampler, screw cap with PTFE-faced septa, 1.8 mL, Varian #96-000099-00 or equivalent.

6.3 MICRO SYRINGES - 10 and 100 µL.

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

6.5 PIPETTES - 2.0 and 5.0 mL transfer.

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

6.7 GAS CHROMATOGRAPHY SYSTEM

6.7.1 The GC must be capable of temperature programming and should be equipped with a linearized electron capture detector and a capillary column splitless injector at 200°C.

6.7.2 Two gas chromatography columns are recommended. Column A (Sect. 6.7.3) is a highly efficient column that provides separations for EDB and DBCP without interferences from

trihalomethanes (Sect. 4.4). Column A should be used as the primary analytical column unless routinely occurring analytes are not adequately resolved. Column B (Sect. 6.7.4) is recommended for use as a confirmatory column when GC/MS confirmation is not viable. Retention times for EDB and DBCP on these columns are presented in Table 1.

6.7.3 Column A - 0.32 mm ID x 30M long fused silica capillary with dimethyl silicone mixed phase (Durawax-DX3, 0.25 μm film, or equivalent). The linear velocity of the helium carrier gas should be about 25 cm/sec at 100°C and 7 psi column head pressure. The column temperature is programmed to hold at 40°C for 4 min, to increase to 190°C at 8°C/min, and hold at 190°C for 25 min or until all expected compounds have eluted. (See Figure 1 for a sample chromatogram.)

6.7.4 Column B (alternative column) - 0.32mm ID x 30M long fused silica capillary with methyl polysiloxane phase (DB-1, 1.0 μm film, 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 270°C at 10°C/min, and hold at 270°C for 10 min or until all expected compounds have eluted.

6.7.5 Column C (alternative column, wide bore) -- 0.53 mm ID x 30 M long, 2.0 μm film thickness, Rt_x-Volatiles (part #10902), dimethyl diphenyl polysiloxane, bonded phase. The hydrogen carrier gas flow is about 80 cm/sec linear velocity, measured at 50°C with about 11.5 psi column head pressure. The oven temperature is programmed to hold at 200°C until all expected compounds have eluted. Injector temperature: 250°C. Detector temperature: 250°C. NOTE: The above parameters were obtained by Restek Corporation during preliminary attempts to improve the separation of EDB and DBCM.

7. REAGENTS AND CONSUMABLE MATERIALS

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 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 (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.

7.2 STANDARD MATERIALS

7.2.1 1,2-Dibromoethane - 99%, available from Aldrich Chemical Company.

7.2.2 1,2-Dibromo-3-chloropropane - 99%, available from USEPA, EMSL-QARD, Cincinnati, Ohio 45268.

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

7.3.1 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.

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

7.3.3 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.

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

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

7.4.1 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.

7.4.2 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 alcohol without contacting the neck of the flask.

7.4.3 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.

7.4.4 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.

7.5 PRIMARY DILUTION STANDARD SOLUTIONS -- Use stock standard solutions to prepare primary dilution standard solutions that contain both analytes in methanol. The primary dilution standards should be prepared at concentrations that can be easily diluted to prepare aqueous calibration standards (Sect. 9.1.1) 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. 7.4.4 also applies to primary dilution standard solutions.

7.6 LABORATORY FORTIFIED BLANK (LFB) SAMPLE CONCENTRATE (0.25 µg/mL) -- Prepare a LFB sample concentrate of 0.25 µg/mL of each analyte from the stock standard solutions prepared in Sect. 7.4.

7.7 MDL CHECK SAMPLE CONCENTRATE (0.02 µg/mL) -- Dilute 2 mL of LFB sample concentrate (Sect. 7.6) 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. 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.

8.1.3 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 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 insure that they will be ≤4°C on arrival at the laboratory.

8.2.2 The addition of sodium thiosulfate as a dechlorinating agent and/or acidification to pH 2 with 1:1 HCl, common preservative procedures for purgeable compounds, have been shown to have no effect on EDB or DBCP (See Table 3). Nonetheless, sodium thiosulfate must be added to avoid the possibility of reactions which may occur between residual chlorine and indeterminant contaminants present in some solvents, yielding compounds which may subsequently interfere with the analysis. The presence of sodium thiosulfate will arrest the formation of DBCM (See Sect. 4.3). Also, samples should be acidified to avoid the possibility of microbial degradation which may periodically affect these analytes contained in other groundwater matrices.

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 Analyze all samples within 28 days of collection. Samples not analyzed within this period must be discarded and replaced.

9. CALIBRATION AND STANDARDIZATION

9.1 CALIBRATION

9.1.1 At least three calibration standards are needed; five are recommended. One should contain EDB and DBCP at a concentration near to but greater than the method detection limit (Table 1) for each compound; the other two should be at concentrations that bracket the range expected in samples. For example, if the MDL is 0.01 µg/L, and a sample expected to contain approximately 0.10 µg/L is to be analyzed, aqueous standards should be prepared at concentrations of 0.02 Mg/L, 0.10 µg/L, and 0.20 µg/L.

9.1.2 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 less than 20 µL of an alcoholic 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.

9.1.3 Each day, 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 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.

9.1.4 Single point calibration is a viable alternative to a calibration curve. Prepare single point standards from the secondary dilution standard solutions. The single point calibration standard should be prepared at a concentration that produces a response close to that of the unknowns, i.e., no more than 20% deviation between response of standard and response of sample.

9.2 INSTRUMENT PERFORMANCE - Check the performance of the entire analytical system daily using data gathered from analyses of reagent water blanks, standards, and the QC check standard (Sect. 10.3).

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

9.2.2 Check the precision between replicate analyses. A properly operating system should perform with an average relative standard deviation of less than 10%: Poor precision is generally traceable to pneumatic leaks, especially at the injection port.

10. QUALITY CONTROL

10.1 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 detection limits capability and an ongoing analysis of laboratory performance check solutions (LPC), 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.

10.1.1 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. 10.2.

10.1.2 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. 10.2.

10.1.3 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.

10.1.4 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. 10.3. The frequency of the LFB analyses is equivalent to 10% of all samples analyzed.

10.1.5 On a weekly basis, the laboratory should demonstrate the ability to analyze low level samples. The procedure for low level LFB samples is described in Sect. 10.4.

10.2 To establish the ability to achieve low detection limits and generate acceptable accuracy and precision, the analyst should perform the following operations:

10.2.1 Prepare four to seven samples at 0.02 µg/L by fortifying 35 µL of the MDL check sample concentrate (Sect. 7.7) into 35-mL aliquots of reagent water in 40-mL bottles. Cap and mix well.

10.2.2 Analyze the well-mixed MDL check samples according to the method beginning in Sect. 11.

10.2.3 Calculate the average concentration found (X) in µg/L, and the standard deviation of the concentrations(s) in µg/L, for each analyte. Then, calculate the MDL for each analyte.

10.2.4 For each analyte, X should be between 80% and 120% of the true value. Additionally, the calculated MDL should meet data quality objectives. If both analytes meet these criteria, the system performance is acceptable and analysis of actual samples can begin. If either analyte fails to meet the data quality objectives on the basis of high variability, correct the source of the problem and repeat the test. It is

recommended that the laboratory repeat the MDL determination on a regular basis. **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 EDB and DBCP.

10.3 The laboratory must demonstrate on a frequency equivalent to 10% of the sample load that the measurement system is in control by analyzing an LFB of both analytes at 0.25 µg/L concentration level.

10.3.1 Prepare an LFB sample (0.25 µg/L) by adding 35 µL of LFB concentrate (Sect. 7.6) to 35 mL of reagent water in a 40-mL bottle.

10.3.2 Immediately analyze the LFB sample according to Sect. 11 and calculate the recovery for each analyte. The recovery should be between 60% and 140% of the expected value.

10.3.3 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.

10.4 On a weekly basis, the laboratory should demonstrate the ability to analyze low level samples.

10.4.1 Prepare an MDL check sample (0.02 µg/L) as outlined in Sect. 10.2.1 and immediately analyze according to the method in Sect. 11.

10.4.2 The instrument response must indicate that the laboratory's MDL is distinguishable from instrument background signal. If not, correct the problem and repeat the MDL test in Sect. 10.2.

10.4.3 For each analyte, the recovery must be between 60% and 140% of the expected value.

10.4.4 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.

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

10.6 At least once in every 20 samples, fortify an aliquot of a randomly selected routine sample with a known amount (see Sect. 4.3). 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.

10.7 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.

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 0.1g and record this weight for subsequent sample volume determination (Sect. 11.3).

11.1.3 For calibration standards, laboratory fortified blanks and laboratory reagent blanks, measure a 35-mL volume using a 50-mL graduated cylinder and transfer it to a 40-mL sample container.

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 shaking by hand for about 20 sec.

11.2.3 Remove the cap and, using a transfer pipette, add 2.0 mL of hexane. Recap and shake vigorously by hand 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 2.0 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 (in g) is equivalent to the volume of water (in mL) extracted. (Sect. 12.3)

12. CALCULATIONS

12.1 Identify EDB and DBCP in the sample chromatogram by comparing the retention time of the suspect peak to retention times generated by the calibration standards and the laboratory control standard.

12.2 Use single point calibrations (Sect. 9.1.4) or use the calibration curve or calibration factor (Sect. 9.1.3) to directly calculate the uncorrected concentration (C_i) of each analyte in the sample (e.g., calibration factor x response).

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. ACCURACY AND PRECISION

13.1 Single laboratory and interlaboratory accuracy and precision at several concentrations in three waters are presented in Tables 2 and 4 (1). The method detection limits are presented in Table 1.

13.2 In a preservation study extending over a 4-week period, the average percent recoveries and relative standard deviations presented in

Table 3 were observed for reagent water (acidified), tap water and groundwater (1). The results for acidified and non-acidified samples were not significantly different.

14. REFERENCES

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TABLE 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS FOR 1,2-DIBROMOETHANE (EDB) AND 1,2-DIBROMO-3-CHLOROPROPANE (DBCP)

Analyte	Retention Time, Min			MDL, µg/L
	Column A	Column B	Column C*	
EDB	9.5	8.9	4.1	0.01
DBCP	17.3	15.0	12.8	0.01

* The MDL experimentally observed by Resteck Corporation during preliminary optimization was 0.3 µg/L.

TABLE 2. SINGLE LABORATORY ACCURACY AND PRECISION FOR EDB AND DBCP IN TAP WATER

Analyte	Number of Samples	Concentration (µg/L)	Average Accuracy (%)	Relative Standard Deviation (%)
EDB	7	0.03	114	9.5
	7	0.24	98	11.8
	7	50.0	95	4.7
DBCP	7	0.03	90	11.4
	7	0.24	102	8.3
	7	50.0	94	4.8

TABLE 3. ACCURACY AND PRECISION AT 2.0 µg/L OVER A 4-WEEK STUDY PERIOD

Analyte	Matrix[1]	Average Number of Samples	Relative Accuracy (% Recovery)	Std. Dev. (%)
EDB	RW-A	16	104	4.7
	GW	15	101	2.5
	GW-A	16	96	4.7
	TW	16	93	6.3
	TW-A	16	93	6.1
DBCP	RW-A	16	105	8.2
	GW	16	105	6.2
	GW-A	16	101	8.4
	TW	16	95	10.1
	TW-A	16	94	6.9

[1]Matrix Identities
RW-A = Reagent water at pH 2
GW = Groundwater, ambient pH
GW-A = Groundwater at pH 2
TW = Tap water, ambient pH
TW-A = Tap water at pH 2.

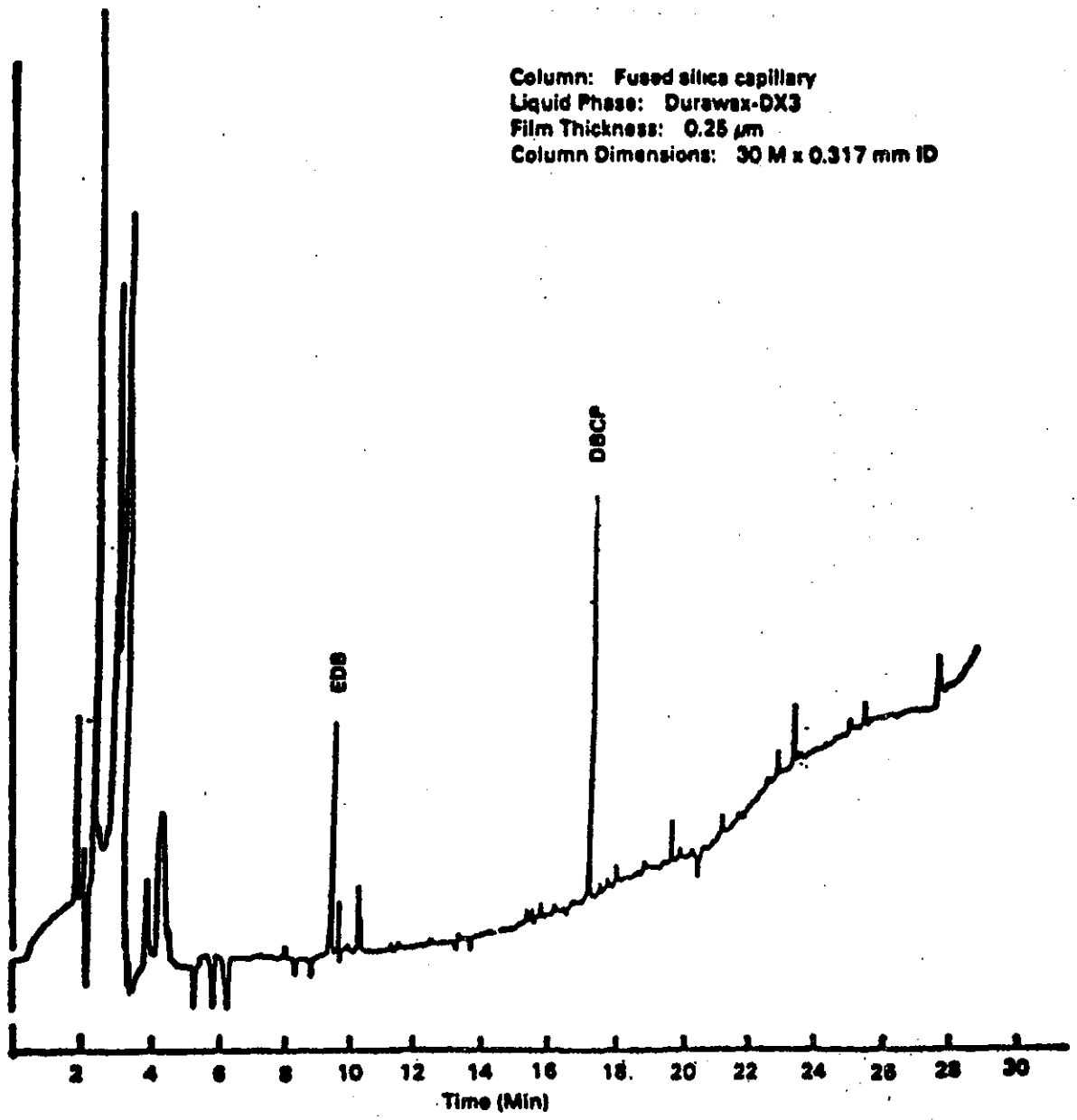

Figure 1. Extract of reagent water spiked at 0.114 μg/L with EDB and DBCP.

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

Revision 2.0

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 For compounds other than the above mentioned analytes or for other sample sources, 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. 13.1). 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.

1.5 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 is used (Sect. 11.4).

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 at least one additional qualitative technique.

1.7 Degradation of Endrin, caused by active sites in the injection port and GC columns, may occur. This is not as much a problem with new capillary columns as with packed columns. However, high boiling sample residue in capillary columns will create the same problem after injection of sample extracts.

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 analysis. Aqueous calibration standards are extracted and analyzed in an identical manner in order to compensate for possible extraction losses.

2.2 The extraction and analysis time is 30 to 50 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.

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. 10.2.

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 wih 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 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 anlayte of interest may be an interferent 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. Positive 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.

4.7 Aldrin, hexachlorocyclopentadiene and methoxychlor are rapidly oxidized by chlorine. Dechlorination with sodium thiosulfate at time of collection will retard 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. APPARATUS AND EQUIPMENT

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 suitable and split/splitless injector 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. 10.3.

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. REAGENTS AND CONSUMABLE MATERIALS - - 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. Place in a bottle and cap.

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.

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. 11.

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. 9.1.1) 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. 7.3.3 also applies to primary dilution standard solutions.

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. Analyte stability may be affected by the matrix; therefore, the analyst should verify that the preservation technique is applicable to the samples under study.

9. CALIBRATION AND STANDARDIZATION

9.1 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 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:

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

9.2 At least three calibration standards are needed; five are recommended. One should contain analytes at a concentration near but greater than the method detection limit for each compound; the other two should be at concentrations that bracket the range expected in samples. For example, if the MDL is 0.01 µg/L, and a sample expected to contain approximately 0.10 µg/L is to be analyzed, aqueous standards should be prepared at concentrations of 0.02 µg/L, 0.10 µg/L, and 0.20 µg/L.

9.2.1 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 alcoholic 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.

9.2.2 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.

9.2.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for an 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 or use a single point calibration standard as described in Sect. 9.2.4.

9.2.4 Single point calibration is an acceptable alternative to a calibration curve. Prepare single point standards from the secondary dilution standard solutions. The single point calibration standard should be prepared at a concentration that produces a response close (±20% or less) to that of the unknowns. Do not use less than 20 µL of the secondary dilution standard solution to produce a single point calibration standard in reagent water.

9.3 INSTRUMENT PERFORMANCE - Check the performance of the entire analytical system daily using data gathered from analyses of laboratory reagent blanks (LRB), (CAL), laboratory duplicate samples (LD1 and LD2), and the laboratory performance check solution (LPC) (Sect. 10.6).

9.3.1 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.

9.3.2 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.

9.3.3 Observed relative area responses of endrin (See 4.5) must meet the following general criteria:

9.3.3.1 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, LPC, 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.

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

10. QUALITY CONTROL

10.1 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).

10.2 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.

10.3 Initial Demonstration of Capability

10.3.1 Select a representative concentration (about 10 times MDL or at the regulatory Maximum Contaminant Level, whichever is lower) for each analyte. Prepare a primary dilution standard solution (in methanol) containing each analyte at 1000 times selected concentration. With a syringe, add 35 μL of the concentrate to each of at least four 35-mL aliquots of reagent water, and analyze each aliquot according to procedures beginning in Sect. 11.

10.3.2 For each analyte the recovery value should for at least three out of four consecutively analyzed samples fall in the range of R±30% (or within R±3S_R if broader) using the values for R and S_R for reagent water in Table 2. For those compounds that meet the acceptance criteria, performance is considered acceptable and sample analysis may begin. For those compounds that fail these criteria, initial demonstration procedures should be repeated.

10.3.3 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.

10.4 The analyst is permitted to modify GC columns, GC conditions, or detectors to improve separations or lower analytical costs. Each time such method modifications are made, the analyst must repeat the procedures in Sect. 10.3.

10.5 Assessing Laboratory Performance - Laboratory Fortified Blank (LFB)

10.5.1 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. The fortifying concentration of each analyte in the LFB sample should be 10 times MDL or the MCL, whichever is less. Calculate accuracy as percent recovery (X_i). If the recovery of any analyte falls outside the control limits (see Sect. 10.5.2), that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

10.5.2 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. 10.3.2 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.

10.5.3 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.

10.5.4 At least each quarter the laboratory should analyze quality control samples (QCS) (if available). If criteria provided with the QCS are not met, corrective action should be taken and documented.

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

10.6.1 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. 10.5). Periodically, samples from all routine sample sources should be fortified.

10.6.2 Calculate the percent recovery (R_i) for each analyte, corrected for background concentrations measured in the unfortified sample, and compare these values to the control limits established in Sect. 10.5.2 from the analyses of LFBs.

10.6.3 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. 10.5), 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.

10.7 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.

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 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 an immediate 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 mL 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. 12.3). By alternately 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 identifiction 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 componenet (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.

12. 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. Select the most sensitive and reproducible peaks to obtain a sum for calculation purposes (See Table 1).

12.2 Use the single point calibration (Sect. 9.2.4) or use the calibration curve or calibration factor (Sect. 9.2.3) to directly calculate the uncorrected concentration (Ci) of each analyte in the sample (e.g., calibration factor x response).

12.3 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).

12.4 Calculate the corrected sample concentration as:

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

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. ACCURACY AND PRECISION

13.1 Single laboratory (EMSL-Cincinnati) accuracy and precision at several concentrations in reagent, ground, and tap water matrices

are presented in Table 2.(11). These results were obtained from data generated with a DB-1 column.

13.2 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.(12).

14. REFERENCES

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10. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

11. Winfield, T., et al. "Analysis of Organohalide Pesticides and Commercial PCB Products in Drinking Water by Microextraction and Gas Chromatography." In preparation.

12. Multilaboratory Method Validation Study #40, conducted by the Quality Assurance Branch, EMSL-Ci. Report in progress.

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		

[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 implicate 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	µg/L	Concentration* µg/L	Accuracy and Standard Deviation Data: Reagent Water R[c]	Reagent Water SR[d]	Groundwater R	Groundwater S_R	Tap Water R	Tap Water S_R
Aldrin	0.075	0.15	86	9.5	100	11.0	69	9.0
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	NA	8.0	-	-	105	12.4
		3.4	NA	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	NA	12.6	-	-	110	9.5
		80	NA	15.3	-	-	114	13.5
Aroclor 1016	0.08	1.0	NA	6.6	-	-	97	7.5
Aroclor 1221	15.0	180	NA	8.3	-	-	92	9.6
Aroclor 1232	0.48	3.9	NA	13.5	-	-	86	7.3
Aroclor 1242	0.31	4.7	NA	6.0	-	-	96	7.4
Aroclor 1248	0.102	3.6	NA	11.5	-	-	-	-
		3.4	-	-	-	-	84	9.9
Aroclor 1254	0.102	1.8	NA	10.4	-	-	-	-
		1.7	-	-	-	-	85	11.8
Aroclor 1260	0.189	2.0	NA	20.7	-	-	-	-
		1.8	NA	-	-	-	88	19.8

Table 2 (Continued)

NA = Not applicable. A separate set of aqueous standards was not analyzed, and the response factor for reagent water was used to calculate a recovery for the tap water matrix.

[a]Data corrected for amount detected in blank and represent 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.

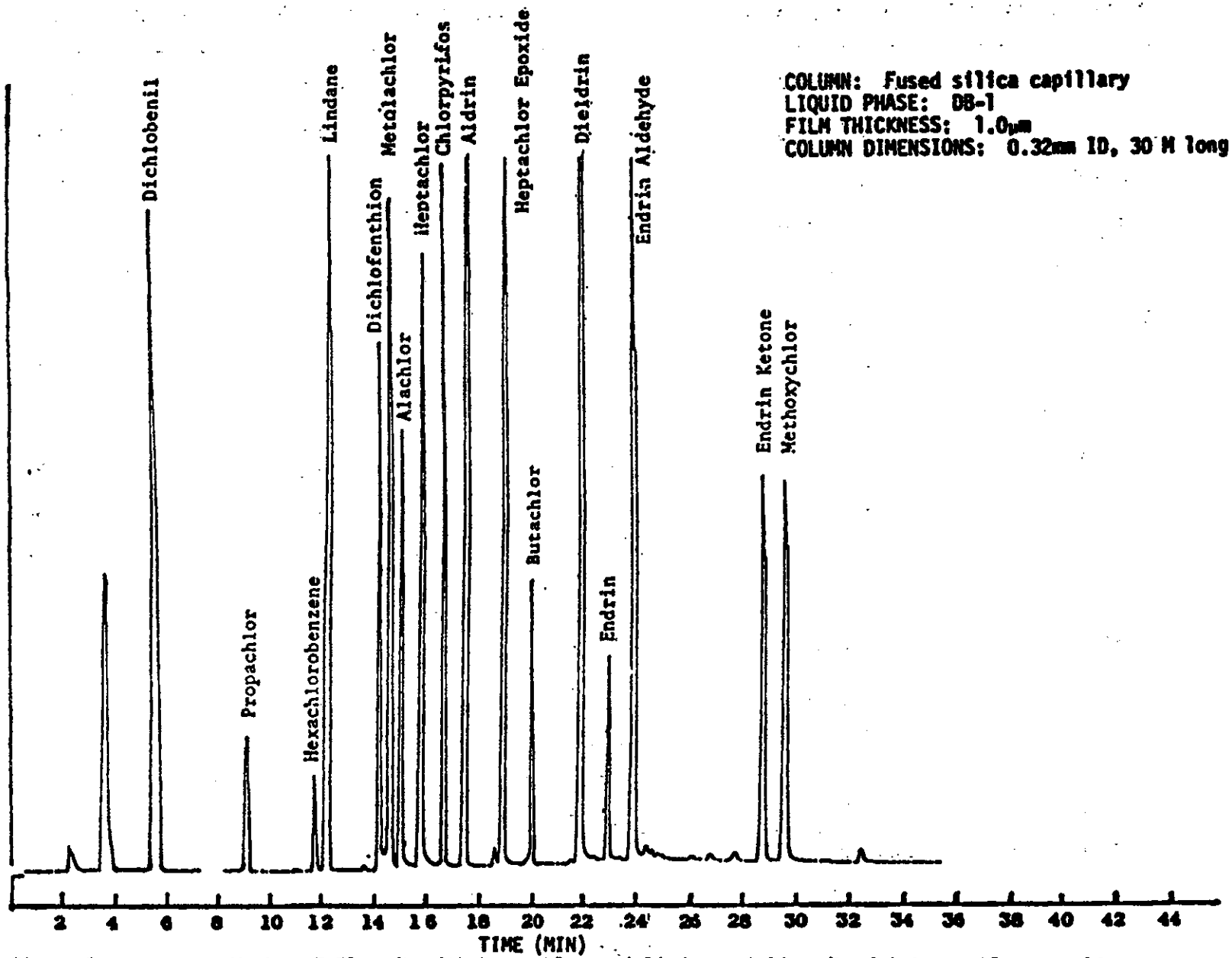

Figure 1. Hexane spiked at 7.71 ug/L with heptachlor and lindane; 9.14 ug/L with heptachlor epoxide; 11.4 ug/L with aldrin and hexachlorobenzene; 23 ug/L with butachlor, chlorpyrifos, chlorpyrifos-methyl, diclobenil, dieldrin, endrin, metolochlor, and propachlor; and 44.9 ug/L with methoxychlor.

COLUMN: Fused silica capillary
LIQUID PHASE: DB-1
FILM THICKNESS: 1.0um
COLUMN DIMENSIONS: 0.32mm ID,
30 M long

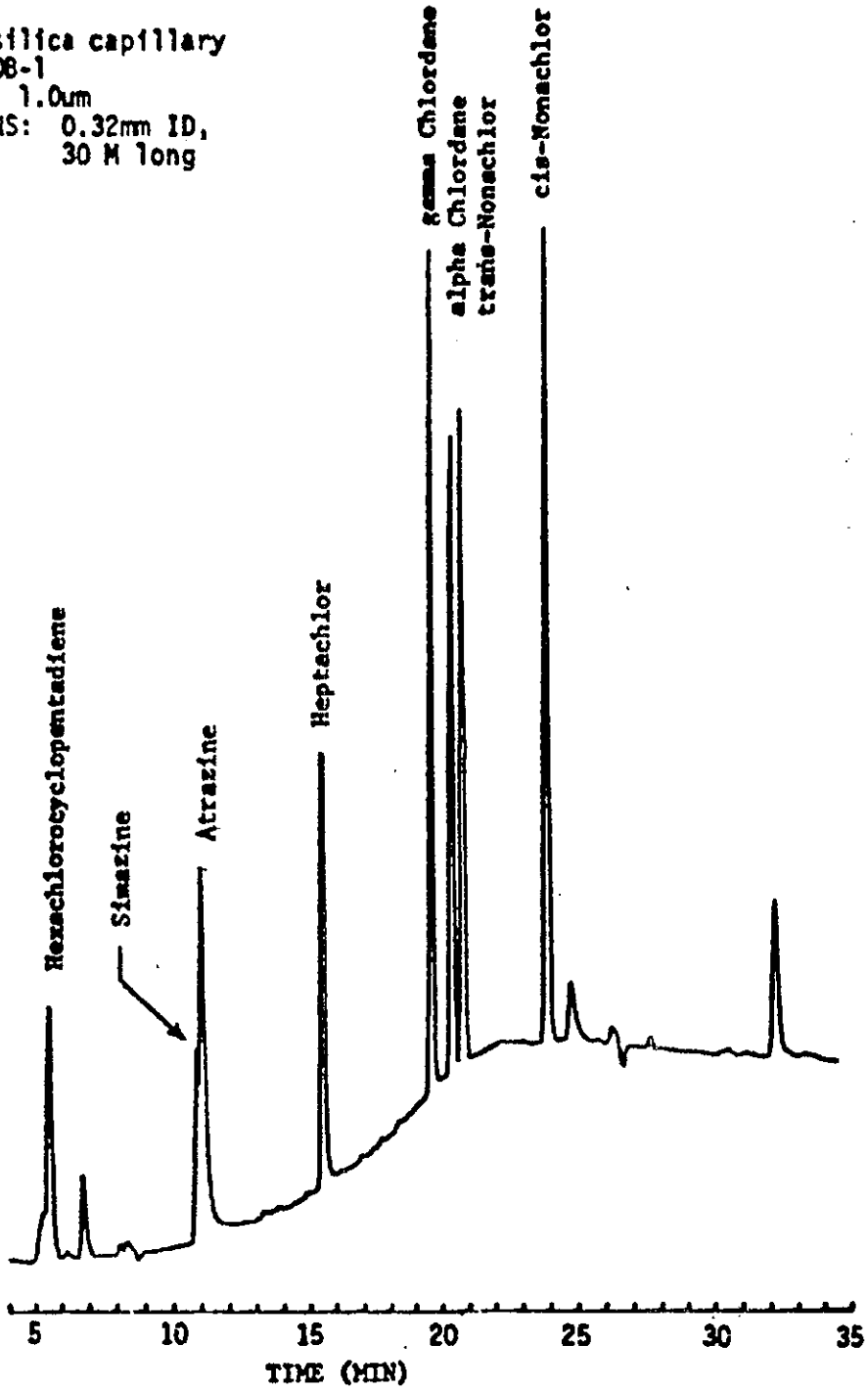

Figure 2. Extract of reagent water spiked at 20 ug/L with atrazine, 60 ug/L with simazine, 0.45 ug/L with cis-nonachlor, and 0.35 ug/L with hexachlorocyclopentadiene, heptachlor, alpha chlordane, gamma chlordane, and trans-nonachlor.

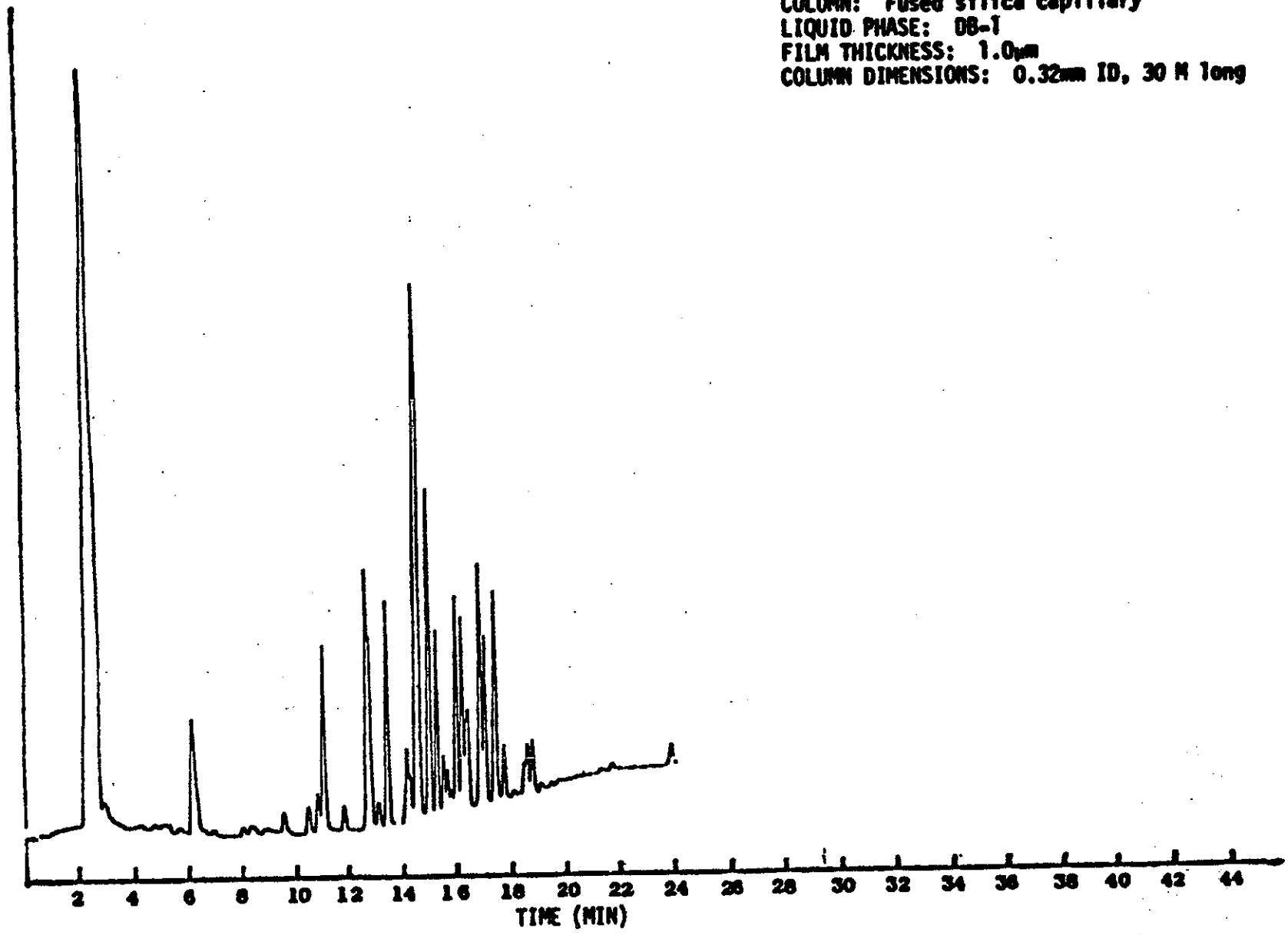

Figure 3. Hexane spiked at 11.4 ug/L with Aroclor 1016.

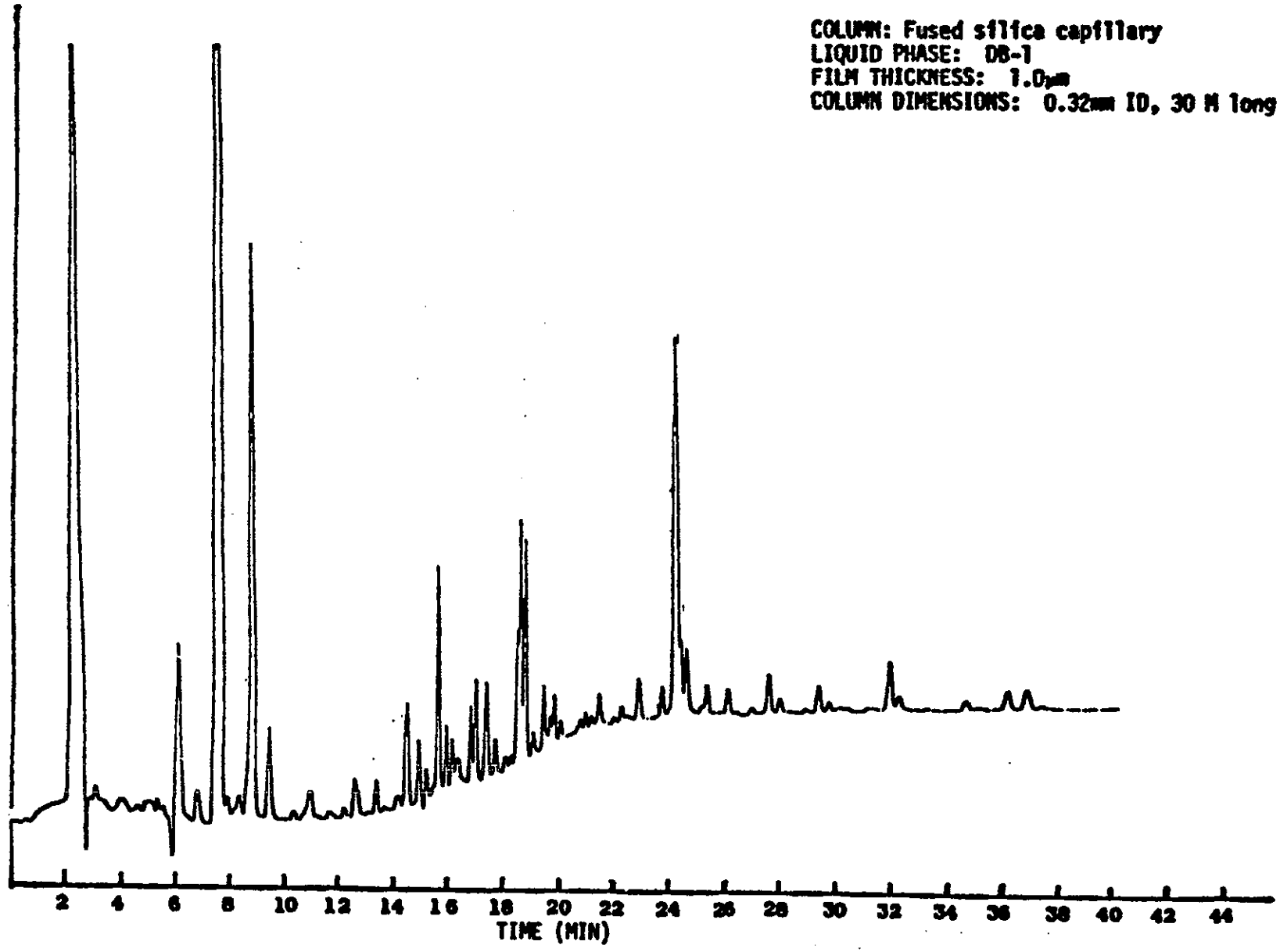

Figure 4. Hexane spiked at 171.4 ug/L with Aroclor 1221.

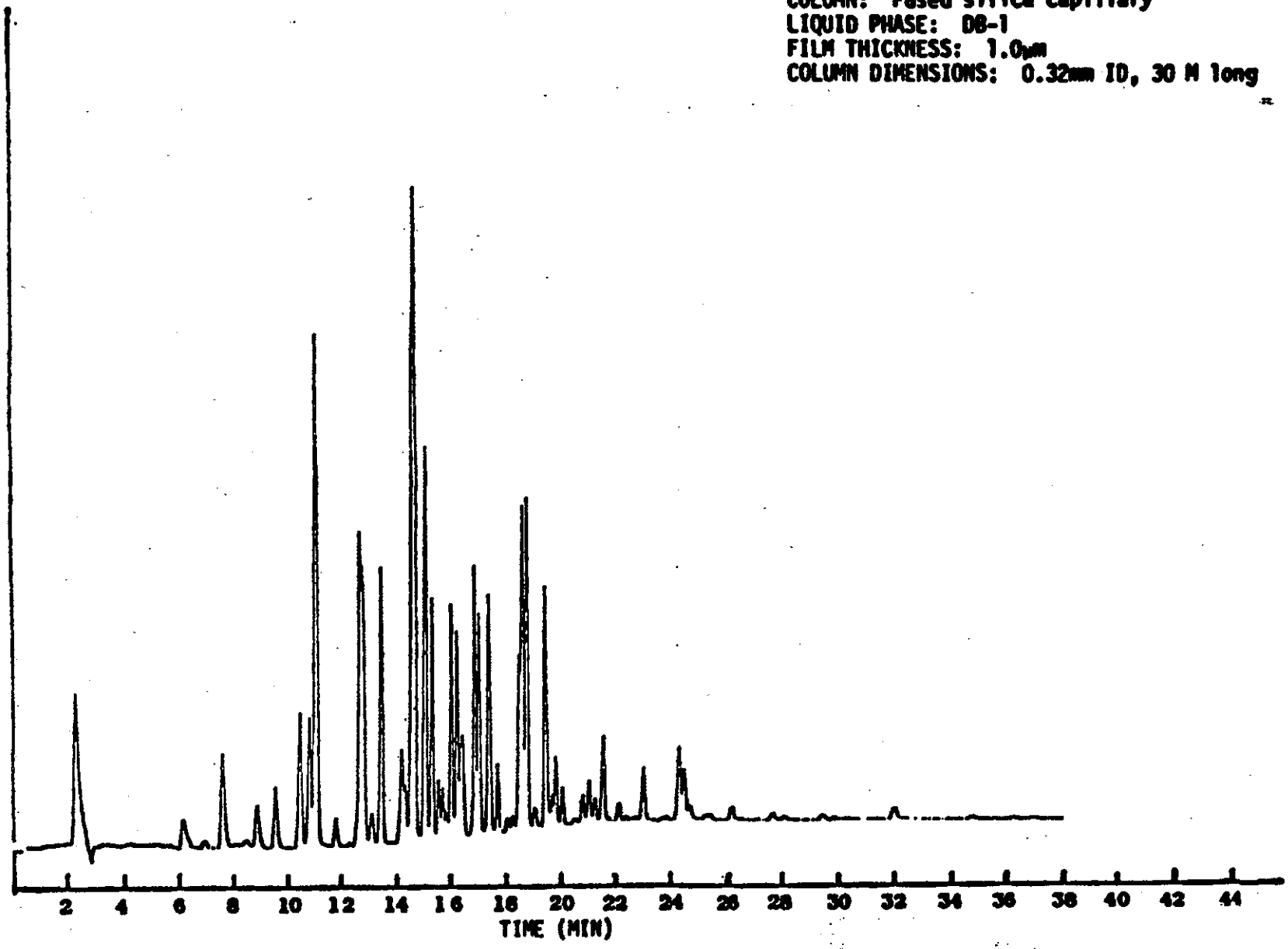

Figure 5. Hexane spiked at 57.1 ug/L with Aroclor 1232.

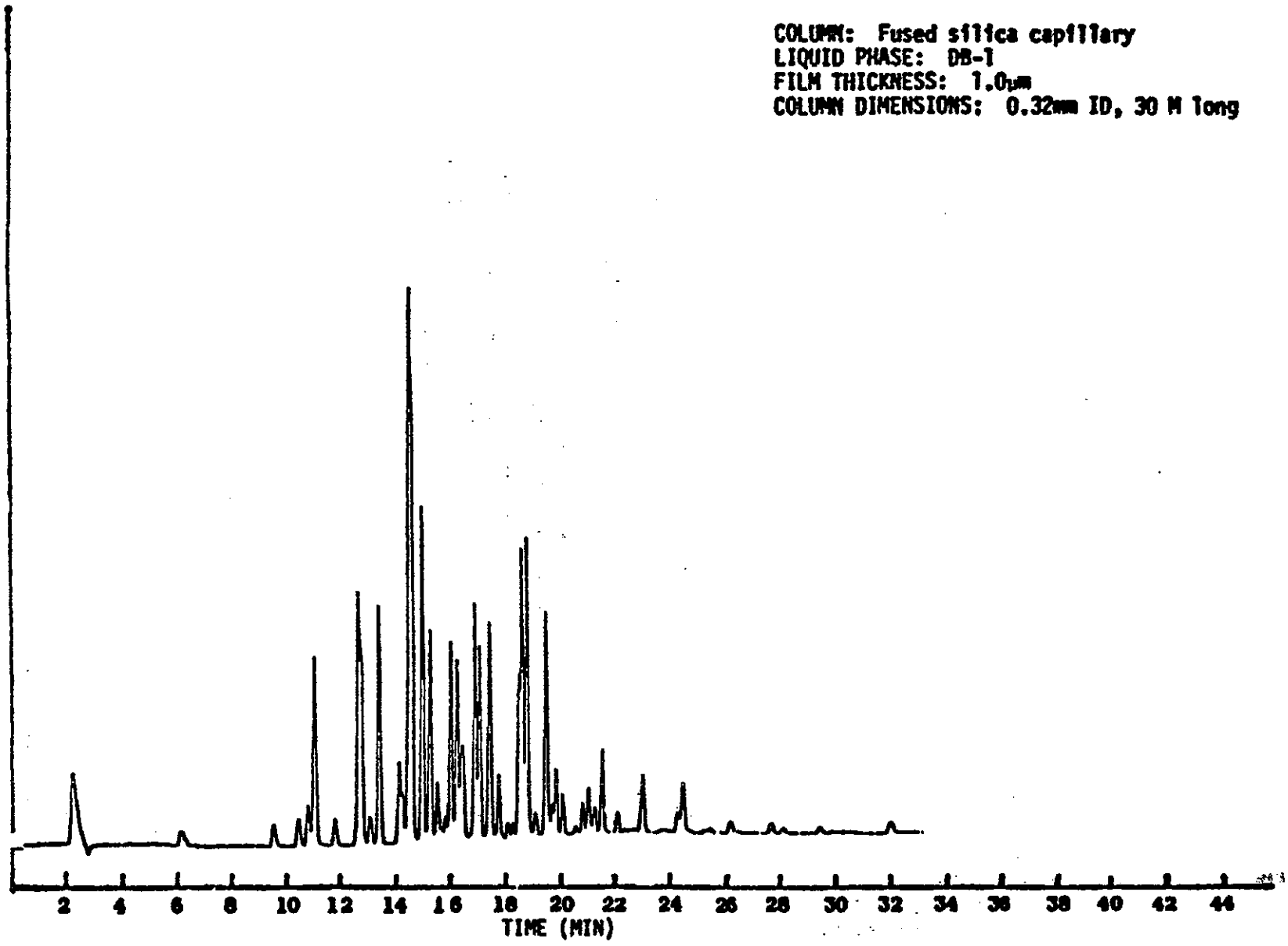

Figure 6. Hexane spiked at 57.1 ug/L with Aroclor 1242.

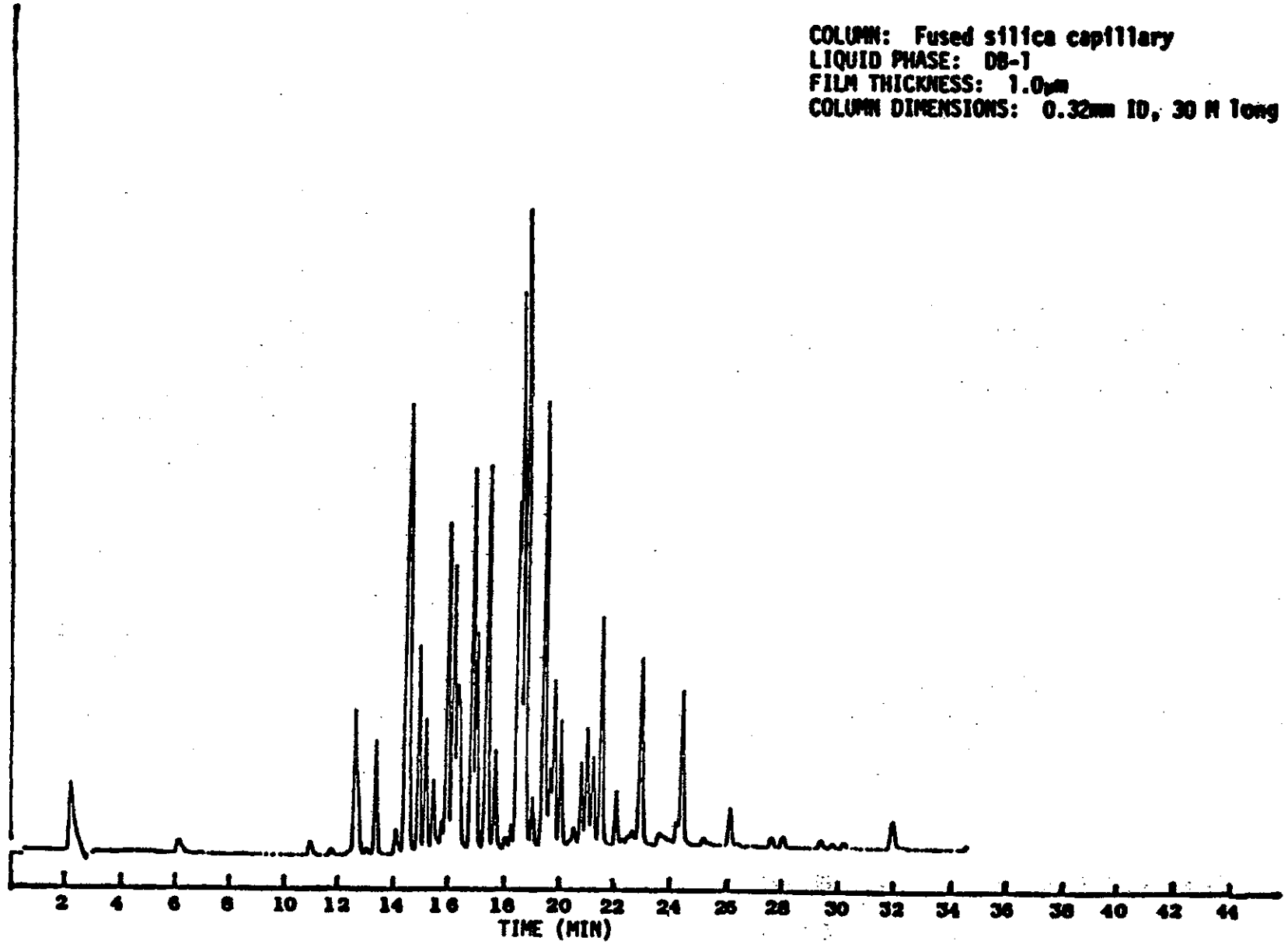

Figure7. Hexane spiked at 57.1 ug/L with Aroclor 1248.

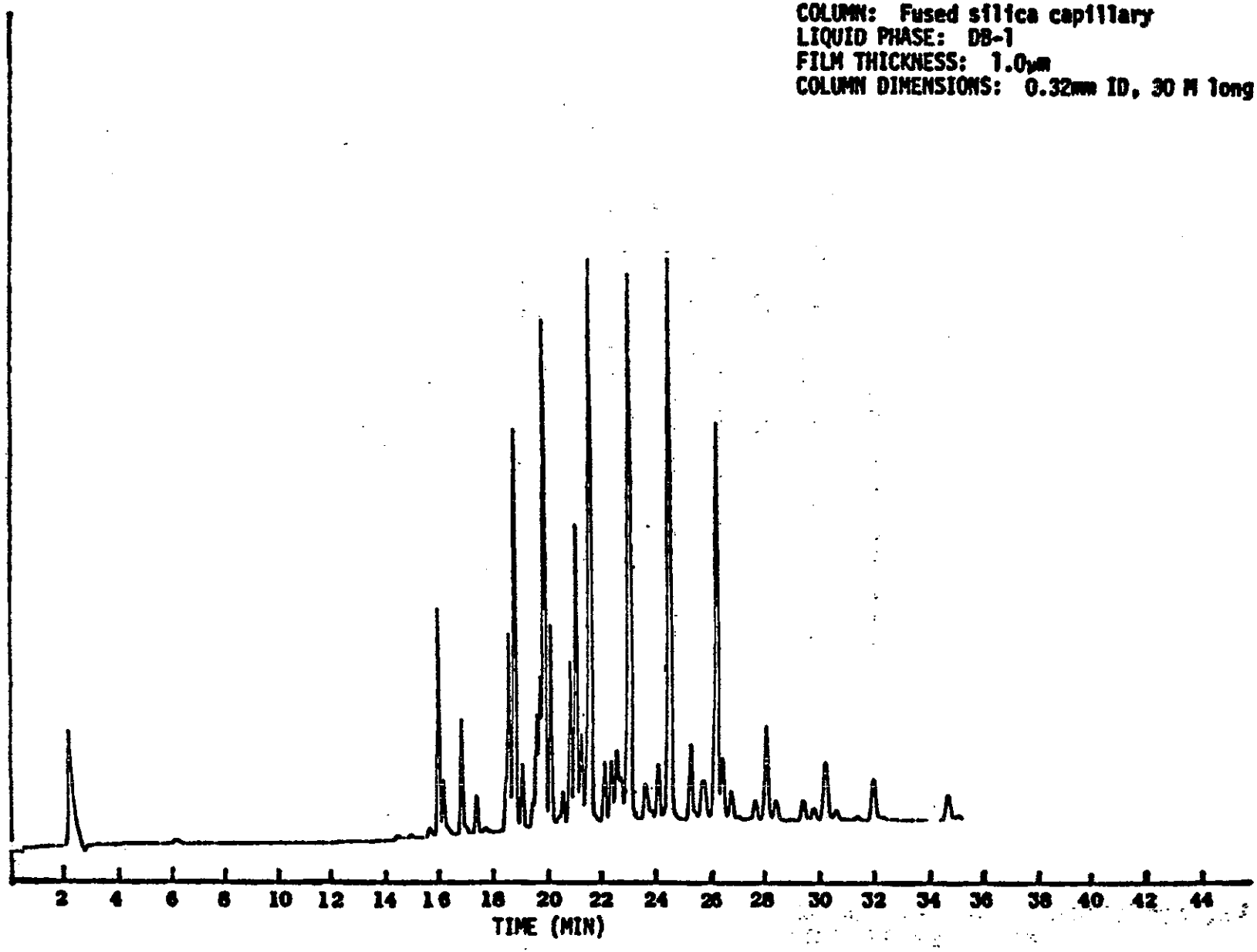

Figure 8. Hexane spiked at 42.9 ug/L with Aroclor 1254.

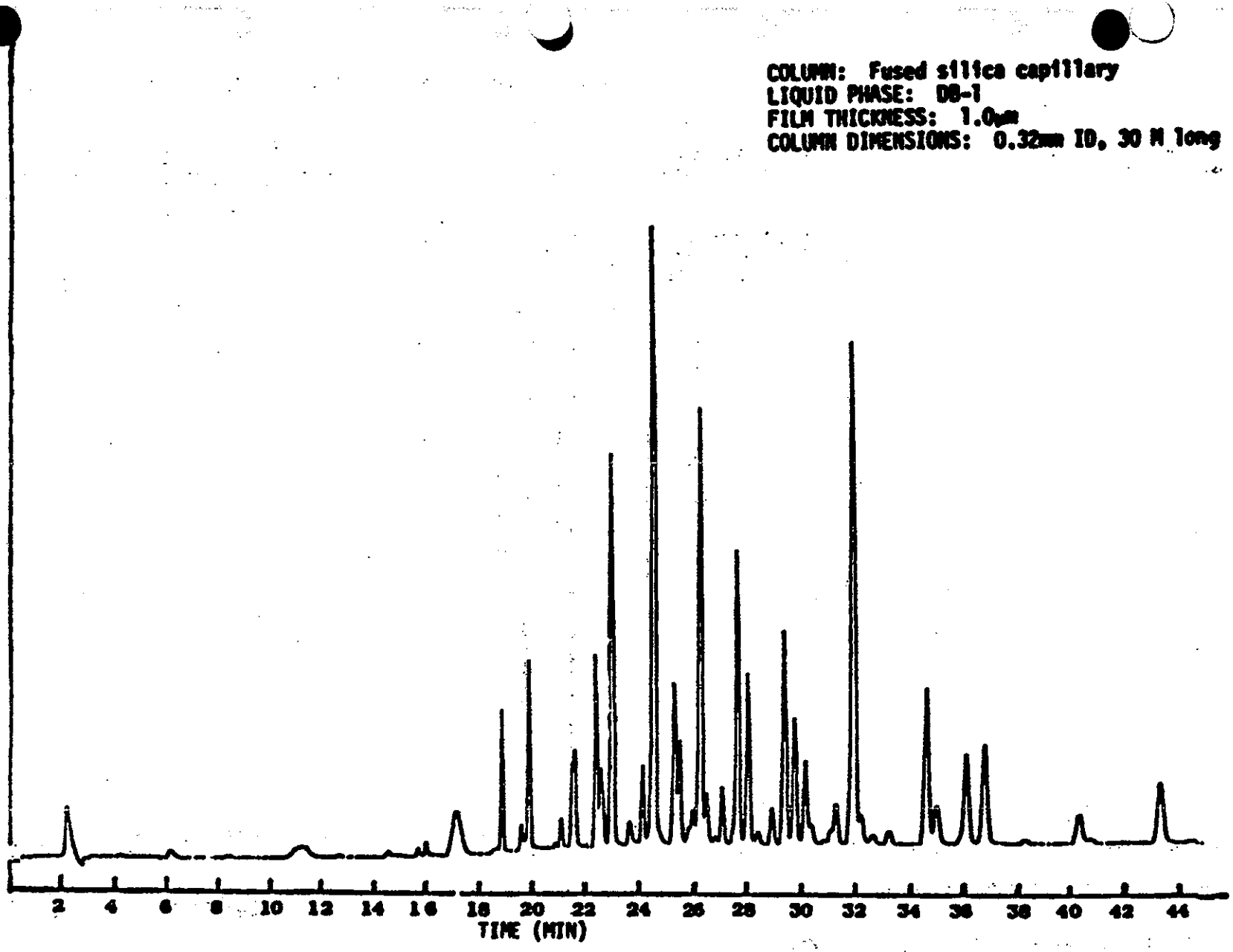

Figure 9. Hexane spiked at 34.3 ug/L with Aroclor 1260.

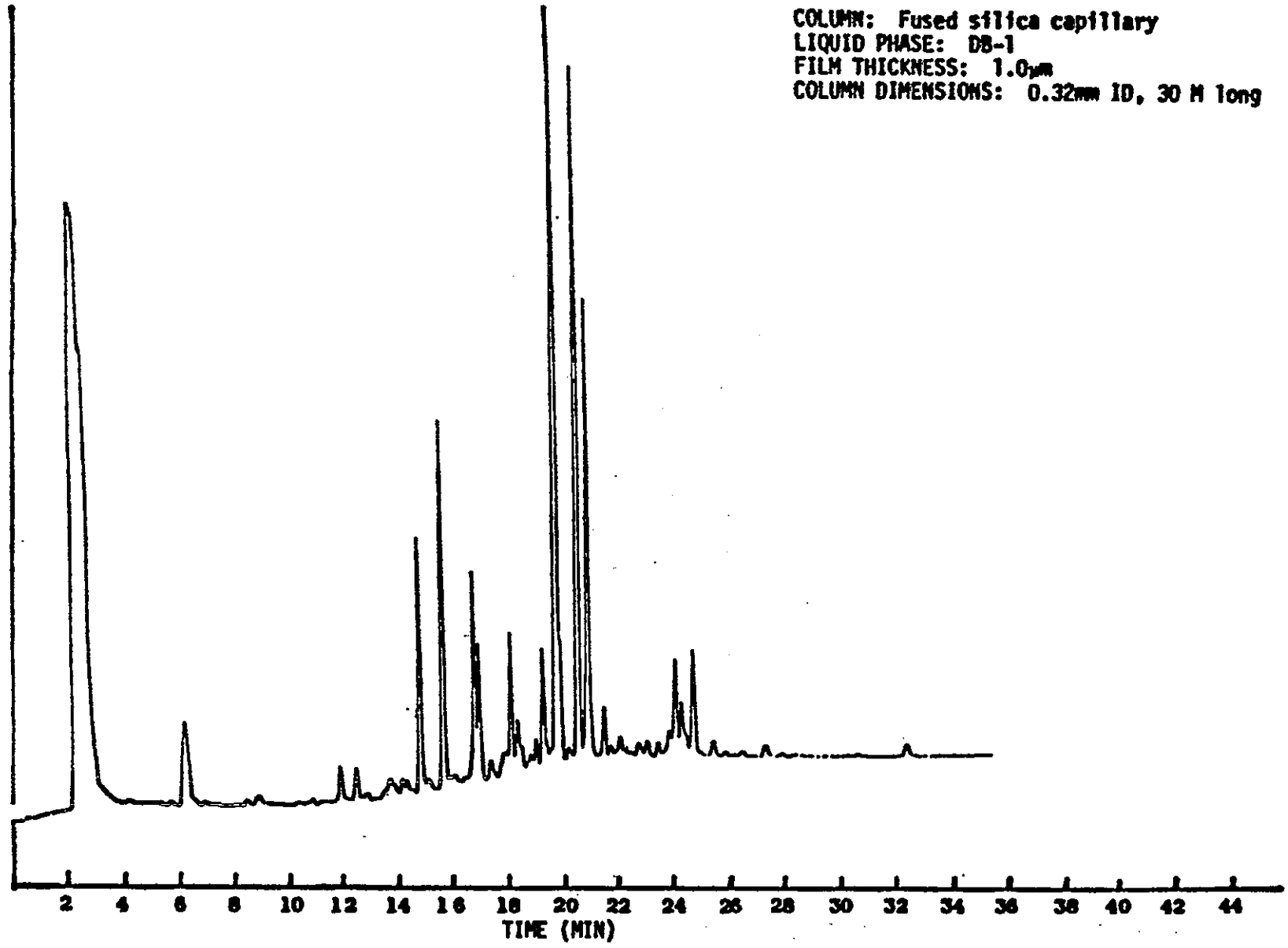

Figure 10. Hexane spiked at 28.6 ug/L with chlordane.

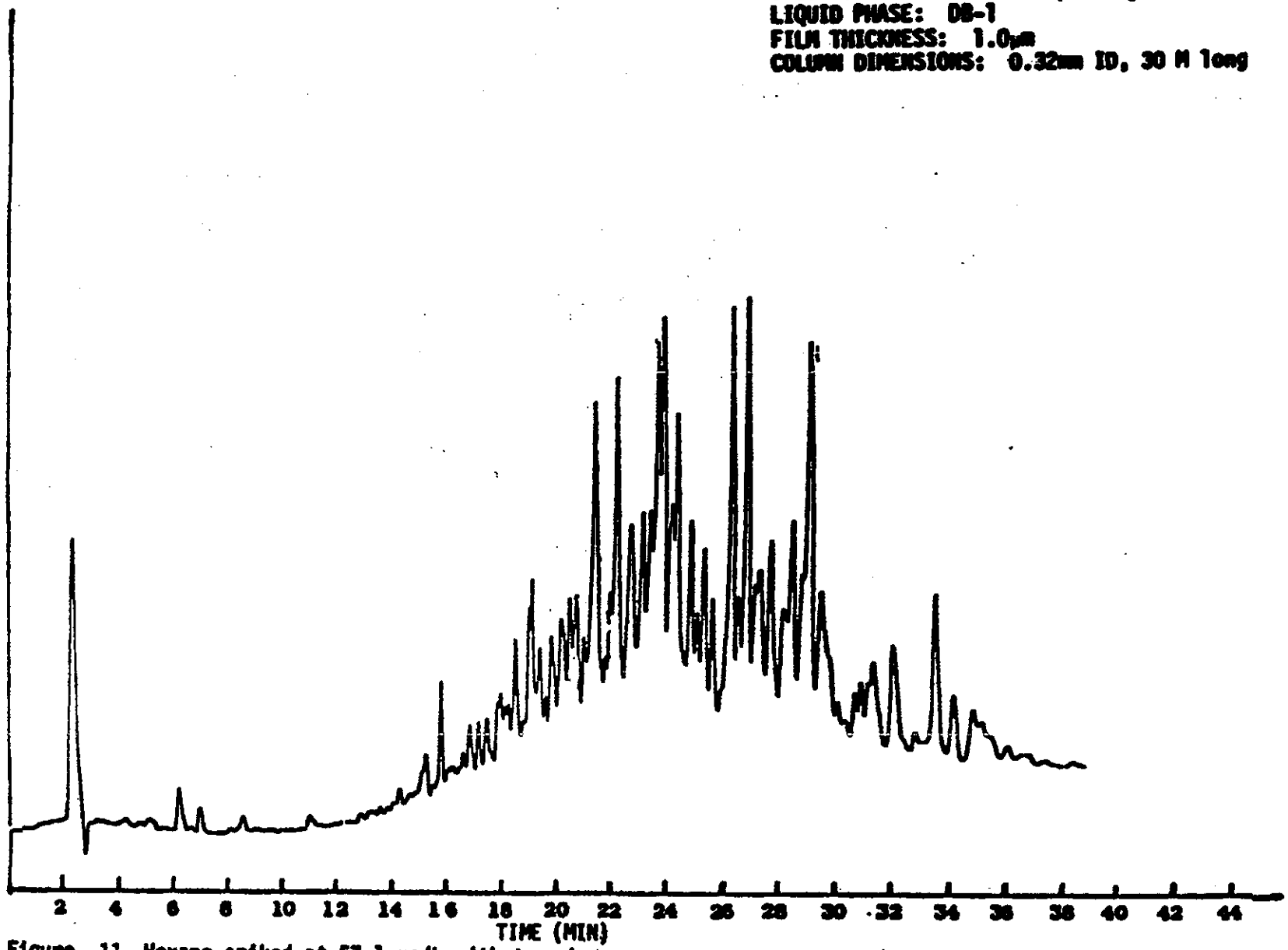

Figure 11. Hexane spiked at 57.1 ug/L with toxaphene.

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

Revision 2.0

T. Engels (Battelle Columbus Laboratories) - 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. (1) 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 in the National Pesticides Survey (NPS) Program. 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) 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. 10.3.

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 (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. 10.2.

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 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 (3-5) 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. APPARATUS AND EQUIPMENT (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 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. 10.4.

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). A NPD was used to generate the validation data presented in this method. Alternative detectors, including a mass spectrometer, may be used in accordance with the provisions described in Sect. 10.4.

7. REAGENTS AND CONSUMABLE MATERIALS - - 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 450°C for a minimum of 4 hours to remove interfering organic substances.

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.

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. If any other bactericide can be shown to work as well as mercuric chloride, it may be used instead.

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. Solution should be replaced when ongoing QC (Sect. 10) indicates a problem. Note that TPP has been shown to be an effective internal standard for the method analytes (1), but other compounds may be used if the quality control requirements in Sect. 10 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. 10) indicates a problem.

Note that 1,3-dimethyl-2-nitrobenzene has been shown to be an effective surrogate standard for the method analytes (1), but other compounds may be used if the quality control requirements in Sect. 10 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 (Section 10) indicates a problem.

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 AND STORAGE

8.2.1 Add mercuric chloride (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.

8.2.2 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 the sample is collected in a bottle containing preservative(s), seal the bottle and shake vigorously for 1 min.

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 indicated that most method analytes present in samples were stable for 14 days when stored under these conditions. (1). 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.

8.3 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. CALIBRATION

9.1 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. 9.2) or the external standard technique (Sect. 9.3). 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. 9.2.5 or 9.3.4). NOTE: Calibration standard solutions must be prepared such that no unresolved analytes are mixed together.

9.2 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.

9.2.1 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. If Merphos is to be determined, calibrate with DEF (S,S,S-tributylphosphoro-trithioate). To each calibration standard, add a known constant amount of one or more of the internal standards, and dilute to volume with MTBE. 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.

9.2.2 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.

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)} \qquad \text{Equation 1}$$

where :

A_s = Response for the analyte.

Ais = 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.

9.2.3 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.

9.2.4 The working calibration curve or RF must be verified on each working shift by the measurement of one or more calibration standards. 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 repetition also fails, a new calibration curve must be generated for that analyte using freshly prepared standards.

9.2.5 Single point calibration is a viable alternative to a calibration curve. Prepare single point standards from the secondary dilution standards in MTBE. The single point standard should be prepared at a concentration that produces a response that deviates from the sample extract response by no more than 20%.

9.2.6 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.

9.3 EXTERNAL STANDARD CALIBRATION PROCEDURE

9.3.1 Prepare calibration standards at a minimum of three (recommend five) concentration levels for each analyte of interest and surrogate compound by adding volumes of one or more stock standards to a volumetric flask. If Merphos is to be determined, calibrate with DEF (S,S,S-tributylphosphorotrithioate). Dilute to volume with MTBE. 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.

9.3.2 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.

9.3.3 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.

9.3.4 Single point calibration is a viable alternative to a calibration curve. Prepare single point standards from the secondary dilution standards in MTBE. The single point standard should be prepared at a concentration that produces a response that deviates from the sample extract response by no more than 20%.

9.3.5 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.

10. QUALITY CONTROL

10.1 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.

10.2 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.

10.3 Initial Demonstration of Capability.

10.3.1 Select a representative fortified concentration (about 10 times EDL or at the regulatory Maximum Contaminant Level, whichever is lower) for each analyte. Prepare a sample concentrate (in methanol) containing each analyte at 1000 times selected concentration. With a syringe, add 1 mL of the concentrate to each of at least four 1-L aliquots of reagent water, and analyze each aliquot according to procedures beginning in Sect. 11.

10.3.2 For each analyte the recovery value for all four of these samples must fall in the range of R ± 30% (or within R ± $3S_R$ if broader) using the values for R and S_R for reagent water in Table 2. For those compounds that meet the acceptance criteria, performance is considered acceptable and sample analysis may begin. For those compounds that fail these criteria, this procedure must be repeated using four fresh samples until satisfactory performance has been demonstrated.

10.3.3 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.

10.4 The analyst is permitted to modify GC columns, GC detectors, GC conditions, continuous extraction techniques, 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. 10.3.

10.5 Assessing Surrogate Recovery

10.5.1 When surrogate recovery from a sample or method blank is <70% or >130%, check (1) calculations to locate possible errors, (2) fortifying solutions for degradation, (3) contamination, and (4) instrument performance. If those steps do not reveal the cause of the problem, reanalyze the extract.

10.5.2 If a blank extract reanalysis fails the 70-130% recovery criterion, the problem must be identified and corrected before continuing.

10.5.3 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.

10.6 Assessing the Internal Standard

10.6.1 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%.

10.6.2 If >30% deviation occurs with an individual extract, optimize instrument performance and inject a second aliquot of that extract.

10.6.2.1 If the reinjected aliquot produces an acceptable internal standard response report results for that aliquot.

10.6.2.2 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.

10.6.3 If consecutive samples fail the IS response acceptance criterion, immediately analyze a calibration check standard.

10.6.3.1 If the check standard provides a response factor (RF) within 20% of the predicted value, then follow procedures itemized in Sect. 10.6.2 for each sample failing the IS response criterion.

10.6.3.2 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.

10.7 Assessing Laboratory Performance - Laboratory Fortified Blank

10.7.1 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 the MCL, whichever is less. Calculate accuracy as percent recovery (X_i). If the recovery of any analyte falls outside the control limits (see Sect. 10.7.2), that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

10.7.2 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. 10.3.2 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 never exceed those established in Sect. 10.3.2.

10.7.3 It is recommended that the laboratory periodically determine and document its detection limit capabilities for analytes of interest.

10.7.4 At least quarterly, analyze a QC sample from an outside source.

10.7.5 Laboratories are encouraged to participate in external performance evaluation studies such as the laboratory certification programs offered by many states or the studies conducted by USEPA. Performance evaluation studies serve as independent checks on the analyst's performance.

10.8 Assessing Analyte Recovery - Laboratory Fortified Sample Matrix

10.8.1 The laboratory must add a known concentration to a minimum of 5% of the routine samples or one sample concentration per set, whichever is greater. The fortified 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. 10.7). Over time, samples from all routine sample sources should be fortified.

10.8.2 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. If the analyzed unfortified sample is found to contain NO background concentrations, and the added concentrations are those specified in Sect. 10.7, then the appropriate control limits would be the acceptance limits in Sect. 10.7. If, on the other hand, the analyzed unfortified sample is found to contain background concentration, b, estimate the standard deviation at the background concentration, s_b, using regressions or comparable background data and, similarly, estimate the mean, X_a, and standard deviation, s_a, of analytical results at the total concentration after fortifying. Then the appropriate percentage control limits would be $\overline{P} \pm 3s_p$, where:

$$\overline{P} = 100\ \overline{X}\ /\ (b + \text{fortifying concentration})$$

$$\text{and } s_p = 100\ \{(s_a^2 + s_b^2)^{1/2} / \text{fortifying concentration}$$

For example, if the background concentration for Analyte A was found to be 1 µg/L and the added amount was also 1 µg/L, and upon analysis the laboratory fortified sample measured 1.6 µ/L, then the calculated P for this sample would be (1.6 µg/L minus 1.0 µg/L)/1 µg/L or 60%. This calculated P is compared to control limits derived from prior reagent water data. Assume it is known that analysis of an interference free sample at 1 µg/L yields an s of 0.12 µg/L and similar analysis at 2.0 µg/L yields X and s of 2.01 µg/L and 0.20

µg/L, respectively. The appropriate limits to judge the reasonableness of the percent recovery, 60%, obtained on the fortified matrix sample is computed as follows:

[100 (2.01 µg/L) / 2.0 µg/L]

$\pm$ 3 (100) $[(0.12\ \mu g/L)^2 + (0.20\ \mu g/L)^2]^{1/2}$ / 1.0 µg/L =

100.5% $\pm$ 300 (0.233) =

100.5% $\pm$ 70% or 30% to 170% recovery of the added analyte.

10.9 ASSESSING INSTRUMENT SYSTEM - LABORATORY PERFORMANCE CHECK (LPC) - Instrument performance should be monitored on a daily basis by analysis of the LPC sample. The LPC sample contains compounds designed to indicate appropriate instrument sensitivity, column performance (primary column) and chromatographic performance. LPC sample components and performance criteria are listed in Table 3. 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 instrument QC standard compounds must be adjusted to be compatible with the laboratory EDLs.

10.10 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.

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 blanks and QC check standards. 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.

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 blanks and QC check standards. 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.

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. 10.3 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 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 adequately

...oved from the final extract, it may cause detector ...blems.

11.3.5 ...nsfer extract to an appropriate- sized TFE-fluorocarbon-...ed screw-cap vial and store, refrigerated at 4°C, until ...lysis by GC-HPD.

11.4 GAS CHR...TOGRAPHY

11.4.1 ...ct. 6.8 summarizes the recommended operating conditions for ... gas chromatograph. Included in Table 1 are retention ... s observed using this method. Other GC columns, ...matographic conditions, or detectors may be used if the ...irements of Sect. 10.3 are met.

11.4.2 ...librate the system daily as described in Sect. 9. The ...ndards and extracts must be in MTBE.

11.4.3 ... the internal standard calibration procedure is used, add ... µL of the internal standard 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 ... e in area units.

11.4.5 ... he response for the peak exceeds the working range of the ...tem, dilute the extract and reanalyze.

11.5 IDENTIFI...ION OF ANALYTES

11.5.1 ...tify a sample component by comparison of its retention ... to the retention time of a reference chromatogram. If the retention time of an unknown compound corresponds, within ...its, 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 ...ntion time variations of standards over the course of a ...y. 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., ...dened 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. 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 calibration procedure described in Sect. 9.

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. 9.2 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. 9.3.2. 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 determined at five concentration levels. Results were used to determine analyte EDLs and demonstrate method range.(1) Analytes were divided into five groups for recovery studies. Analyte EDLs

and 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.(1) Analyte recoveries from the two synthetic matrices are given in Table 2.

14. REFERENCES

1. National Pesticide Survey Method No. 1: Determination of Nitrogen- and Phosphorus-Containing Pesticides in Groundwater by Gas Chromatography with a Nitrogen-Phosphorus Detector.

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.

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 11, Volume 11.01, D3370-82, "Standard Practice for Sampling Water," American Society for Testing and Materials, Philadelphia, PA, 1986.

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	25.42
Cycloate	28.58	29.67
Chlorpropham	29.09	(b)
Atraton	31.26	29.97
Simazine	31.39	31.32
Prometon	31.58	30
Atrazine	31.87	31.23
Propazine	32.01	31.13
Terbufos	32.37	(b)
Pronamide	32.76	32.63
Diazinon	33.23	(b)
Disulfoton	33.42	30.9
Terbacil	33.73	(b)
Metribuzin	35.20	34.73
Methyl paraoxon	35.38	34.1
Simetryn	35.72	34.55
Alachlor	35.95	34.1
Ametryn	36.00	34.52
Prometryn	36.41	34.23
Terbutryn	36.70	34.8
Bromacil	38.32	30
Metolachlor	37.74	35.7
Triademefon	38.12	37
MGK 264 (c)	38.73	35.73
Diphenamid	41.17	34.97
Stirofos	41.27	39.55
Disulfoton sulfone	41.41	39.42
Butachlor	41.56	
Fenamiphos	41.93	1
Napropamide	41.93	(b)
Tricyclazole	42.35	41.33
Merphos (d)	42.55	39.78
Carboxin	42.77	39.95
Norflurazon	43.02	41.68
Triphenyl phosphate (int. std.)	47	45.4

TABLE 1 (CONTINUED)

Analyte	Retention Time[a] Col.1	Col.2
Hexazinone	46.58	47.8
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, PRECISION AND ESTIMATED DETECTION LIMITS (EDLS) FOR ANALYTES FROM REAGENT WATER AND SYNTHETIC GROUNDWATERS(A)

Analyte	EDL[b] µg/L	Conc. µg/L	Reagent Water R[c]	Reagent Water S_R[d]	Synthetic Water 1 R	Synthetic Water 1 S_R	Synthetic Water 2 R	Synthetic Water 2 S_R
Alachlor	0.38	3.8	95	11	82	6	90	8
Ametryn	2	20	91	10	102	11	96	4
Ametraton	0.6	6	91	11	84	7	91	8
Atrazine	0.13	1.3	92	8	89	6	92	5
Bromacil	2.5	25	91	9	81	5	88	8
Butachlor	0.38	3.8	96	4	93	15	84	5
Butylate	0.15	1.5	97	21	36	8	83	8
Carboxin	0.6	6	102	4	98	13	87	5
Chlorpropham	0.5	5	93	11	82	7	93	8
Cycloate	0.25	2.5	89	9	97	14	93	3
Diazinon	0.25	2.5	115	7	83	8	84	3
Dichlorvos	2.5	25	97	6	86	6	106	16
Diphenamid	0.6	6	93	8	88	4	93	5
Disulfoton	0.3	3	89	10	107	12	95	5
Disulfoton sulfone	3.8	7.5	98	10	92	5	96	3
Disulfoton sulfoxide	0.38	3.8	87	11	83	22	54	19
EPTC	0.25	2.5	85	9	83	5	86	4
Ethoprop	0.19	1.9	103	5	91	7	79	3
Fenamiphos	1.	10	90	8	87	5	89	2
Fenarimol	0.38	3.8	99	5	89	6	89	6
Fluridone	3.8	38	87	9	91	11	86	10
Hexazinone	0.76	7.6	90	7	95	6	95	9
Merphos	0.25	2.5	96	8	99	4	92	4
Methyl paraoxon	2.5	25	98	10	97	8	94	4
Metolachlor	0.75	7.5	93	4	92	10	84	4
Metribuzin	0.15	1.5	101	5	99	10	86	4
Mevinphos	5.	50	95	11	93	6	92	4
MGK 264	0.5	5	100	4	91	11	83	6
Molinate	0.15	1.5	98	18	93	8	89	9
Napropamide	0.25	2.5	101	6	99	5	104	18
Norflurazon	0.5	5.	94	5	101	15	87	4
Pebulate	0.13	1.3	94	9	99	6	98	15
Prometon	0.3	3	78	9	99	5	83	2
Prometryn	0.19	1.9	93	8	91	8	93	4
Pronamide	0.76	7.6	91	10	91	7	92	8
Propazine	0.13	1.3	92	8	99	6	92	5
Simazine	0.075	0.75	100	7	95	5	103	14
Simetryn	0.25	2.5	99	5	93	4	103	14
Stirofos	0.76	7.6	98	6	91	6	95	10
Tebuthiuron	1.3	13	84	9	95	10	98	13
Terbacil	4.5	45	97	6	96	5	102	12
Terbufos	0.5	5	97	4	99	6	77	7
Terbutryn	0.25	2.5	94	9	91	8	92	4

TABLE 2. (CONTINUED)

Analyte	EDL[b]	Conc. µg/L	Reagent Water R[c]	Reagent Water S_R[d]	Synthetic Water R	Synthetic Water S_R	Synthetic Water 2[f] R	Synthetic Water 2[f] S_R
Triademefon	0.65	6.5	93	8	94	5	95	5
Tricyclazole	1.	10	86	7	90	6	90	11
Vernolate	0.13	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] 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.

[c] R = average percent recovery.

[d] S = standard deviation of the percent recovery.

[e] Corrected for amount found in blank; Absopure Nature Artesian Spring Water Obtained from the Absopure Water Company in Plymouth, Michigan.

[f] 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. 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	0.30	Resolution > 0.7 (b)
	Atrazine	0.15	

* PGF - peak Gaussian factor. Calculated using the equation:

$$PGF = \frac{1.83 \times W(1/2)}{W(1/10)}$$

W(1/2) is the peak width at half height and W(1/10) is the peak width at tenth height.

The resolution for two peaks is 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.

METHOD 508. DETERMINATION OF CHLORINATED PESTICIDES IN WATER BY GAS CHROMATOGRAPHY WITH AN ELECTRON CAPTURE DETECTOR

Revision 3.0

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)

T. Engels (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.(1) The following compounds can be determined using this method:

Compound	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	1897-45-6
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 Method 505 (capillary column). The columns used in this method may well be adequate, however, no data were collected for these constituents during methods development.

(a) These compounds are only qualitatively identified in the National Pesticides Survey (NPS) Program. 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) 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. 10.3.

1.4 Degradation of DDT and Endrin caused by active sites in the injection port and GC columns may occur. This is not as much a problem with new capillary columns as with packed columns. However, high boiling sample residue in capillary columns will create the same problem after injection of sample extracts.

1.5 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).

1.6 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 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. 10.2.

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 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 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.(3,4)

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. Cleanup of sample extracts may be necessary. Positive 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.

4.6 WARNING: A dirty injector insert will cause the late eluting compounds to drop off.

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 WARNING: When a solvent is purified stabilizers added by the manufacturer are removed thus potentially making the solvent hazardous.

6. APPARATUS AND EQUIPMENT (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 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 3 (See

Section 10.9). Alternative columns may be used in accordance with the provisions described in Sect. 10.4.

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 spiked reagent and artificial ground waters. An ECD was used to generate the validation data presented in this method. Alternative detectors, including a mass spectrometer, may be used in accordance with the provisions described in Sect. 10.4.

7. REAGENTS AND CONSUMABLE MATERIALS - - 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, pH7 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 450°C for a minimum of 4 hours to remove interfering organic substances.

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.

7.5 SODIUM THIOSULFATE, granular, anhydrous, ACS grade.

7.6 PENTACHLORONITROBENZENE (PCNB) 98% purity, for use as internal standard.

7.7 4,4'-DICHLOROBIPHENYL (DCB) 96% purity, for use as surrogate standard (available from Chemicals Procurement Inc.).

7.8 MERCURIC CHLORIDE -- ACS grade -- for use as a bactericide. If any other bactericide can be shown to work as well as mercuric chloride, it may be used instead.

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 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. 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. 10) indicates a problem. Note that PCNB has been shown to be an effective internal standard for the method analytes (1), but other compounds may be used if the quality control requirements in Section 10 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. 10) indicates a problem. Note DCB has been shown to be an effective surrogate standard for the method analytes (1), but other compounds may be used if the quality control requirements in Section 10 are met.