METHOD 551.1

DETERMINATION OF CHLORINATION DISINFECTION BYPRODUCTS, CHLORINATED SOLVENTS, AND HALOGENATED PESTICIDES/HERBICIDES IN DRINKING WATER BY LIQUID-LIQUID EXTRACTION AND GAS CHROMATOGRAPHY WITH ELECTRON-CAPTURE DETECTION

Revision 1.0

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1.0 SCOPE AND APPLICATION

1.1 This method[1-9] is applicable to the determination of the following analytes in finished drinking water, drinking water during intermediate stages of treatment, and raw source water. The particular choice of analytes from this list should be a function of the specific project requirements.

	Analyte	CAS No.
Disinfection Byproducts (DBPs):		
Trihalomethanes	Chloroform	67-66-3
	Bromodichloromethane	75-27-4
	Bromoform	75-25-2
	Dibromochloromethane	124-48-1
Haloacetonitriles	Bromochloroacetonitrile	83463-62-1
	Dibromoacetonitrile	3252-43-5
	Dichloroacetonitrile	3018-12-0
	Trichloroacetonitrile	545-06-2
Other DBPs	Chloral Hydrate	75-87-6
	Chloropicrin	76-06-2
	1,1-Dichloro-2-propanone	513-88-2
	1,1,1-Trichloro-2-propanone	918-00-3
Chlorinated Solvents:		
	Carbon Tetrachloride	56-23-5
	1,2-Dibromo-3-chloropropane [DBCP]	96-12-8
	1,2-Dibromoethane [EDB]	106-93-4
	Tetrachloroethylene	127-18-4
	1,1,1-Trichloroethane	71-55-6
	1,1,2-Trichloroethane	79-00-5
	Trichloroethylene	79-01-6
	1,2,3-Trichloropropane	96-18-4
Pesticides/Herbicides:		
	Alachlor	15972-60-8
	Atrazine	1912-24-9
	Bromacil	314-40-9
	Cyanazine	21725-46-2
	Endrin	72-20-8

Analyte	CAS No.
Endrin Aldehyde	7421-93-4
Endrin Ketone	53494-70-5
Heptachlor	76-44-8
Heptachlor Epoxide	1024-57-3
Hexachlorobenzene	118-74-1
Hexachlorocyclopentadiene	77-47-4
Lindane (gamma-BHC)	58-89-9
Metolachlor	51218-45-2
Metribuzin	21087-64-9
Methoxychlor	72-43-5
Simazine	122-34-9
Trifluralin	1582-09-8

1.2 This analyte list includes 12 commonly observed chlorination disinfection byproducts,[3,4] eight commonly used chlorinated organic solvents and 16 halogenated pesticides and herbicides.

1.3 This method is intended as a stand-alone procedure for either the analysis of only the trihalomethanes (THMs) or for all the chlorination disinfection by-products (DBPs) with the chlorinated organic solvents or as a procedure for the total analyte list. The dechlorination/preservation technique presented in Section 8.0 details two different dechlorinating agents. Results for the THMs and the eight solvents may be obtained from the analysis of samples employing either dechlorinating agent. (Section 8.1.2)

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

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

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of GC and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 9.4.

1.7 Methyl-t-butyl ether (MTBE) is recommended as the primary extraction solvent in this method since it effectively extracts all of the target analytes listed in Section 1.1. However, due to safety concerns associated with MTBE and the current use of pentane by some laboratories for certain method analytes, pentane is offered as an optional extraction solvent for all analytes except

chloral hydrate. If project requirements specify the analysis of chloral hydrate, MTBE must be used as the extracting solvent. This method includes sections specific for pentane as an optional solvent.

2.0 SUMMARY OF METHOD

2.1 A 50 mL sample aliquot is extracted with 3 mL of MTBE or 5 mL of pentane. Two µL of the extract is then injected into a GC equipped with a fused silica capillary column and linearized electron capture detector for separation and analysis. Procedural standard calibration is used to quantitate method analytes.

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

3.0 DEFINITIONS

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

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

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

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

cannot be analyzed, the collection and analysis of field duplicates for this method is critical.

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

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

3.7 Laboratory Fortified Blank (LFB) -- An aliquot of reagent water, or other blank matrix, to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise analyte quantitation at various concentrations including the required method detection limit.

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

3.9 Stock Standard Solution (SSS) -- A concentrated solution containing one or more method analytes which is prepared in the laboratory using assayed reference materials or purchased as certified from a reputable commercial source.

3.10 Primary Dilution Standard Solution (PDS) -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.11 Calibration Standard (CAL) -- A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standard(s) and surrogate analyte(s). The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.12 Quality Control Sample (QCS) -- A solution of method analytes which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a

source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.13 Laboratory Performance Check Solution (LPC) -- A solution of selected method analytes, surrogate(s), internal standard(s), or other test substances used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.14 Method Detection Limit (MDL) -- The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero. (Appendix B to 40 CFR Part 136)

3.15 Estimated Detection Limit (EDL) -- Defined as either the MDL or a level of compound in a sample yielding a peak in the final extract with a signal to noise (S/N) ratio of approximately five, whichever is greater.

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

4.0 INTERFERENCES

4.1 Impurities contained in the extracting solvent usually account for the majority of the analytical problems. Each new bottle of solvent should be analyzed for interferences before use. An interference free solvent is a solvent containing no peaks yielding data at ≥MDL (Tables 2 and 8) at the retention times of the analytes of interest. Indirect daily checks on the extracting solvent are obtained by monitoring the laboratory reagent blanks (Section 9.3). Whenever an interference is noted in the reagent blank, the analyst should analyze the solvent separately to determine if the source of the problem is the solvent or another reagent.

4.2 Glassware must be scrupulously cleaned[13]. Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot water and detergent and thoroughly rinsing with tap and reagent water. Drain dry, and heat in an oven or muffle furnace at 400°C for one hour. Do not muffle volumetric ware but instead rinse three times with HPLC grade or better acetone. Thoroughly rinsing all glassware with HPLC grade or better acetone may be substituted for heating provided method blank analysis confirms no background interferant contamination is present. After drying and cooling, seal and store all glassware in a clean environment free of all potential contamination. To prevent any accumulation of dust or other contaminants, store glassware inverted on clean aluminum foil or capped with aluminum foil.

4.3 Commercial lots of the extraction solvents (both MTBE and pentane) often contain observable amounts of chlorinated solvent impurities, e.g., chloroform, trichloroethylene, carbon tetrachloride. When present, these impurities can normally be removed by double distillation.

4.4 This liquid/liquid extraction technique efficiently extracts a wide boiling range of non-polar and polar organic components of the sample. Thus, confirmation is quite important, particularly at lower analyte concentrations. A confirmatory column (Section 6.9.2.2) is suggested for this purpose. Alternatively, GC/MS may also be used for confirmation if sufficient concentration of analyte is present.

4.5 Special care must be taken in the determination of endrin since it has been reported to breakdown to aldo and keto derivatives upon reaction with active sites in the injection port sleeve[14]. The active sites are usually the result of micro fragments of the injector port septa and high boiling sample residual deposited in the injection port sleeve or on the inner wall at the front of the capillary column. The degradation of endrin is monitored using the Laboratory Performance Check Standard (Section 9.2).

4.6 Interfering and erratic peaks have been observed in method blanks within the retention windows of metribuzin, alachlor, cyanazine and heptachlor. These are believed to be due to phthalate contamination. This contamination can be reduced by paying special attention to reagent preparation (See solvent rinsing the dry buffer and the dechlorination/ preservative salts, Section 7.1.7.5) and elimination of all forms of plastic from the procedure (i.e., HDPE bottles, plastic weighing boats, etc.). After NaCl or Na_2SO_4 is muffled or phosphate buffer and dechlorination/preservative salts are solvent rinsed, they should be stored in sealed glass containers. NaCl, Na_2SO_4, phosphate buffer, and dechlorination/preservative salts should be weighed using glass beakers, never plastic weighing boats.

5.0 SAFETY

5.1 The toxicity and carcinogenicity of chemicals used in this method have not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available[15-17] for the information of the analyst.

5.2 The following have been tentatively classified as known or suspected human or mammalian carcinogens:

Chloroform, 1,2-Dibromo-3-Chloropropane, 1,2-Dibromoethane, Heptachlor, and Hexachlorobenzene.

5.3 The toxicity of the extraction solvent, MTBE, has not been well defined. Susceptible individuals may experience adverse affects upon skin contact or inhalation of vapors. Therefore, protective clothing and gloves should be used and MTBE should be used only in a chemical fume hood or glove box. The same precaution applies to pure standard materials.

6.0 <u>EQUIPMENT AND SUPPLIES</u> (All specifications in Sections 6.0 and 7.0 are suggested. Catalog numbers are included for illustration only.)

6.1 Sample Containers -- 60 mL screw cap glass vials (Kimble #60958A-16, Fisher #03-339-5E or equivalent) each equipped with size 24-400 cap and PTFE-faced septa (Kimble #73802-24400, Fisher #03-340-14A or equivalent). Prior to use or following each use, wash vials and septa with detergent and tap water then rinse thoroughly with distilled water. Allow the vials and septa to dry at room temperature, place only the vials in an oven and heat to 400°C for 30 minutes. After removal from the oven allow the vials to cool in an area known to be free of organics. After rinsing caps with distilled water, rinse in a beaker with HPLC grade or better acetone and place in a drying oven at 80°C for one hour.

6.2 Vials -- Autosampler, 2.0 mL vial with screw or crimp cap and a Teflon-faced septa.

6.3 Micro Syringes -- 10 µL, 25 µL, 50 µL, 100 µL, 250 µL, and 1000 µL.

6.4 Pipettes -- 3.0 mL or 5.0 mL, Type A, TD, glass.

6.5 Volumetric Flask -- 10 mL, 100 mL, 250 mL, and 500 mL glass stoppered.

6.6 Disposable Pasteur Pipets, 9 inch -- Used for extract transfer.

6.7 Standard Solution Storage (SSS) Containers -- 30 mL Boston round, amber glass bottles with TFE-lined caps or equivalent.

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

6.9 Gas Chromatography System

6.9.1 The GC must be capable of temperature programming and should be equipped with a linearized electron capture detector (ECD), fused silica capillary column, and on-column or splitless injector (splitless mode, 30 second delay). If simultaneous confirmation is employed the GC must have a second ECD. An auto-sampler/injector is desirable.

6.9.1.1 Special Precaution: During method development, a problem was encountered with the syringe on the autosampler. The syringe plunger, after repeated sample extract injections, developed resistance when withdrawn or inserted into the

syringe barrel. This resistance was due to salt deposits in the syringe barrel which were left behind following the evaporation of hydrated MTBE. To minimize this problem, a unique syringe wash procedure was employed. After sample injection, the syringe was first rinsed three times with reagent water then three times with MTBE. This effectively removed all the residual salt after each injection from the syringe and surmounted the problem. Some autosampler designs may not encounter this problem but this precaution has been mentioned to alert the analyst. When pentane was used as the extraction solvent, this was not a problem.

6.9.2 Two GC columns are recommended. Column A is recommended as the primary analytical column unless routinely occurring analytes are not adequately resolved. Column B is recommended for use as a confirmatory column when GC/MS confirmation is not sensitive enough or unavailable. Other GC columns or conditions may be employed provided adequate analyte resolution is attained and all the quality assurance criteria established in Section 9.0 are met.

6.9.2.1 Column A - 0.25 mm ID x 30 m fused silica capillary with chemically bonded methyl polysiloxane phase (J&W, DB-1, 1.0 m film thickness or equivalent). As a result of the different boiling points of MTBE (b.p. 55°C) and pentane (b.p. 35°C), two different GC oven temperature programs are specified in Table 1 for MTBE and Table 12 for pentane. Retention times for target analytes were slightly different using the pentane oven temperature program but elution order, analyte resolution, and total analysis time were not effected. Injector temperature: 200°C equipped with 4 mm ID deactivated sleeve with wool plug (Restek #20781 for HP GC's or equivalent). This sleeve design was found to give better analyte response than the standard 2 mm sleeve. Detector temperature: 290°C.

6.9.2.2 Column B - 0.25 mm ID x 30 m with chemically bonded 6% cyanopropylphenyl/94% dimethyl polysiloxane phase (Restek, Rtx-1301, 1.0 µm film thickness or equivalent). The column oven was temperature programmed exactly as indicated for column A (Tables 1 and 12). Injector and detector temperatures at 200°C and 290°C, respectively. The same temperature program was utilized to allow for simultaneous confirmation analysis.

6.9.3 To perform simultaneous confirmation from a single injection onto both the primary and confirmation columns, two injector setups can be employed.

6.9.3.1 Using a two hole graphite ferrule (Restek #20235, or equivalent) both columns can be inserted into one injection port. To ensure the column ends are centered in the injection port sleeve and not angled to the side, an inlet adaptor fitting is installed at the base of the injection port (Restek #20633, or equivalent). Use caution when installing columns in this manner to ensure the column does not break at the base of the injector due to the two columns twisting as the ferrule nut is tightened. To minimize this hazard, the ferrule nut can be reverse twisted four to five times once the ferrule has been seated.

6.9.3.2 An alternate procedure involves installing a 1 mr portion of 0.25 mm deactivated, uncoated fused silica capillary tubing (Restek #10043, or equivalent) into the injector as a normal single column is installed. Then using a Y-press tight union (Restek #20403 or equivalent) join the 1 m uncoated column to the primary and secondary columns. Using this procedure will reduce detection limits when compared to the procedure outline in Section 6.9.3.1 since only one column is positioned in the injection port to receive the injected sample extract.

6.9.4 The analyst is permitted to modify GC columns, GC conditions, internal standard or surrogate compounds. Each time such method modifications are made, the analyst must repeat the procedures in Section 9.4.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 MTBE -- High purity grade. It may be necessary to double distill the solvent if impurities are observed which coelute with some of the more volatile compounds.

7.1.2 Pentane (Optional Extraction Solvent), High Purity Grade -- It may be necessary to double distill the solvent if impurities are observed which coelute with some of the more volatile compounds.

7.1.3 Acetone, High Purity -- Demonstrated to be free of analytes.

7.1.4 Methanol, High Purity -- Demonstrated to be free of analytes.

7.1.5 Sodium Chloride, NaCl, ACS Reagent Grade -- Before using a batch of NaCl, place in muffle furnace, increase temperature to 400°C and hold for 30 minutes. Store in a capped glass bottle, not in a plastic container.

7.1.6 Sodium Sulfate, Na_2SO_4, ACS Reagent Grade -- Before using a batch of Na_2SO_4, place in muffle furnace, increase temperature to 400°C and hold for 30 minutes. Store in a capped glass bottle not in a plastic container.

7.1.7 Sample Preservation Reagents

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

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

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

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

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

Note: If a laboratory is not conducting analyses for the high molecular weight herbicides and pesticides, this cleanup may not be required if no interfering peaks are observed within the retention time window (Section 12.2) for any target analytes in the laboratory reagent blank.

SOLVENT RINSE CLEANUP PROCEDURE

Prepare two separate homogeneous mixtures of the phosphate buffer salts (Section 7.1.7.1) in a 500 mL beaker. To one, add the correct amount of ammonium chloride and to the other add the correct amount of sodium sulfite. Three separate solvents are then used to rinse the mixture. (This solvent rinsing must be performed in a fume hood or glove box.) First, add approx. 100 mL of methanol, or enough to cover the salt to a depth of approx. 1 cm, and using a clean spatula, stir the solvent salt mixture for one minute. Allow the buffer/solvent mixture to settle for one minute and then decant the methanol, being careful not to pour off the rinsed buffer. It may be necessary to perform this procedure up to four times with methanol.

Note: By softly lifting and tapping the base of the beaker against the fume hood counter surface, more of the solvent is brought to the surface of the buffer.

Next, perform the identical procedure up to two times using acetone. Finally, perform two final rinses with the appropriate extracting solvent (MTBE or Pentane). After the final solvent rinse, place the "wet" buffer on a hot plate at approx. 60°C for 30 minutes or until dry. Stir the mixture every five minutes to aid the evaporation of excess solvent. Once dry, place the buffer in a glass bottle with either a ground glass stopper or TFE-faced septum.

7.2 Reagent Water -- Reagent water is defined as purified water which does not contain any measurable quantities of any target analytes or any other interfering species.

7.2.1 A Millipore Super-Q water system or its equivalent may be used to generate deionized reagent water. Distilled water that has been charcoal filtered may also be suitable.

7.2.2 Test reagent water each day it is used by analyzing according to Section 11.0.

7.3 Stock Standard Solutions (SSS) -- These solutions may be obtained as certified solutions or prepared from neat materials using the following procedures:

7.3.1 For analytes which are solids in their pure form, prepare stock standard solutions (1 mg/mL) by accurately weighing approximately 0.01 g of pure material in a 10 mL volumetric flask. Dilute to volume with acetone. Due to the low solubility of simazine, this stock should be prepared at 0.5 mg/mL by weighing 0.005 g diluted to volume with acetone in a 10 mL volumetric flask. Alternatively, simazine stock standard solutions may be prepared in ethyl acetate at approximately 0.01 g/10 mL. Stock standard solutions for analytes which are liquid in their pure form at room temperature can be accurately prepared in the following manner.

7.3.1.1 Place about 9.8 mL of acetone into a 10 mL ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes to allow solvent film to evaporate from the inner walls of the volumetric flask, and weigh to the nearest 0.1 mg.

7.3.1.2 Use a 10 µL syringe and immediately add 10.0 µL of standard material to the flask by keeping the syringe needle just above the surface of the acetone. Caution should be observed to be sure that the standard material falls dropwise directly into the acetone without contacting the inner wall of the volumetric flask.

7.3.1.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in milligrams per milliliter from the net gain in weight. Final concentration should be between 0.800-1.50 mg/mL.

7.3.2 Larger volumes of standard solution may be prepared at the discretion of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard.

7.3.3 Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source. When purchasing commercially prepared stock standards, every effort should be made to avoid solutions prepared in methanol (chloral hydrate is an exception, Section 7.3.3.1). Methanol can cause degradation of most of the haloacetonitriles. In addition, some commercial suppliers have reported instability with solutions of simazine and atrazine prepared in methanol[18]. For these reasons, acetone should be used as the primary solvent for stock standard and primary dilution standard preparation and all sources of methanol introduction into these acetone solutions should be eliminated.

7.3.3.1 It is extremely difficult to acquire chloral hydrate in its pure form since it is classified as a controlled substance. Consequently, if pure chloral hydrate cannot be acquired, a commercially prepared solution of this analyte (most often at 1.0 mg/mL) must be purchased. Most manufactures provide certified chloral hydrate solutions in methanol. Since chloral hydrate is unstable, standards from a separate vendor must be utilized to confirm the accuracy of the primary supplier's solution.

7.3.4 Outside source stock solutions, which are independently prepared or purchased from an outside source different from the source for the original stock standard solutions, must be used as a means of verifying the accuracy of the original stock standard solutions for all analytes. Prepare a dilution of both stocks in acetone and perform a final dilution in MTBE such that each stock dilution is at the same concentration. Analyze as outlined in Section 11.3. The relative percent difference (RPD as defined below) between the analytes' response (area counts) from both solutions should not exceed 25% for any one analyte. The RPD must be less than 20% for 90% or greater of the total number of target analytes analyzed.

$$\text{RPD} = \frac{(\text{DUP 1} - \text{DUP 2})}{1/2(\text{DUP 1} + \text{DUP 2})} \text{ X } 100$$

7.3.4.1 If this criteria cannot be met, a third outside source should be purchased and tested in the same manner. When two sources of stock solutions agree, the accuracy of the stock solutions is confirmed. This should be done prior to preparing the primary dilution standards.

7.3.5 Stock Solution of Surrogate -- Prepare a stock solution of the surrogate standard in acetone by weighing approx. 0.010 g decafluorobiphenyl in a 10 mL volumetric flask. When diluted to volume this yields a concentration of 1.00 mg/mL. Alternate surrogate analytes may be selected provided they are similar in analytical behavior to the compounds of interest, are highly unlikely to be found in any sample, and do not coelute with target analytes.

7.3.6 Stock Solution of Internal Standard (IS) -- Use of an IS is optional when MTBE is the extraction solvent but mandatory if pentane is used. This is due to the high volatility of pentane when compared to MTBE (see boiling points, SectION 6.9.2.1). Prepare an internal standard stock solution of bromofluorobenzene (BFB) in acetone. Since this compound is a liquid at room temperature, the procedure outlined in Sections 7.3.1.1 through 7.3.1.3 should be followed but add approximately 65 µL of neat BFB rather than 10 µL as specified in

Section 7.3.1.2. When diluted to volume this yields a concentration near 10.0 mg/mL. Alternate internal standard analytes may be selected provided they are highly unlikely to be found in any sample and do not coelute with target analytes.

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

7.3.8 When stored in a freezer at <-10°C, the THM stock standards have been shown to be stable for up to six months. The other analyte stock standards, with the exception of chloral hydrate, have been shown to be stable for at least four months when stored in a freezer (<-10°C). Chloral hydrate stock standards, when stored in a freezer (<-10°C), have been shown to be stable for two months, however, since freezers can hold at various temperatures below -10°C, fresh chloral hydrate standards should be initially prepared weekly, until the stability of this analyte is determined for a specific laboratory setting.

7.4 Primary Dilution Standards (PDS) -- Two separate groups of primary dilution standards must be prepared; one set in acetone for all the method analytes except chloral hydrate and the second set in methanol for chloral hydrate. Although preparation of separate chloral hydrate standards may seem laborious, due to the stability problems encountered with this analyte, making fresh chloral hydrate primary dilution standards is more efficient. Prepare primary dilution standards by combining and diluting stock standards in acetone (methanol for chloral hydrate). The primary dilution standards should be prepared such that when 25 µL of this primary dilution standard are added to 50 mL of buffered/dechlorinated reagent water (Section 10.1.2), aqueous concentrations will bracket the working concentration range. Store the primary dilution standard solutions in vials or bottles, with caps using TFE faced liners, in a freezer (<-10°C) with minimal headspace and check frequently for signs of deterioration or evaporation, especially just before preparing calibration standards. The same comments on storage stability in Section 7.3.8 apply to primary dilution standards.

7.4.1 Surrogate Primary Dilution Standard -- Dilute 500 µL of the surrogate stock solution to volume with acetone in a 50 mL volumetric flask. This yields a primary dilution standard at 10.0 µg/mL. Addition of 50 µL of this standard to 50 mL of aqueous sample yields a final concentration in water of 10.0 µg/L. This solution is fortified into the aqueous sample prior to extraction of all calibration standards (Section 10.1.3), quality control samples (Section 9.0), LRBs (Section 9.3.1) and actual field samples (Section 11.1.3) in the extraction set.

7.4.2 Internal Standard (IS) Primary Dilution Standard -- Prepare a IS primary dilution standard at 100 µg/mL by diluting the appropriate amount of internal standard stock solution (500 µL if stock is 10.0 mg/mL) to volume with acetone in a 50 mL volumetric flask. When 10 µL of this solution are added to 1.0 mL of extract, the resultant final concentration is 1.00 µg/mL. The internal standard is used in order to perform an internal standard calibration and is added to an analytically precise volume of the extract following extraction. This solution is added to all extracts.

7.4.3 Reserve approximately a 10 mL aliquot of the same lot of both the acetone and methanol used in the preparation of the primary dilution standards. When validating the accuracy of the calibration standards (Section 7.3.4), fortify a laboratory reagent blank with 25 µL of both the acetone and the methanol which was used to prepare the primary dilution standards. Analysis of this laboratory reagent blank will confirm no target analyte contamination in the solvents used to prepare the primary dilution standards.

7.5 Laboratory Performance Check Solution (LPC) -- To insure proper instrument performance, a Laboratory Performance Check Solution is prepared. This solution is prepared in MTBE for direct injection on the GC and is used to evaluate the parameters of instrument sensitivity, chromatographic performance, column performance and analyte breakdown. These parameters are listed in Table 7 along with the method analytes utilized to perform this evaluation, their concentration in MTBE and the acceptance criteria. To prepare this solution at the concentrations listed in Table 7, a double dilution of the analyte stock solutions must be made. First prepare a primary stock dilution mix at 1000 times the concentrations listed in Table 7, by adding the appropriate volume of each stock solution to a single 50 mL volumetric flask containing approximately 25 mL of MTBE. Dilute to volume with MTBE. Then the LPC working solution is prepared in MTBE by diluting 50 µL of the primary stock dilution mix in MTBE to 50 mL in a volumetric flask. The best way to accomplish this is to add approximately 48 mL MTBE to the 50 mL volumetric flask and add 50 µL of the primary stock dilution mix, then dilute to volume with MTBE. Store this solution in a vial or bottle, with TFE faced cap, in a freezer (<-10°C) with minimal headspace and check frequently for signs of deterioration or evaporation.

7.5.1 If a laboratory is not conducting analyses for the high molecular weight pesticides and herbicides, a modified LPC may be prepared. This modified LPC can omit the endrin analyte breakdown component as well as the resolution requirement for bromacil and alachlor under column performance. In addition, substitute analytes in place of lindane for the sensitivity check and hexachlorocyclopentadiene for chromatographic performance can be selected. These substitute compounds must meet the same criteria as listed in Table 7 with the concentration for sensitivity check near the substitute analyte's EDL and the concentration for chromatographic performance near 50 times the

substitute analyte's EDL. The column performance criteria for resolution between bromodichloromethane and trichloroethylene cannot be modified.

7.5.2 If pentane is selected as an alternate extraction solvent the LPC must also be prepared in pentane.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Vial Preparation

8.1.1 To conduct analyses for the total analyte list, two sets of 60 mL vials must be prepared for sampling. One set of vials, prepared for the analysis of all target analytes except chloral hydrate, contains ammonium chloride as a dechlorinating agent. Due to concerns over low recoveries for chloral hydrate in matrices preserved with ammonium chloride (Section 8.1.2), a separate sample set must be collected and preserved with sodium sulfite. Both sets of vials are prepared as follows.

8.1.1.1 Using the homogeneous phosphate buffer/dechlorinating agent mixtures prepared in Section 7.1.7.4, 1 g of the appropriate mixture are added to the corresponding vials.

8.1.2 If the sample assay is for only the THMs and/or solvents, either dechlorinating agent can be added. However, sodium sulfite promotes the decomposition of the haloacetonitriles, 1,1-dichloro-2-propanone, 1,1,1-trichloro-2-propanone and chloropicrin and therefore ammonium chloride must be used as the dechlorination reagent in their analysis. In addition, some fortified matrices, dechlorinated with ammonium chloride, have displayed recoveries of chloral hydrate which have been up to 50% lower than expected, when compared to the same sample matrix dechlorinated with sodium sulfite. In other matrices, recoveries have been consistent regardless of dechlorinating agent. The reason for these differences has not been determined. Due to this uncertainty, a separate sample, dechlorinated with 100 mg/L sodium sulfite must be collected for the analysis of chloral hydrate.

8.1.3 The dechlorinating agents, if not added within the homogeneous mixture of the buffer, must be added to the sampling vials as a dry salt. Solutions of the dechlorinating agents should not be used due to concerns over the stability of these salts dissolved in solution and the potential chemical interactions of aqueous solutions of these salts with the dry phosphate buffer.

8.1.4 Samples must contain either 100 mg/L ammonium chloride or sodium sulfite, as appropriate for the analysis being performed. This amount will eliminate free chlorine residual in typical chlorinated drinking

water samples. If high chlorine doses are used, such as in a maximum formation potential test, additional dechlorinating reagent may be required.

8.2 Sample Collection

8.2.1 Collect all samples in duplicate. Fill sample bottles to just overflowing but take care not to flush out the buffer/dechlorination reagents. No air bubbles should pass through the sample as the bottle is filled, or be trapped in the sample when the bottle is sealed.

8.2.2 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about three to five minutes). Remove the aerator and adjust the flow so that no air bubbles are visually detected in the flowing stream.

8.2.3 When sampling from an open body of water, fill a 1 q wide-mouth glass bottle or 1 L beaker with sample from a representative area, and carefully fill duplicate 60 mL sample vials from the container.

8.2.4 The samples must be chilled to 4°C on the day of collection and maintained at that temperature until analysis. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to ensure they will be at 4°C on arrival at the laboratory. Synthetic ice (i.e., Blue ice) is not recommended.

8.3 Sample Storage/Holding Times

8.3.1 Store samples at 4°C and extracts in a freezer (<-10°C) until analysis. The sample storage area must be free of organic solvent vapors.

8.3.2 Extract all samples within 14 days of collection and analyze within 14 days following extraction. This applies to either MTBE or pentane extracts). Samples not analyzed within these time periods must be discarded and replaced.

9.0 QUALITY CONTROL

9.1 Each laboratory that uses this method is required to operate a formal quality control (QC) program. Minimum QC requirements include the laboratory performance check standard, initial demonstration of laboratory capability, method detection limit determination, analysis of laboratory reagent blanks, continuing calibration check standard, laboratory fortified sample matrices, field duplicates and monitoring surrogate and/or internal standard peak response in each sample and blank. Additional quality control practices may be added.

9.2 Assessing Instrument System -- Laboratory Performance Check Standard (LPC) -- Prior to any sample analyses, a laboratory performance check standard must be analyzed. The LPC sample contains compounds designed to indicate appropriate instrument sensitivity, endrin breakdown, column performance (primary column), and chromatographic performance. LPC sample components and performance criteria are listed in Table 7. Inability to demonstrate acceptable instrument performance indicates the need for reevaluation of the instrument system. The sensitivity requirement is based on the Estimated Detection Limits (EDLs) published in this method. If laboratory EDLs differ from those listed in this method, concentrations of the LPC standard must be adjusted to be compatible with the laboratory EDLs. If endrin breakdown exceeds 20%, the problem can most likely be solved by performing routine maintenance on the injection port including replacing the injection port sleeve, and all associated seals and septa. If column or chromatographic performance criteria cannot be met, new columns may need to be installed, column flows corrected, or modifications adapted to the oven temperature program. During early method development work, significant chromatographic and column performance problems were observed while using a DB-1 column which had been used for several years for drinking water extract analysis. By installing a new DB-1 column, these performance problems were overcome. If the columns to be used for this method have been used for several years or have had extended use with extracts from harsh sample matrices (i.e., wastewater, acidified sample extracts, hazardous waste samples) it may be difficult to meet the criteria established for this LPC standard and column replacement may be the best alternative.

9.3 Laboratory Reagent Blanks (LRB) -- Before processing any samples, the analyst must analyze an LRB to demonstrate that all glassware and reagent interferences are under control. In addition, each time a set of samples is extracted or reagents are changed, a LRB must be analyzed. If the LRB produces a peak within the retention time window of any analyte (Section 12.2) preventing the quantitation of that analyte, determine the source of the contamination and eliminate the interference before processing samples. LRB samples must contain the appropriate buffer for the target analytes (buffered/NH_4Cl dechlorinated and/or buffered/Na_2SO_3 dechlorinated reagent water).

9.3.1 Prepare the two LRBs in the appropriate buffered/dechlorinated reagent water. Add 50 µL of surrogate primary dilution standard (Section 7.4.1) to each blank and follow the procedure outlined in Section 11.2.

9.4 Initial Demonstration of Capability (IDC)

9.4.1 Preparation of the IDC Laboratory Fortified Blank (LFB) -- Select a concentration for each of the target analyte which is approximately 50 times the EDL or close to the expected levels observed in field samples. Concentrations near analyte levels in Table 3.A are

recommended. Prepare a LFB by adding the appropriate concentration of the primary dilution standard (Section 7.4) to each of four to seven 50 mL aliquots of buffered/NH_4Cl dechlorinated reagent water. Separate Na_2SO_3 preserved matrices need not be analyzed (Section 9.4.1.1). Analyze the aliquots according to the method beginning in Section 11.0.

9.4.1.1 Chloral hydrate is included in the buffered/NH_4Cl dechlorinated reagent water, containing all the other target analytes since no matrix induced recovery problems have been found from reagent water preserved with NH_4Cl.

9.4.2 Following procedural calibration standard analysis and subsequent instrument calibration, analyze a set of at least seven IDC samples and calculate the mean percent recovery (R) and the relative standard deviation of this recovery (RSD). The percent recovery is determined as the ratio of the measured concentration to the actual fortified concentration. For each analyte, the mean recovery value must fall within the range of 80-120% and the RSD must not exceed 15%. For those compounds that meet these criteria, performance is considered acceptable, and sample analysis may begin. For those compounds that fail these criteria, this procedure must be repeated using eight fresh samples until satisfactory performance has been demonstrated.

9.4.3 The initial demonstration of capability is used primarily to preclude a laboratory from analyzing and reporting unknown samples without obtaining some experience with an unfamiliar method. It is expected that as laboratory personnel gain experience with this method, the quality of data will improve beyond those specified in Section 9.4.2.

9.4.4 Method Detection Limits (MDL) -- Prior to the analysis of any field samples the method detection limits must be determined. Initially, estimate the concentration of an analyte which would yield a peak equal to five times the baseline noise and drift. Prepare a primary dilution standard with analyte concentrations at 1000 times this level in acetone (or methanol for chloral hydrate).

9.4.4.1 Prepare a 500 mL aliquot of buffered/ammonium chloride dechlorinated reagent water. Fill a minimum of seven replicate, 60 mL vials with 50 mL of the buffered/dechlorinated (NH_4Cl) reagent water.

9.4.4.2 Fortify the 50 mL buffered/dechlorinated (NH_4Cl) reagent water with 50 µL of both the MDL concentrate prepared in acetone and the chloral hydrate MDL concentrate in methanol. Separate preparation of a reagent water containing Na_2SO_3 as the dechlorinating agent for chloral hydrate MDL determination is not necessary. (See Section 9.4.1.1)

9.4.4.3 Extract and analyze these samples as outlined in Section 11.0. MDL determination can then be performed as discussed in Section 13.1.

9.5 Laboratory Fortified Blank (LFB) -- Since this method utilizes procedural calibration standards, which are fortified reagent water, there is no difference between the LFB and the continuing calibration check standard. Consequently, there is not a requirement for the analysis of an LFB. However, the criteria established for the continuing calibration check standard (Section 10.4) should be evaluated as the LFB.

9.6 Laboratory Fortified Sample Matrix (LFM) -- The laboratory must add known concentrations of analytes to a minimum of 10% of the routine samples or one fortified sample per sample set, whichever is greater, for both NH_4Cl and Na_2SO_3 dechlorinated sample matrices. The concentrations should be equal to or greater than the background concentrations in the sample selected for fortification. Over time, samples from all routine sample sources should be fortified. By fortifying sample matrices and calculating analyte recoveries, any matrix induced analyte bias is evaluated. When an analyte recovery falls outside the acceptance criteria outlined below, a bias is concluded and that analyte for that matrix is reported to the data user as suspect.

9.6.1 First, follow the procedure outlined in Section 11.1.

9.6.2 Next, prepare the LFM by adding 50 µL of an acetone based standard solution into the remaining 50 mL of the buffered / NH_4Cl dechlorinated sample matrix in the vial in which it was sampled. This sample vial will have had the required amount of aqueous sample removed as specified in Section 11.1.2. Add 50 µL of surrogate primary dilution standard (Section 7.4.1) and follow procedure outlined in Sections 11.0 and 12.0.

9.6.3 When chloral hydrate is being determined, prepare the LFM by adding 50 µL of a methanol based chloral hydrate standard solution into 50 mL of the buffered / Na_2SO_3 dechlorinated sample matrix in the vial in which it was sampled. Add 50 µL of surrogate primary dilution standard (Section 7.4.1) and follow procedure outlined in Sections 11.0 and 12.0.

9.6.4 Calculate the percent recovery, R, of the concentration for each analyte, after correcting the total measured concentration, A, from the fortified sample for the background concentration, B, measured in the unfortified sample, i.e.:

$$R = 100\ (A - B) / C$$

where: C = the fortifying concentration.

The recoveries of all analytes being determined must fall between 75% and 125% and the recoveries of at least 90% of these analytes must fall between 80% and 120%. This criteria is applicable to both external and internal standard calibrated quantitation.

9.6.5 If a recovery falls outside of this acceptable range, a matrix induced bias can be assumed for the respective analyte and the data for that analyte in that sample matrix must be reported to the data user as suspect.

9.6.6 If the unfortified matrix has analyte concentrations equal to or greater than the concentration fortified, a duplicate sample vial needs to be fortified at a higher concentration. If no such sample is available the recovery data for the LFM sample should not be reported for this analyte to the data user.

9.7 Field Duplicates (FD1 and FD2) -- The laboratory must analyze a field sample duplicate for a minimum of 10% of the total number of field samples or at least one field sample duplicate per sample set, whichever is greater. Duplicate results must not reflect a relative percent difference (RPD as defined below) greater than 25% for any one analyte and the RPD for 90% of the analytes being determined must be less than 20%.

$$RPD = \frac{(FD1 - FD2)}{1/2(FD1 + FD2)} \times 100$$

where: FD1 and FD2 = the quantified concentration on an individual analyte for the initial and duplicate field sample analysis, respectively

If this criteria is not met the analysis must be repeated. Upon repeated failure, the sampling must be repeated or the analyte out of control must be reported as suspect to the data user.

9.8 Assessing Surrogate Recovery

9.8.1 The surrogate analyte is fortified into the aqueous portion of all calibration standards, quality control samples and field samples. By monitoring the surrogate response, the analyst generates useful quality control information from extraction precision through quantitative analysis. Deviations in surrogate recovery may indicate an extraction problem. If using external standard calibration the surrogate retention time functions as a reference for identification of target analytes.

9.8.2 Using the mean surrogate response from the calibration standard analyses (Cal_{SR}), determine the surrogate percent recovery ($\%REC_S$) in all calibration standards, LFBs, and LFMs, and field samples. This

recovery is calculated by dividing the surrogate response from the sample (Sam_{SR}) by the mean response from the initial calibration standards (Section 10.2 or Section 10.3) and multiplying by 100, as shown below.

$$\% \ REC_s = \frac{Sam_{SR}}{Cal_{SR}} \ x \ 100$$

Recoveries must fall within the range of 80-120%. If a sample provides a recovery outside of this range, the extract must be reanalyzed. If upon reanalysis, the recovery continues to fall outside the acceptable range a fresh sample should be extracted and analyzed. If this is not possible the data for all the analytes from this sample should be reported to the data user as suspect due to surrogate recovery outside acceptable limits.

9.8.3 If consecutive samples fail the surrogate response acceptance criterion, immediately analyze a continuing calibration standard.

9.8.3.1 If the continuing calibration standard provides a recovery within the acceptable range of 80-120%, then follow procedures itemized in Section 9.8.2 for each sample failing the surrogate response criterion.

9.8.3.2 If the check standard provides a surrogate recovery which falls outside the acceptable range or fails the acceptance criteria specified in Section 10.4 for the target analytes, then the analyst must recalibrate, as specified in Section 10.0.

9.9 Assessing the Internal Standard (IS)

9.9.1 When using the internal standard calibration procedure, the analyst must monitor the internal standard response (peak area or peak height) of all samples during each analysis day. The internal standard response should not deviate from mean internal standard response of the past five continuing calibration standards by >20%.

9.9.2 If >20% deviation occurs with an individual extract, optimize instrument performance and inject a second aliquot of that extract.

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

9.9.2.2 If a deviation of >20% is obtained for the reinjected extract, analysis of a calibration check standard must be performed (Section 10.4).

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

9.9.3.1 If the check standard provides a response factor (RF) within 20% of the predicted value for the internal standard and the criteria for all the target analytes as specified in Section 10.4 is met, the previous sample(s) failing the IS response criteria need to be reextracted provided the sample is still available. In the event that reextraction is not possible, report results obtained from the reinjected extract (Section 9.9.2) but annotate as suspect due to internal standard recovery being outside acceptable limits.

9.9.3.2 If the check standard provides a response factor which deviates more than 20% of the predicted value for the internal standard or the criteria for the target analytes, as specified in Section 10.4 are not met, then the analyst must recalibrate, as specified in Section 10.3 and all samples analyzed since the previous calibration check standard need to be reanalyzed.

9.10 Confirmation Column Analysis -- If a positive result is observed on the primary column, a confirmation analysis should be performed using either the confirmation column or by GC/MS.

9.11 The laboratory may adapt additional quality control practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. For example, field reagent blanks may be used to assess contamination of samples under site conditions, transportation and storage.

9.12 Quality control samples (QCS) from an outside source, as defined in Section 3.12, should be analyzed at least quarterly.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Preparation of Calibration Standards

10.1.1 Five calibration standards are required. One should contain the analytes at a concentration near to but greater than the method detection limit (Table 2) for each compound; the others should be evenly distributed throughout the concentration range expected in samples or define the working range of the detector. Guidance on the number of standards is as follows: A minimum of three calibration standards are required to calibrate a range of a factor of 20 in concentration. For a factor of 50 use at least four standards, and for a factor of 100 at least five standards. For example, if the MDL is 0.1 µg/L, and a sample concentrations are expected to range from

1.0-10.0 µg/L, aqueous standards should be prepared at 0.20 µg/L, 0.80 µg/L, 2.0 µg/L, 5.0 µg/L, and 15.0 µg/L.

10.1.2 As a means of eliminating any matrix effects due to the use of the phosphate buffer and dechlorinating agents, the procedural calibration standards are prepared in reagent water which has been buffered to pH 4.8-5.5 and dechlorinated with ammonium chloride. To prepare this buffered/dechlorinated reagent water, add 8.3 g of phosphate buffer/dechlorinating agent (Section 7.1.7.4, ammonium chloride type) to 500 mL of reagent water (Section 7.2).

10.1.3 Next, add 25 µL of the desired concentration primary dilution standards (acetone and methanol based, Section 7.4) to a 50 mL aliquot of the buffered/dechlorinated reagent water in a 60 mL vial. Use a 50 µL micro syringe and rapidly inject 25 µL of the standard into the middle point of the water volume. Remove the needle as quickly as possible after injection. Next, add 50 µL of the surrogate standard solution (Section 7.4.1) in the same manner. Mix by slowly and carefully inverting the sample vial two times with minimal sample agitation. Aqueous standards must be prepared fresh daily and extracted immediately after preparation (Section 11.2).

10.1.3.1 By including chloral hydrate into the total NH_4Cl analyte matrix, a separate calibration standard analysis for Na_2SO_3 preserved reagent water fortified with chloral hydrate is avoided. Chloral hydrate is included in the buffered/NH_4Cl dechlorinated reagent water, containing all the other target analytes since no matrix induced recovery problems have been found from reagent water preserved with NH_4Cl.

Warning: Do not attempt to analyze chloral hydrate in field samples preserved with NH_4Cl, low recoveries may result due to matrix effects.

Caution: DO NOT prepare procedural calibration standards in a volumetric flask and transfer the sample to an extraction vial either directly for weight determination of volume or into a graduated cylinder with a subsequent additional transfer into the extraction vial. Volatility experiments reflected as much as a 30% loss in volatile low molecular weight analytes following such transfers. All fortified samples and field samples must be extracted in the vial or bottle in which they were fortified and collected.

10.2 External Standard Calibration Procedure

10.2.1 Extract and analyze each calibration standard according to Section 11.0 and tabulate peak height or area response versus the concentration of the standard. The results are used to prepare a calibration curve for each compound by plotting the peak height or area response versus the concentration. This curve can be defined as either first or second order. Alternatively, if the ratio of response to concentration (response factor) is constant over the working range (≤10% relative standard deviation,[RSD]), linearity through the origin can be assumed, and the average ratio or calibration factor can be used in place of a calibration curve.

10.2.2 Surrogate analyte recoveries must be verified as detailed in Section 9.8.

10.3 Internal Standard (IS) Calibration Procedure

10.3.1 Extract each calibration standard according to Section 11.0. Remove a 1.00 mL portion of the MTBE or pentane extract from the sample extraction vial and place this into a 2.0 mL autosampler vial. To this extract, add the 10 µL of the internal standard primary dilution standard, cap the vial and analyze. Following analysis, tabulate peak height or area responses against concentration for each compound and the internal standard. Calculate relative response factor (RRF) for each compound using the following equation.

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

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

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

10.4 Continuing Calibration Check Standard

10.4.1 Preceding each analysis set, after every 10th sample analysis and after the final sample analysis, a calibration standard should be analyzed as a continuing calibration check. These check standards should be at two different concentration levels to verify the calibration curve. This criteria is applicable to both external and internal standard calibrated

quantitation. Surrogate and internal standard recoveries must be verified as detailed in Sections 9.8 and 9.9, respectively.

10.4.2 In order for the calibration to be considered valid, analyte recoveries for the continuing calibration check standard must fall between 75% and 125% for all the target analytes. The recoveries of at least 90% of the analytes determined must fall between 80% and 120%.

10.4.3 If this criteria cannot be met, the continuing calibration check standard is reanalyzed in order to determine if the response deviations observed from the initial analysis are repeated. If this criteria still cannot be met then the instrument is considered out of calibration for those specific analytes beyond the acceptance range. The instrument needs to be recalibrated and the previous samples reanalyzed or those analytes out of acceptable range should be reported as suspect to the data user for all the previously analyzed samples.

11.0 PROCEDURE

11.1 Sample Preparation

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

11.1.2 Remove the vial caps. Remove a 10 mL volume of the sample. Check the pH of this 10 mL aliquot to verify that it is within a pH range of 4.5 and 5.5. If the pH is out of this range a new sample must be collected. Replace the vial caps and weigh the containers with contents to the nearest 0.1 g and record these weights for subsequent sample volume determination. (See Section 11.2.4 for continuation of weighing and calculation of true volume). Alternatively, the sample vials may be precalibrated by weighing in 50 mL of water and scoring the meniscus on the bottle. This will eliminate the gravimetric step above and in Section 11.2.4.

11.1.3 Inject 50 µL of the surrogate analyte fortification solution (Section 7.4.1) into the sample. The aqueous concentration of surrogate analyte must be the same as that used in preparing calibration standards (Section 9.1.3). Mix by slowly and carefully inverting the sample vial two times with minimal sample agitation.

11.2 Sample Extraction

11.2.1 With MTBE as Extraction Solvent

11.2.1.1 After addition of the surrogate (Section 11.1.3) add exactly 3.0 mL of MTBE with a Type A, TD, transfer or automatic dispensing pipet.

11.2.1.2 Add 10 g NaCl or 20 g Na_2SO_4 to the sample vial. (See Section 13.7 for an important notice concerning the use of NaCl when analyzing for DBPs.) Recap and extract the NaCl or Na_2SO_4/MTBE/sample mixture by vigorously and consistently shaking the vial by hand for four minutes. Invert the vial and allow the water and MTBE phases to separate (approx. two minutes).

If a series of samples are being prepared for extraction using Na_2SO_4, immediately after the addition of the Na_2SO_4, the sample should be recapped, agitated and placed in a secure horizontal position with the undissolved Na_2SO_4 distributed along the length of the vial. If the vial is left in a vertical position, while additional samples have solvent and salt added, the Na_2SO_4 will solidify in the bottom of the vial and it will not dissolve during sample extraction.

Note: Previous versions of this method call for the addition of the salt by "shaking the vial vigorously" before the MTBE has been added. Please make a note that this procedural order has been changed in an effort to minimize volatile analyte losses.

11.2.1.3 By using a disposable Pasteur pipet (Section 6.2), transfer a portion of the solvent phase from the 60 mL vial to an autosampler vial (Section 6.2). Be certain no water has carried over onto the bottom of the autosampler vial. If a dual phase appears in the autosampler vial, the bottom layer can be easily removed and discarded by using a Pasteur pipet. The remaining MTBE phase may be transferred to a second autosampler vial as a backup extract or for separate confirmation analysis. Approximately 2.5 mL of the solvent phase can be conveniently transferred from the original 3 mL volume.

11.2.1.3.1 If using an internal standard quantitation, the extract transfer into the autosampler vial must be performed in a quantitative manner. This may be done using a 1.00 mL syringe or a 2.00 mL graduated disposable pipet to accurately transfer 1.00 mL of sample extract to the autosampler vial where 10 µL of internal standard primary dilution standard (Section 7.4.2) solution can be added.

11.2.2 With Pentane as Extraction Solvent

11.2.2.1 After addition of the surrogate (Section 11.1.3) add exactly 5.0 mL of pentane with a Type A, TD, transfer or automatic dispensing pipet.

11.2.2.2 Add 20 g Na_2SO_4 to the sample vial. Recap and extract the Na_2SO_4/pentane/sample mixture by vigorously and consistently shaking the vial by hand for four minutes. Invert the vial and allow the water and pentane phases to separate (approx. two minutes).

Note: Previous versions of this method call for the addition of NaCl by "shaking the vial vigorously" before the pentane has been added. Please make a note that this procedural order has been changed in an effort to minimize volatile analyte losses.

If a series of samples are being prepared for extraction, immediately after the addition of the Na_2SO_4, the sample should be recapped, agitated and placed in a secure horizontal position with the undissolved Na_2SO_4 distributed along the length of the vial. If the vial is left in a vertical position, while additional samples have solvent and salt added, the Na_2SO_4 will solidify in the bottom of the vial and it will not dissolve during sample extraction.

11.2.2.3 Using a disposable Pasteur pipet, transfer a portion of the solvent phase from the 60 mL vial to an autosampler vial. Be certain no water has carried over onto the bottom of the autosampler vial. If a dual phase appears in the autosampler vial, the bottom layer can be easily removed and discarded using a Pasteur pipet. The remaining pentane phase may be transferred to a second autosampler vial as a backup extract or for separate confirmation analysis.

11.2.2.3.1 The extract transfer into the autosampler vial must be performed in a quantitative manner. This may be done using a 1.00 mL syringe or a 2.00 mL graduated disposable pipet to accurately transfer 1.00 mL of sample extract to the autosampler vial where 10 µL of internal standard primary dilution standard (Section 7.4.2) solution can be added.

11.2.3 Discard the remaining contents of the sample vial. Shake off the last few drops with short, brisk wrist movements.

11.2.4 Reweigh the empty vial with the original cap and calculate the net weight of sample by difference to the nearest 0.1 g (Section 11.1.2 minus Section 11.2.4). This net weight (in grams) is equivalent to the volume of water (in mL) extracted, V_s.

11.2.5 The sample extract may be stored in a freezer (<-10°C) for a maximum of fourteen days before chromatographic analysis but no more than 24 hours at room temperature (i.e., on an autosampler rack). Due to the volatility of the extraction solvent, if the septum on a vial has been pierced, the crimp top or screw cap septum needs to be replaced immediately or the extract cannot be reanalyzed at a later time.

11.3 Sample Analysis

11.3.1 The recommended GC operating conditions are described in Sections 6.9.2.1 and 6.9.2.2 along with recommended primary and confirmation columns. Retention data for the primary and confirmation columns are given in Table 1.

11.3.2 Inject 2 µL of the sample extract and record the resulting peak response. For optimum performance and precision, an autosampler for sample injection and a data system for signal processing are strongly recommended.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Identify sample components by comparison of retention times to retention data from the calibration standard analysis. If the retention time of an unknown compound corresponds, within limits (Section 12.2), to the retention time of a standard compound, then identification is considered positive.

12.2 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms. Use the initial demonstration of capability retention time data as an initial means of determining acceptable retention time windows. Throughout the development of this method a retention time window of 1.0% of the total analyte retention time was used.

12.3 Identification requires expert judgment when sample components are not resolved chromatographically, that is, when GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima). Whenever doubt exists over the

identification of a peak in a chromatogram, confirmation is suggested by the use of a dissimilar column or by GC-MS when sufficient concentrations of analytes are present.

12.4 If the peak response exceeds the linear range of the calibration curve, the final extract should be diluted with the appropriate extraction solvent and reanalyzed. The analyst is not permitted to extrapolate beyond the concentration range of the calibration curve.

12.5 Calculate the uncorrected concentrations (C_i) of each analyte in the sample from the response factors or calibration curves generated in Section 10.2.1 or Section 10.3.1. Do not use the daily calibration check standard to calculate amounts of method analytes in samples.

12.6 Calculate the corrected sample concentration as:

$$\text{Concentration } \mu g/L = C_i \times \frac{50}{V_s}$$

where: V_s = equivalent to the net sample weight in grams determined in Section 11.1.2 and Section 11.2.4

13.0 METHOD PERFORMANCE

13.1 In a single laboratory, analyte recoveries from reagent water with MTBE as the extracting solvent, were determined at three concentration levels, Tables 2A through 4B. Results from the lowest fortified level were used to determine the analyte MDLs[11] listed in Table 2. These MDLs along with the estimated detection limit (EDL) were determined in the following manner. EDLs are provided for informational purposes.

13.1.1 For each analyte, calculate the mean concentration and the standard deviation of this mean between the seven replicates. Multiply the student's t-value at 99% confidence and n-1 degrees of freedom (3.143 for seven replicates) by this standard deviation to yield a statistical estimate of the detection limit. This estimate is the MDL.

13.1.2 Since the statistical estimate is based on the precision of the analysis, an additional estimate of detection can be determined based upon the noise and drift of the baseline as well as precision. This estimate, known as the "EDL" is defined as either the MDL or a level of compound in a sample yielding a peak in the final extract with a signal to noise (S/N) ratio of approximately five, whichever is greater.

13.1.3 These MDL determinations were conducted on both the primary (DB-1) and the confirmation (Rtx-1301) columns and are presented in Tables 2A through 2D.

13.2 Analyte recoveries were also determined for reagent water with pentane as the extracting solvent. Two concentration levels were studied and the results are presented in Tables 8 and 9. Results from the lowest fortified level were used to determine the analyte MDLs[11] listed in Table 8. These MDLs along with the estimated detection limit (EDL) were determined in a manner analogous to that described in Section 13.1.1 through 13.1.2.

13.3 In a single laboratory, method precision and accuracy were evaluated using analyte recoveries from replicate buffered / dechlorinated (both NH_4Cl and Na_2SO_3) matrices with MTBE as the extracting solvent. The matrices studied included; fulvic acid fortified reagent water and ground water displaying a high $CaCO_3$ content. The results for these are presented in Tables 3A through 6B. These matrices were fortified using outside source analyte solutions (except for the pesticides and herbicides) to assess accuracy and eight replicate analyses were conducted to assess precision.

13.4 Holding time studies were conducted for buffered / dechlorinated reagent water and tap water. Holding studies were also conducted on MTBE sample extracts from these two matrices. Results indicated that analytes were stable in these water matrices stored at 4°C.

13.5 MTBE and pentane extracts holding studies indicated the analytes were stable for 14 days when stored in a freezer at <-10°C.

13.6 Chromatograms of a fortified, buffered / NH_4Cl dechlorinated reagent water extract are presented as Figures 1 through 3. In the chromatograms of Figures 1 and 2, the elution of the method analytes from a MTBE extract can be seen on the primary DB-1 column and the confirmation Rtx-1301 column, respectively. Figure 3 shows the elution of the method analytes from a pentane extract, using a modified temperature program, on the primary DB-1 column. Analyte numerical peak identification, retention time and fortified concentrations are presented for information purposes only in Tables 10, 11, and 12 for Figures 1, 2, and 3, respectively.

Important Notice: All demonstration data presented in Section 17 using MTBE as the extracting solvent, was obtained using NaCl as the salt. A recent report[19] indicated elevated recoveries (via synthesis) of some brominated DBPs when NaCl was used in the extraction process, due to the inevitable presence of bromide impurities in the NaCl. This phenomenon has been confirmed by the authors of this method in samples from chlorinated water systems that were not extracted immediately after the NaCl was added. Significant effects can be seen if extraction is delayed for as little as 15 minutes after the addition of the NaCl. For this reason, the use of Na_2SO_4 is strongly recommended over NaCl for MTBE extraction of DBPs. Although less method validation data

have been obtained for the Na_2SO_4 option, sufficient data have been collected to indicate that it is equivalent or superior to NaCl in salting out the method analytes, and has no observed negative effect on precision or accuracy.

14.0 POLLUTION PREVENTION

14.1 This method is a micro-extraction procedure which uses a minimal amount of extraction solvent per sample. This microextraction procedure reduces the hazards involved with handling large volumes of potentially harmful organic solvents needed for conventional liquid-liquid extractions.

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

15.0 WASTE MANAGEMENT

15.1 Due to the nature of this method, there is little need for waste management. No large volumes of solvents or hazardous chemicals are used. The matrices of concern are finished drinking water or source water. However, the Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations, and that laboratories protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel", also available from the American Chemical Society at the address in Section 14.2.

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TABLE 1. RETENTION TIME DATA USING MTBE

Analyte	Column A[a] Retention Time minutes	Column B[b] Retention Time minutes
Chloroform	7.04	7.73
1,1,1-Trichloroethane	8.64	7.99
Carbon Tetrachloride	9.94	8.36
Trichloroacetonitrile	10.39	10.35
Dichloroacetonitrile	12.01	25.21
Bromodichloromethane	12.42	15.28
Trichloroethylene	12.61	11.96
Chloral Hydrate	13.41	NR[c]
1,1-Dichloro-2-Propanone	14.96	20.50
1,1,2-Trichloroethane	19.91	25.01
Chloropicrin	23.10	23.69
Dibromochloromethane	23.69	26.32
Bromochloroacetonitrile	24.03	29.86
1,2-Dibromoethane (EDB)	24.56	26.46
Tetrachloroethylene	26.24	24.77
1,1,1-Trichloropropanone	27.55	28.47
Bromoform	29.17	30.36
Dibromoacetonitrile	29.42	32.77
1,2,3-Trichloropropane	30.40	31.73
1,2-Dibromo-3-chloropropane (DBCP)	35.28	36.11
Hexachlorocyclopentadiene	40.33	39.53
Trifluralin	45.17	45.43
Simazine	46.27	48.56[d]
Atrazine	46.55	48.56[d]
Hexachlorobenzene	47.39	46.47
Lindane (gamma-BHC)	47.95	49.68
Metribuzin	50.25	53.92
Bromacil	52.09	59.60
Alachlor	52.25	54.38
Cyanazine	53.43	59.89
Heptachlor	53.72	53.15
Metolachlor	55.44	57.07
Heptachlor Epoxide	58.42	59.05
Endrin	64.15	65.24
Endrin Aldehyde	65.46	71.56
Endrin Ketone	72.33	81.28
Methoxychlor	73.53	76.73
Surrogate: Decafluorobiphenyl	36.35	36.28
Internal Standard: Bromofluorobenzene	31.00	31.30

TABLE 1. RETENTION TIME DATA USING MTBE

Analyte	Column A[a] Retention Time minutes	Column B[b] Retention Time minutes

[a]Column A - 0.25 mm ID x 30 m fused silica capillary with chemically bonded methyl polysiloxane phase (J&W, DB-1, 1.0 µm film thickness or equivalent). The linear velocity of the helium carrier is established at 25 cm/sec.at 35°C.

The column oven is temperature programmed as follows:

[1] HOLD at 35°C for 22 minutes
[2] INCREASE to 145°C at 10°C/min and hold at 145°C for two minutes
[3] INCREASE to 225°C at 20°C/min and hold at 225°C for 15 minutes
[4] INCREASE to 260°C at 10°C/min and hold at 260°C for 30 minutes or until all expected compounds have eluted.

Injector temperature: 200°C
Detector temperature: 290°C

[b]Column B - 0.25 mm ID x 30 m with chemically bonded 6% cyanopropylphenyl/94% dimethyl polysiloxane phase (Restek, Rtx-1301, 1.0 µm film thickness or equivalent). The linear velocity of the helium carrier gas is established at 25 cm/sec. at 35°C.

The column oven is temperature programmed exactly as indicated for Column A, above. The same temperature program is utilized to allow for simultaneous confirmation analysis.

[c]There is no retention time for this analyte since it does not separate into a discreet peak on the Rtx-1301.
[d]Atrazine and simazine coelute on the confirmation column.

TABLE 2A. METHOD DETECTION LIMIT USING MTBE NH_4Cl PRESERVED REAGENT WATER ON PRIMARY DB-1 COLUMN

Analyte	Fort. Conc. µg/L	Obser.[a] Conc. µg/L	Avg. % Rec.	% RSD	MDL[b] µg/L	EDL[c] µg/L
Alachlor	0.327	0.384	117	2.13	0.025	0.500
Atrazine	0.633	0.764	121	3.56	0.082	0.324
Bromacil	0.094	0.099	105	10.05	0.030	0.055
Bromochloroacetonitrile	0.010	0.011	110	5.42	0.002	0.009
Bromodichloromethane	0.010	0.012	120	7.50	0.003	0.005
Bromoform	0.010	0.018	180	8.12	0.004	0.006
Carbon Tetrachloride	0.010	0.011	110	6.32	0.002	0.004
Chloral Hydrate	0.025	0.029	116	5.61	0.005	0.011
Chloropicrin	0.010	0.009	90	7.65	0.002	0.014
Chloroform	0.050	0.054	108	34.04	0.055	0.075
Cyanazine	0.567	0.757	134	13.93	0.316	0.685
Dibromoacetonitrile	0.010	0.016	160	12.78	0.006	0.010
Dibromochloromethane	0.010	0.011	110	4.55	0.001	0.007
1,2-Dibromo-3-Chloropropane	0.010	0.020	200	15.15	0.009	0.009
1,2-Dibromoethane	0.010	0.020	200	12.54	0.008	0.008
Dichloroacetonitrile	0.010	0.009	90	4.28	0.001	0.005
1,1-Dichloro-2-Propanone	0.010	0.011	110	6.22	0.002	0.007
Endrin	0.016	0.023	144	2.57	0.002	0.011
Endrin Aldehyde	0.022	0.023	105	2.25	0.002	0.010
Endrin Ketone	0.016	0.016	100	5.14	0.002	0.020
Heptachlor	0.047	0.062	132	43.65	0.081	0.081
Heptachlor Epoxide	0.044	0.050	114	1.64	0.002	0.030
Hexachlorobenzene	0.006	0.006	100	5.44	0.001	0.006
Hexachlorocyclopentadiene	0.019	0.019	100	31.81	0.018	0.022
Lindane (g-BHC)	0.009	0.015	167	9.89	0.004	0.016
Methoxychlor	0.063	0.057	90	4.85	0.008	0.046
Metolachlor	0.219	0.254	116	3.20	0.024	0.146
Metribuzin	0.062	0.100	161	12.45	0.037	0.037
Simazine	0.625	0.794	127	5.95	0.142	0.431
Tetrachloroethylene	0.010	0.012	120	5.04	0.002	0.004
Trichloroacetonitrile	0.010	0.010	100	5.31	0.002	0.004
1,1,1-Trichloroethane	0.010	0.013	130	12.35	0.005	0.005
1,1,2-Trichloroethane	0.140	0.124	89	3.27	0.012	0.040
Trichloroethylene	0.010	0.008	80	8.68	0.002	0.008
1,2,3-Trichloropropane	0.156	0.137	88	1.95	0.008	0.028
1,1,1-Trichloro-2-propanone	0.010	0.027	270	20.53	0.016	0.016
Trifluralin	0.022	0.026	118	3.89	0.003	0.010
Surrogate ===> Decafluorobyphenyl	10.0	10.8	108	2.38		

[a]Based upon the analysis of eight replicate MTBE sample extracts.
[b]MDL designates the statistically derived MDL and is calculated by multiplying the standard deviation of the eight replicates by the student's t-value (2.998) appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.
[c]Estimated Detection Limit (EDL) -- Defined as either the MDL or a level of compound in a sample yielding a peak in the final extract with a signal to noise (S/N) ratio of approximately five, whichever is greater.

TABLE 2B. METHOD DETECTION LIMIT USING MTBE NH_4Cl PRESERVED REAGENT WATER ON CONFIRMATION Rtx-1301 COLUMN

Analyte	Fort. Conc. µg/L	Obser.[a] Conc. µg/L	Avg. % Rec.	% RSD	MDL[b] µg/L	EDL[c] µg/L
Alachlor	0.109	0.107	98	1.70	0.005	0.076
Bromacil	0.094	0.134	143	11.65	0.047	0.071
Bromochloroacetonitrile	0.010	0.008	80	9.49	0.002	0.015
Bromodichloromethane	0.010	0.012	120	4.34	0.002	0.006
Bromoform	0.010	0.015	150	29.51	0.013	0.013
Carbon Tetrachloride	0.010	0.011	110	18.70	0.006	0.006
Chloropicrin	0.010	NR[d]	NR	NR	NR	0.062
Chloroform	0.010	0.059	590	2.82	0.005	0.008
Cyanazine	0.189	0.279	148	7.56	0.063	0.065
Dibromoacetonitrile	0.010	0.010	100	4.87	0.001	0.007
Dibromochloromethane	0.010	0.021	210	29.30	0.018	0.018
1,2-Dibromo-3-Chloropropane	0.010	0.020	200	9.95	0.006	0.024
1,2-Dibromoethane	0.010	0.039	390	6.44	0.007	0.007
Dichloroacetonitrile	0.010	0.010	100	4.11	0.001	0.003
1,1-Dichloro-2-Propanone	0.010	0.009	90	11.65	0.003	0.015
Endrin	0.016	0.025	156	4.09	0.003	0.015
Endrin Aldehyde	0.022	0.034	155	22.45	0.023	0.030
Endrin Ketone	0.047	0.049	104	5.49	0.008	0.047
Heptachlor	0.016	0.018	113	3.79	0.002	0.010
Heptachlor Epoxide	0.044	0.079	180	84.71	0.202	0.202
Hexachlorobenzene	0.006	0.006	100	16.47	0.003	0.011
Hexachlorocyclopentadiene	0.019	NR	NR	NR		0.327
Lindane (g-BHC)	0.009	0.011	122	6.09	0.002	0.009
Methoxychlor	0.188	0.221	118	3.53	0.023	0.041
Metolachlor	0.219	0.280	128	1.45	0.012	0.268
Metribuzin	0.062	0.076	123	2.17	0.005	0.013
Simazine / Atrazine	1.26[e]	1.619	129	2.48	0.121	0.629
Tetrachloroethylene	0.010	0.012	120	6.97	0.002	0.003
Trichloroacetonitrile	0.010	0.006	60	16.01	0.003	0.010
1,1,1-Trichloroethane	0.010	0.020	200	19.22	0.012	0.012
1,1,2-Trichloroethane	0.140	0.133	95	3.40	0.014	0.020
Trichloroethylene	0.010	0.009	90	13.77	0.004	0.007
1,2,3-Trichloropropane	0.156	0.160	103	3.11	0.015	0.114
1,1,1-Trichloro-2-Propanone	0.010	0.011	110	7.11	0.002	0.010
Trifluralin	0.022	0.024	109	3.07	0.002	0.006
Surrogate ===> Decafluorobyphenyl	10.0	10.6	106	1.78		

[a]Based upon the analysis of eight replicate MTBE sample extracts.
[b]MDL designates the statistically derived MDL and is calculated by multiplying the standard deviation of the eight replicates by the student's t-value (2.998) appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.
[c]Estimated Detection Limit (EDL) -- Defined as either the MDL or a level of compound in a sample yielding a peak in the final extract with a signal to noise (S / N) ratio of approximately 5, whichever is greater.
[d]NR indicates Not Reported since there was no peak detected for the eight replicate MDL determination.
[e]The concentration of atrazine and simazine were added together for this determination since these two peaks coelute on the confirmation column.

TABLE 3A. PRECISION AND ACCURACY RESULTS USING MTBE[a] NH_4Cl PRESERVED FORTIFIED REAGENT WATER ON THE PRIMARY DB-1 COLUMN

Analyte	Fortified Conc., µg/L	Mean Meas. Conc., µg/L	% RSD	Percent Recovery
Alachlor	2.18	2.40	1.47	110
Atrazine	12.6	12.4	1.71	98
Bromacil	1.88	1.85	3.13	98
Bromochloroacetonitrile	5.00	5.69	0.71	114
Bromodichloromethane	5.00	4.94	1.14	99
Bromoform	5.00	5.07	0.72	101
Carbon Tetrachloride	5.00	5.07	1.72	101
Chloropicrin	5.00	5.32	1.38	106
Chloroform	5.00	5.10	1.30	102
Cyanazine	3.77	3.89	2.85	103
Dibromoacetonitrile	5.00	5.78	1.43	116
Dibromochloromethane	5.00	4.87	0.71	97
1,2-Dibromo-3-chloropropane	5.00	5.11	0.59	102
1,2-Dibromoethane	5.00	4.96	0.73	99
Dichloroacetonitrile	5.00	5.35	0.57	107
1,1-Dichloro-2-propanone	5.00	5.08	0.72	102
Endrin	0.31	0.337	1.40	108
Endrin Aldehyde	0.437	0.503	1.32	115
Endrin Ketone	0.310	0.319	1.52	103
Heptachlor	0.313	0.351	2.84	112
Heptachlor Epoxide	0.875	0.968	0.65	111
Hexachlorobenzene	0.124	0.137	0.89	110
Hexachlorocyclopentadiene	0.374	0.368	1.18	98
Lindane (g-BHC)	0.188	0.199	1.41	106
Methoxychlor	1.26	1.48	2.84	117
Metolachlor	4.39	4.89	0.87	111
Metribuzin	1.24	1.21	3.94	97
Simazine	12.5	13.1	2.02	105
Tetrachloroethylene	5.00	5.07	1.62	101
Trichloroacetonitrile	5.00	5.73	1.34	115
1,1,1-Trichloroethane	5.00	5.02	1.22	100
1,1,2-Trichloroethane	2.80	2.92	0.91	104
Trichloroethylene	5.00	4.87	1.48	97
1,2,3-Trichloropropane	3.12	3.08	0.62	99
1,1,1-Trichloro-2-Propanone	5.00	5.30	0.81	106
Trifluralin	0.439	0.503	1.09	115
Surrogate ===> Decafluorobyphenyl	10.0	10.4	1.93	104

[a]Based upon the analysis of eight replicate MTBE sample extracts.

TABLE 3B. PRECISION AND ACCURACY RESULTS USING MTBE[a] Na_2SO_3 PRESERVED FORTIFIED REAGENT WATER ON THE PRIMARY DB-1 COLUMN

Analyte	Fortified Conc., µg/L	Mean Meas. Conc., µg/L	% RSD	Percent Recovery
Bromodichloromethane	5.00	4.91	1.49	98
Bromoform	5.00	5.05	1.32	101
Carbon Tetrachloride	5.00	5.08	2.24	102
Chloral Hydrate	1.00	0.93	1.81	93
Chloroform	5.00	4.96	1.71	99
Dibromochloromethane	5.00	4.83	1.43	97
1,2-Dibromo-3-Chloropropane	5.00	5.07	1.04	101
1,2-Dibromoethane	5.00	4.90	1.02	98
Tetrachloroethylene	5.00	5.06	2.53	101
1,1,1-Trichloroethane	5.00	5.01	2.11	100
Trichloroethylene	5.00	4.81	2.21	96
Surrogate ===> Decafluorobyphenyl	10.0	10.2	1.88	102

[a]Based upon the analysis of eight replicate MTBE sample extracts.

TABLE 3C. PRECISION AND ACCURACY RESULTS USING MTBE[a] NH_4Cl PRESERVED FORTIFIED REAGENT WATER ON THE CONFIRMATION Rtx-1301 COLUMN

Analyte	Fortified Conc., µg/L	Mean Meas. Conc., µg/L	% RSD	Percent Recovery
Alachlor	2.18	2.26	0.81	104
Bromacil	1.88	1.77	3.50	94
Bromochloroacetonitrile	5.00	5.59	0.86	112
Bromodichloromethane	5.00	4.92	1.02	98
Bromoform	5.00	5.04	0.73	101
Carbon Tetrachloride	5.00	4.90	1.72	98
Chloropicrin	5.00	5.24	1.20	105
Chloroform	5.00	5.05	1.20	101
Cyanazine	3.77	3.90	2.30	103
Dibromoacetonitrile	5.00	5.47	0.58	109
Dibromochloromethane	5.00	5.04	0.90	101
1,2-Dibromo-3-Chloropropane	5.00	5.12	0.54	102
1,2-Dibromoethane	5.00	5.09	1.82	102
Dichloroacetonitrile	5.00	5.30	0.55	106
1,1-Dichloro-2-Propanone	5.00	4.94	0.70	99
Endrin	0.310	0.335	2.08	108
Endrin Aldehyde	0.440	0.490	2.13	111
Endrin Ketone	0.310	0.317	1.63	102
Heptachlor	0.310	0.349	1.06	113
Heptachlor Epoxide	0.880	0.978	0.80	111
Hexachlorobenzene	0.124	0.135	0.59	109
Hexachlorocyclopentadiene	0.374	0.474	7.19	127
Lindane (g-BHC)	0.188	0.205	0.75	109
Methoxychlor	1.26	1.42	2.30	113
Metolachlor	4.39	4.57	3.43	104
Metribuzin	1.24	1.29	1.15	104
Simazine / Atrazine	25.1[b]	30.0	1.11	119
Tetrachloroethylene	5.00	4.93	1.65	99
Trichloroacetonitrile	5.00	5.48	1.31	110
1,1,1-Trichloroethane	5.00	4.87	1.66	97
1,1,2-Trichloroethane	2.80	2.76	1.52	98
Trichloroethylene	5.00	4.87	1.52	97
1,2,3-Trichloropropane	3.12	3.07	0.88	98
1,1,1-Trichloro-2-Propanone	5.00	4.90	0.89	98
Trifluralin	0.440	0.486	0.93	110
Surrogate ===> Decafluorobyphenyl	10.0	10.6	1.96	106

[a]Based upon the analysis of eight replicate MTBE sample extracts.
[b]Simazine and atrazine coelute on the confirmation column and therefore these results were added together.

TABLE 3D. PRECISION AND ACCURACY RESULTS USING MTBE[a] Na_2SO_3 PRESERVED FORTIFIED REAGENT WATER ON THE CONFIRMATION Rtx-1301 COLUMN

Analyte	Fortified Conc., µg/L	Mean Meas. Conc., µg/L	% RSD	Percent Recovery
Bromodichloromethane	5.00	4.88	1.53	98
Bromoform	5.00	5.03	1.19	101
Carbon Tetrachloride	5.00	4.90	2.27	98
Chloroform	5.00	4.90	1.58	98
Dibromochloromethane	5.00	5.15	1.78	103
1,2-Dibromo-3-Chloropropane	5.00	5.07	0.94	101
1,2-Dibromoethane	5.00	5.02	0.82	100
Tetrachloroethylene	5.00	4.89	2.47	98
1,1,1-Trichloroethane	5.00	4.84	2.18	97
Trichloroethylene	5.00	4.83	2.06	97
Surrogate ===> Decafluorobyphenyl	10.0	10.3	1.64	103

[a]Based upon the analysis of eight replicate MTBE sample extracts.

TABLE 4A. PRECISION AND ACCURACY RESULTS USING MTBE[a] NH_4Cl PRESERVED FORTIFIED REAGENT WATER ON THE PRIMARY DB-1 COLUMN

Analyte	Fortified Conc., µg/L	Mean Meas. Conc., µg/L	% RSD	Percent Recovery
Alachlor	0.436	0.515	1.84	118
Atrazine	2.520	2.994	1.95	119
Bromacil	0.376	0.376	3.32	100
Bromochloroacetonitrile	0.250	0.281	1.57	113
Bromodichloromethane	0.250	0.276	1.42	110
Bromoform	0.250	0.260	1.62	104
Carbon Tetrachloride	0.250	0.299	1.60	120
Chloropicrin	0.250	0.285	2.03	114
Chloroform	0.250	0.264	1.94	105
Cyanazine	0.754	0.761	1.97	101
Dibromoacetonitrile	0.250	0.276	1.89	110
Dibromochloromethane	0.250	0.266	1.20	106
1,2-Dibromo-3-Chloropropane	0.250	0.261	1.82	104
1,2-Dibromoethane	0.250	0.274	1.89	110
Dichloroacetonitrile	0.250	0.268	1.12	107
1,1-Dichloro-2-Propanone	0.250	0.261	0.91	105
Endrin	0.062	0.073	2.65	117
Endrin Aldehyde	0.087	0.108	1.29	123
Endrin Ketone	0.062	0.062	0.76	100
Heptachlor	0.063	0.059	10.29	93
Heptachlor Epoxide	0.175	0.206	0.90	118
Hexachlorobenzene	0.025	0.030	3.77	120
Hexachlorocyclopentadiene	0.075	0.074	3.22	99
Lindane (g-BHC)	0.038	0.047	2.74	125
Methoxychlor	0.252	0.298	3.24	118
Metolachlor	0.878	1.056	1.00	120
Metribuzin	0.248	0.264	2.15	107
Simazine	2.500	2.960	2.71	118
Tetrachloroethylene	0.250	0.263	1.93	105
Trichloroacetonitrile	0.250	0.291	1.02	116
1,1,1-Trichloroethane	0.250	0.291	3.65	116
1,1,2-Trichloroethane	0.560	0.531	0.85	95
Trichloroethylene	0.250	0.252	1.20	101
1,2,3-Trichloropropane	0.624	0.595	0.83	95
1,1,1-Trichloro-2-Propanone	0.250	0.286	3.72	114
Trifluralin	0.088	0.106	1.50	121
Surrogate ===> Decafluorobyphenyl	10.0	10.9	2.49	109

[a]Based upon the analysis of eight replicate MTBE sample extracts.

TABLE 4B. PRECISION AND ACCURACY RESULTS USING MTBE[a] Na_2SO_3 PRESERVED FORTIFIED REAGENT WATER ON THE PRIMARY DB-1 COLUMN

Analyte	Fortified Conc., µg/L	Mean Meas. Conc., µg/L	% RSD	Percent Recovery
Bromodichloromethane	0.250	0.270	1.77	108
Bromoform	0.250	0.257	2.04	103
Carbon Tetrachloride	0.250	0.287	5.18	115
Chloral Hydrate	0.250	0.258	4.12	103
Chloroform	0.250	0.248	1.88	99
Dibromochloromethane	0.250	0.261	1.36	105
1,2-Dibromo-3-Chloropropane	0.250	0.258	1.26	103
1,2-Dibromoethane	0.250	0.243	0.90	97
Tetrachloroethylene	0.250	0.256	1.95	102
1,1,1-Trichloroethane	0.250	0.276	5.72	110
Trichloroethylene	0.250	0.246	1.01	98
Surrogate ===> Decafluorobyphenyl	10.0	10.6	3.51	106

[a]Based upon the analysis of eight replicate MTBE sample extracts.

TABLE 5A. PRECISION AND ACCURACY RESULTS USING MTBE[a] NH_4Cl PRESERVED FORTIFIED FULVIC ACID ENRICHED REAGENT WATER[b] ON THE PRIMARY DB-1 COLUMN

Analyte	Fortified Conc., µg/L	Mean Meas. Conc., µg/L	% RSD	Percent Recovery
Alachlor	2.18	2.38	1.57	109
Atrazine	12.6	11.6	2.31	92
Bromacil	1.88	1.89	3.33	101
Bromochloroacetonitrile	1.00	1.11	1.51	111
Bromodichloromethane	1.00	0.87	1.93	87
Bromoform	1.00	0.97	1.50	97
Carbon Tetrachloride	1.00	0.88	3.91	88
Chloropicrin	1.00	1.13	2.49	113
Chloroform	1.00	1.03	2.47	103
Cyanazine	3.77	4.02	3.99	107
Dibromoacetonitrile	1.00	1.14	1.61	114
Dibromochloromethane	1.00	0.89	1.78	89
1,2-Dibromo-3-chloropropane	1.00	0.93	1.37	93
1,2-Dibromoethane	1.00	0.96	1.58	96
Dichloroacetonitrile	1.00	1.05	0.98	105
1,1-Dichloro-2-propanone	1.00	1.03	0.90	103
Endrin	0.311	0.325	3.50	104
Endrin Aldehyde	0.437	0.505	1.99	116
Endrin Ketone	0.310	0.319	2.62	103
Heptachlor	0.313	0.358	5.45	114
Heptachlor Epoxide	0.875	0.978	1.28	112
Hexachlorobenzene	0.124	0.139	1.82	112
Hexachlorocyclopentadiene	0.374	0.363	3.55	97
Lindane (g-BHC)	0.188	0.206	1.79	110
Methoxychlor	1.26	1.41	4.78	112
Metolachlor	4.39	4.84	1.27	110
Metribuzin	1.24	1.30	2.08	105
Simazine	12.5	12.0	1.09	96
Tetrachloroethylene	1.00	0.90	4.02	90
Trichloroacetonitrile	1.00	1.11	2.41	111
1,1,1-Trichloroethane	1.00	0.96	3.89	96
1,1,2-Trichloroethane	2.80	2.81	2.89	100
Trichloroethylene	1.00	0.93	3.55	93
1,2,3-Trichloropropane	3.12	2.92	0.82	93
1,1,1-Trichloro-2-propanone	1.00	1.10	2.05	110
Trifluralin	0.439	0.517	1.27	118
Surrogate ===> Decafluorobyphenyl	10.0	10.4	1.84	104

[a]Based upon the analysis of eight replicate MTBE sample extracts.
[b]Reagent water fortified at 1.0 mg/L with fulvic acid extracted from Ohio River water. Sample simulated high TOC matrix.

TABLE 5B. PRECISION AND ACCURACY RESULTS USING MTBE[a] Na_2SO_3 PRESERVED FORTIFIED FULVIC ACID ENRICHED REAGENT WATER ON THE PRIMARY DB-1 COLUMN

Analyte	Fortified Conc., µg/L	Mean Meas. Conc., µg/L	% RSD	Percent Recovery
Bromodichloromethane	1.00	0.87	1.13	87
Bromoform	1.00	0.97	1.28	97
Carbon Tetrachloride	1.00	0.88	1.71	88
Chloral Hydrate	1.00	0.90	0.95	90
Chloroform	1.00	0.96	1.51	96
Dibromochloromethane	1.00	0.88	1.25	88
1,2-Dibromo-3-chloropropane	1.00	0.92	0.98	92
1,2-Dibromoethane	1.00	0.93	1.01	93
Tetrachloroethylene	1.00	0.90	2.07	90
1,1,1-Trichloroethane	1.00	0.97	1.57	97
Trichloroethylene	1.00	0.94	1.62	94
Surrogate ===>				
Decafluorobyphenyl	10.0	10.6	2.56	106

[a]Based upon the analysis of eight replicate MTBE sample extracts.
[b]Reagent water fortified at 1.0 mg/L with fulvic acid extracted from Ohio River water. Sample simulated high TOC matrix.

TABLE 6A. PRECISION AND ACCURACY RESULTS USING MTBE[a] NH_4Cl PRESERVED FORTIFIED GROUND WATER[b] ON THE PRIMARY DB-1 COLUMN

Analyte	Unfort. matrix conc., µg/L	Fort. Conc., µg/L	Mean Meas. Conc., µg/L	% RSD	Percent Recovery
Alachlor	ND[c]	8.72	9.01	2.93	103
Atrazine	ND	50.4	46.7	3.30	93
Bromacil	ND	7.52	6.53	7.81	87
Bromochloroacetonitrile	ND	5.00	5.74	1.38	115
Bromodichloromethane	1.70	5.00	6.68	2.59	100
Bromoform	20.1	5.00	24.8	1.61	95
Carbon Tetrachloride	ND	5.00	4.99	6.65	100
Chloropicrin	ND	5.00	5.29	3.59	106
Chloroform	0.571	5.00	5.73	3.68	103
Cyanazine	ND	15.1	15.4	6.07	102
Dibromoacetonitrile	ND	5.00	5.84	1.59	117
Dibromochloromethane	6.00	5.00	11.1	1.89	102
1,2-Dibromo-3-Chloropropane	ND	5.00	5.04	1.64	101
1,2-Dibromoethane	ND	5.00	4.87	1.90	97
Dichloroacetonitrile	ND	5.00	5.29	1.52	106
1,1-Dichloro-2-Propanone	ND	5.00	5.01	1.30	100
Endrin	ND	1.24	1.32	4.81	106
Endrin Aldehyde	ND	1.75	1.91	2.36	109
Endrin Ketone	ND	1.24	1.22	3.77	98
Heptachlor	ND	1.25	1.33	4.46	106
Heptachlor Epoxide	ND	3.50	3.67	2.92	105
Hexachlorobenzene	ND	0.50	0.509	3.42	103
Hexachlorocyclopentadiene	ND	1.50	1.41	3.70	94
Lindane (g-BHC)	ND	0.75	0.773	1.91	103
Methoxychlor	ND	5.04	5.60	5.86	111
Metolachlor	ND	17.6	18.2	3.06	103
Metribuzin	ND	4.96	4.85	6.15	98
Simazine	ND	50.0	48.3	3.30	97
Tetrachloroethylene	ND	5.00	4.97	6.29	99
Trichloroacetonitrile	ND	5.00	5.59	4.89	112
1,1,1-Trichloroethane	1.77	5.00	6.62	4.60	97
1,1,2-Trichloroethane	ND	11.2	10.4	2.98	93
Trichloroethylene	ND	5.00	4.74	5.78	95
1,2,3-Trichloropropane	0.340	12.5	12.5	3.92	97
1,1,1-Trichloro-2-Propanone	ND	5.00	5.21	1.58	104
Trifluralin	ND	1.76	1.94	3.38	110
Surrogate ===> Decafluorobyphenyl		10.0	10.4	2.25	104

[a]Based upon the analysis of eight replicate MTBE sample extracts.
[b]Chlorinated ground water from a water source displaying a hardness of 460 mg/L as $CaCO_3$.
[c]ND indicates not detected above the EDL.

TABLE 6B. PRECISION AND ACCURACY RESULTS USING MTBE[a] Na_2SO_3 PRESERVED FORTIFIED GROUND WATER[b] ON THE PRIMARY DB-1 COLUMN

Analyte	Unfort. matrix conc., µg/L	Fort. Conc., µg/L	Mean Meas. Conc., µg/L	% RSD	Percent Recovery
Bromodichloromethane	1.77	5.00	6.64	1.70	97
Bromoform	20.5	5.00	24.6	1.63	82
Carbon Tetrachloride	ND[c]	5.00	4.99	2.72	100
Chloral Hydrate	ND	2.00	1.84	1.38	92
Chloroform	0.600	5.00	5.22	1.89	92
Dibromochloromethane	6.16	5.00	11.0	1.53	98
1,2-Dibromo-3-Chloropropane	ND	5.00	5.01	1.19	100
1,2-Dibromoethane	ND	5.00	4.79	1.86	96
Tetrachloroethylene	ND	5.00	4.95	2.49	99
1,1,1-Trichloroethane	1.91	5.00	6.73	3.18	96
Trichloroethylene	ND	5.00	4.69	2.38	94
Surrogate ===>					
Decafluorobyphenyl		10.0	10.1	8.71	101

[a]Based upon the analysis of eight replicate MTBE sample extracts.
[b]Chlorinated ground water from a water source displaying a hardness of 460 mg/L as $CaCO_3$.
[c]ND indicates Not Detected above the detection limit.

TABLE 7. LABORATORY PERFORMANCE CHECK SOLUTION

Parameter	Analyte	Conc., µg/mL in MTBE or pentane	Acceptance Criteria
Instrument Sensitivity	Lindane (gamma-BHC)	0.000200	Detection of Analyte; Signal to Noise >3
Chromatographic Performance	Hexachlorocyclopentadiene	0.0200	PGF between 0.80 and 1.15[a]
Column Performance	Bromodichloromethane	0.0300	Resolution >0.50[b]
	Trichloroethylene	0.0300	
	Bromacil	0.0830	Resolution >0.50
	Alachlor	0.0830	
Analyte Breakdown	Endrin	0.0300	%BD[c] <20%

[a]PGF -- peak Gaussian factor. Calculated using the equation:

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

where: W(1/2) = the peak width at half height in seconds
W(1/10) = the peak width in seconds at 10th height

[b]Resolution between the two peaks as defined by the equation:

$$R = \frac{t}{W}$$

where: t = the difference in elution times between the two peaks
W = the average peak width, at the baseline, of the two peaks

[c]%BD = Percent breakdown. Endrin breakdown calculated using the equation.

$$\%BD = \frac{(\text{AREA Endrin Ketone} + \text{AREA Endrin Aldehyde})}{(\text{AREA Endrin Ketone} + \text{AREA Endrin Aldehyde} + \text{AREA Endrin})} \times 100$$

Note: If laboratory EDLs differ from those listed in this method, concentrations of the LPC standard must be adjusted to be compatible with the laboratory EDLs.

TABLE 8. METHOD DETECTION LIMIT USING PENTANE NH_4Cl PRESERVED REAGENT WATER ON PRIMARY DB-1 COLUMN

Analyte	Fort. Conc. µg/L	Observ.[b] Conc. µg/L	Avg. % Rec.	% RSD	MDL[c] µg/L	EDL[d] µg/L
Alachlor	0.109	0.095[a]	87.00	5.37	0.015	0.050
Atrazine	0.633	0.663	105.00	5.00	0.099	0.390
Bromacil	0.094	0.058	62.00	21.44	0.037	0.330
Bromochloroacetonitrile	0.040	0.047	118.00	3.61	0.005	0.026
Bromodichloromethane	0.040	0.054	135.00	42.05	0.068	0.068
Bromoform	0.040	0.033	83.00	20.60	0.020	0.035
Carbon Tetrachloride	0.040	0.060	150.00	27.76	0.050	0.050
Chloropicrin	0.040	0.045	113.00	4.25	0.006	0.023
Chloroform	0.040	0.110	275.00	24.36	0.080	0.080
Cyanazine	0.189	0.170[a]	90.00	13.37	0.068	0.200
Dibromoacetonitrile	0.040	0.046	115.00	3.84	0.005	0.030
Dibromochloromethane	0.040	0.050	125.00	5.48	0.008	0.026
1,2-Dibromo-3-Chloropropane	0.040	0.053	133.00	5.39	0.009	0.017
1,2-Dibromomethane	0.040	0.053	133.00	19.85	0.032	0.032
Dichloroacetonitrile	0.040	0.037	93.00	20.09	0.022	0.042
1,1-Dichloro-2-Propanone	0.040	0.042	105.00	4.86	0.006	0.022
Endrin	0.016	0.019	119.00	4.69	0.003	0.016
Endrin Aldehyde	0.022	0.023	105.00	5.52	0.004	0.022
Endrin Ketone	0.016	0.014	88.00	9.50	0.004	0.020
Heptachlor	0.016	0.011[a]	69.00	18.14	0.006	0.009
Heptachlor Epoxide	0.044	0.045	102.00	5.02	0.007	0.016
Hexachlorobenzene	0.0062	0.008	129.00	9.56	0.002	0.002
Hexachloropentadiene	0.040	0.022	55.00	24.42	0.016	0.016
Lindane (g-BHC)	0.0094	0.006	64.00	91.20	0.017	0.017
Methoxychlor	0.063	0.069	110.00	12.76	0.026	0.066
Metolachlor	0.219	0.267	122.00	10.35	0.083	0.172
Metribuzin	0.062	0.076	123.00	18.15	0.041	0.041
Simazine	0.625	0.662	106.00	9.42	0.187	0.420
Tetrachloroethylene	0.040	0.052	130.00	5.33	0.008	0.016
Trichloroacetonitrile	0.040	0.048	120.00	2.79	0.004	0.014
1,1,1-Trichloroethane	0.040	0.058	145.00	4.26	0.007	0.017
1,1,2-Trichloroethane	0.140	0.141	101.00	4.01	0.017	0.052
Trichloroethylene	0.040	0.064	160.00	21.80	0.042	0.042
1,2,3-Trichloropropane	0.156	0.151	97.00	3.54	0.016	0.116
1,1,1-Trichloro-2-Propanone	0.040	0.045	113.00	3.65	0.005	0.024
Trifluralin	0.040	0.021	53.00	19.28	0.012	0.012
Surrogate ===> Decafluorobyphenyl	10.0	11.2	112.00	3.98		

[a]Quantitated from confirmation column due to baseline interference on primary column.
[b]Based upon the analysis of eight replicate pentane sample extracts.
[c]MDL designates the statistically derived MDL and is calculated by multiplying the standard deviation of the eight replicates by the student's t-value (2.998) appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.
[d]Estimated Detection Limit (EDL) -- Defined as either the MDL or a level of compound in a sample yielding a peak in the final extract with a signal to noise (S/N) ratio of approximately 5, whichever is greater.

TABLE 9. PRECISION AND ACCURACY RESULTS[a] USING PENTANE NH_4Cl PRESERVED FORTIFIED REAGENT WATER ON THE PRIMARY DB-1 COLUMN

Analyte	Fortified Conc., µg/L	Mean Meas. Conc., µg/L	% RSD	Percent Recovery
Alachlor	2.18	1.98[b]	5.09	91
Atrazine	12.6	12.0	3.09	95
Bromacil	1.88	1.74	2.95	93
Bromochloroacetonitrile	5.00	4.63	3.18	93
Bromodichloromethane	5.00	4.46	4.07	89
Bromoform	5.00	4.81	2.76	96
Carbon Tetrachloride	5.00	4.61	4.14	92
Chloropicrin	5.00	4.51	2.46	90
Chloroform	5.00	4.95	2.90	99
Cyanazine	3.77	4.00[b]	2.59	106
Dibromoacetonitrile	5.00	4.80	2.87	96
Dibromochloromethane	5.00	4.23	3.38	85
1,2-Dibromo-3-Chloropropane	5.00	4.73	3.00	95
1,2-Dibromoethane	5.00	4.69	2.54	94
Dichloroacetonitrile	5.00	4.73	3.39	95
1,1-Dichloro-2-Propanone	5.00	4.78	3.04	96
Endrin	0.311	0.312	2.61	100
Endrin Aldehyde	0.437	0.443	2.29	101
Endrin Ketone	0.310	0.311	2.10	100
Heptachlor Epoxide	0.875	0.866	2.11	99
Heptachlor	0.313[b]	0.30	3.47	97
Hexachlorobenzene	0.124	0.123	2.51	99
Hexachlorocyclopentadiene	0.374	0.384	3.30	103
Lindane (g-BHC)	0.188	0.176	10.23	94
Methoxychlor	1.26	1.28	3.03	102
Metolachlor	4.39	4.42	2.36	101
Metribuzin	1.24	1.34	2.13	108
Simazine	12.5	12.5	2.20	100
Tetrachloroethylene	5.00	4.46	3.67	89
Trichloroacetonitrile	5.00	5.07	4.02	101
1,1,1-Trichloroethane	5.00	4.70	3.39	94
1,1,2-Trichloroethane	2.80	2.62	2.03	93
Trichloroethylene	5.00	4.84	2.98	97
1,2,3-Trichloropropane	3.12	3.13	1.76	100
1,1,1-Trichloro-2-Propanone	5.00	4.88	2.80	98
Trifluralin	0.439	0.446	2.74	102
Surrogate===> Decafluorobyphenyl	10.0	10.7	1.88	107

[a]Based upon the analysis of eight replicate pentane sample extracts.
[b]Quantitated from confirmation column due to baseline interference on primary column.

TABLE 10. ANALYTE PEAK IDENTIFICATION, RETENTION TIMES, CONCENTRATIONS AND CONDITIONS USING MTBE FOR FIGURE 1 NH_4Cl PRESERVED FORTIFIED REAGENT WATER ON THE PRIMARY DB-1 COLUMN

Peak #	Analyte	Retention Time[a] minutes	Conc. µg/L
1	Chloroform	7.04	5.00
2	1,1,1-Trichloroethane	8.64	5.00
3	Carbon Tetrachloride	9.94	5.00
4	Trichloroacetonitrile	10.39	5.00
5	Dichloroacetonitrile	12.01	5.00
6	Bromodichloromethane	12.42	5.00
7	Trichloroethylene	12.61	5.00
8	Chloral Hydrate	13.41	5.00
9	1,1-Dichloro-2-Propanone	14.96	5.00
10	1,1,2-Trichloroethane	19.91	44.8
11	Chloropicrin	23.10	5.00
12	Dibromochloromethane	23.69	5.00
13	Bromochloroacetonitrile	24.03	5.00
14	1,2-Dibromoethane (EDB)	24.56	5.00
15	Tetrachloroethylene	26.24	5.00
16	1,1,1-Trichloropropanone	27.55	5.00
17	Bromoform	29.17	5.00
18	Dibromoacetonitrile	29.42	5.00
19	1,2,3-Trichloropropane	30.40	50.0
20	1,2-Dibromo-3-Chloropropane (DBCP)	35.28	5.00
21	Surrogate: Decafluorobiphenyl	36.35	10.0
22	Hexachlorocyclopentadiene	40.33	28.0
23	Trifluralin	45.17	7.04
24	Simazine	46.27	200
25	Atrazine	46.55	200
26	Hexachlorobenzene	47.39	1.98
27	Lindane (gamma-BHC)	47.95	30.1
28	Metribuzin	50.25	19.9
29	Bromacil	52.09	30.1
30	Alachlor	52.25	34.9
31	Cyanazine	53.43	60.4
32	Heptachlor	53.72	5.00
33	Metolachlor	55.44	70.0
34	Heptachlor Epoxide	58.42	14.0

TABLE 10. ANALYTE PEAK IDENTIFICATION, RETENTION TIMES, CONCENTRATIONS AND CONDITIONS USING MTBE FOR FIGURE 1 NH_4Cl PRESERVED FORTIFIED REAGENT WATER ON THE PRIMARY DB-1 COLUMN

Peak #	Analyte	Retention Time[a] minutes	Conc. µg/L
35	Endrin	64.15	5.00
36	Endrin Aldehyde	65.46	7.00
37	Endrin Ketone	72.33	4.96
38	Methoxychlor	73.53	20.1

Note: Bromofluorobenzene (ret. time 31.00 minutes) as the internal standard was not included in this chromatogram.

[a]Column A - 0.25 mm ID x 30 m fused silica capillary with chemically bonded methyl polysiloxane phase (J&W, DB-1, 1.0 µm film thickness or equivalent). The linear velocity of the helium carrier is established at 25 cm/sec. at 35°C.

The column oven is temperature programmed as follows:

[1] HOLD at 35°C for 22 minutes
[2] INCREASE to 145°C at 10°C/mi. and hold at 145°C for two minutes.
[3] INCREASE to 225°C at 20°C/min and hold at 225°C for 15 minutes.
[4] INCREASE to 260°C at 10°C/min and hold at 260°C for 30 minutes or until all expected compounds have eluted.

Injector temperature: 200°C
Detector temperature: 290°C

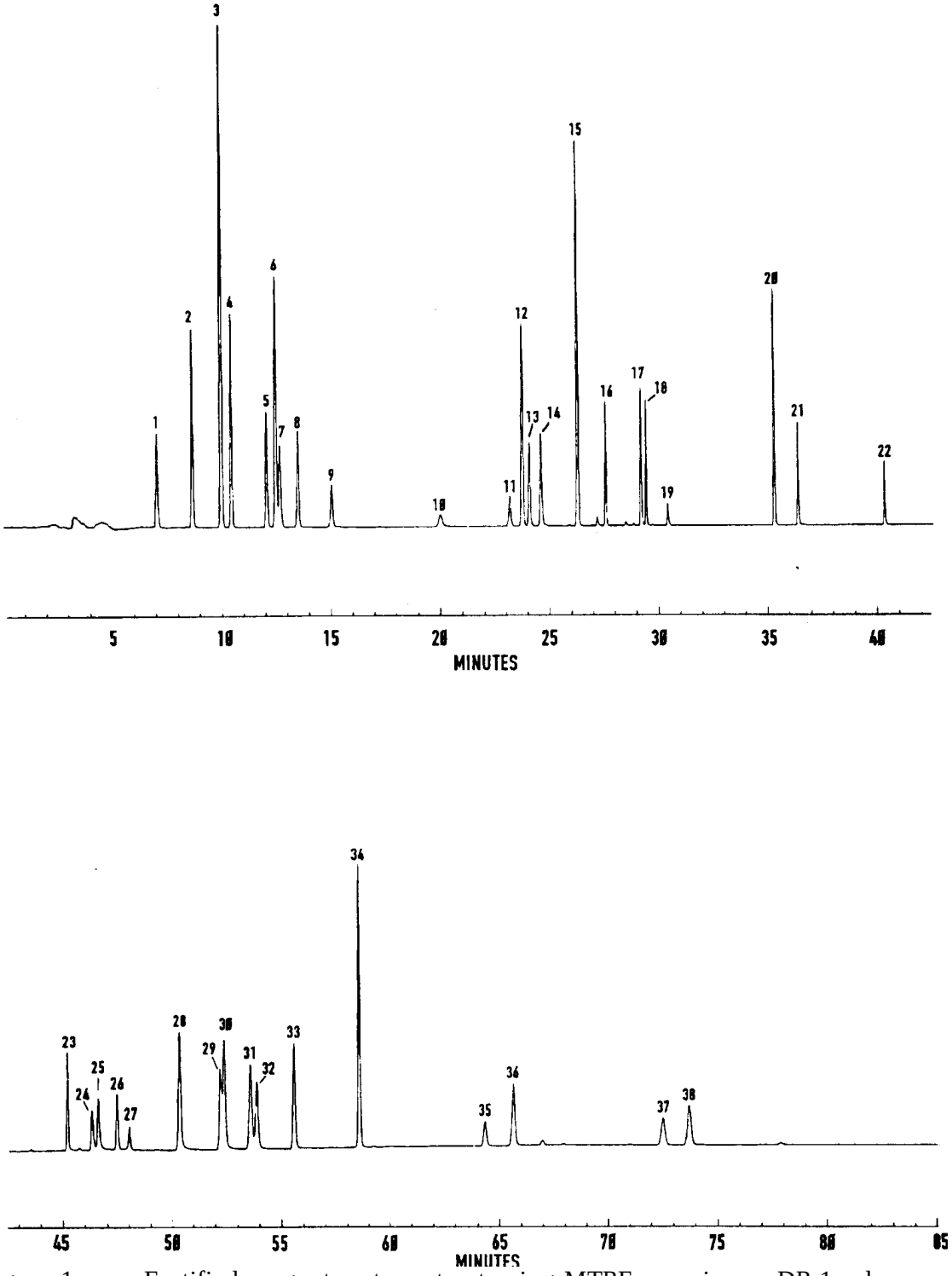

Figure 1. Fortified reagent water extract using MTBE on primary DB-1 column

TABLE 11. ANALYTE PEAK IDENTIFICATION, RETENTION TIMES, CONCENTRATIONS AND CONDITIONS USING MTBE FOR FIGURE 2 NH_4Cl PRESERVED FORTIFIED REAGENT WATER ON THE CONFIRMATION Rtx-1301

Peak #	Analyte	Retention Time[a] minutes	Conc. µg/L
1	Chloroform	7.73	5.00
2	1,1,1-Trichloroethane	7.99	5.00
3	Carbon Tetrachloride	8.36	5.00
4	Trichloroacetonitrile	10.35	5.00
5	Trichloroethylene	11.96	5.00
6	Bromodichloromethane	15.28	5.00
7	1,1-Dichloro-2-Propanone	20.50	5.00
8	Chloropicrin	23.69	5.00
9	Tetrachloroethylene	24.77	5.00
10	1,1,2-Trichloroethane	25.01	44.8
11	Dichloroacetonitrile	25.21	5.00
12	Dibromochloromethane	26.32	5.00
13	1,2-Dibromoethane (EDB)	26.46	5.00
14	1,1,1-Trichloropropanone	28.47	5.00
15	Bromochloroacetonitrile	29.86	5.00
16	Bromoform	30.36	5.00
17	1,2,3-Trichloropropane	31.73	50.0
18	Dibromoacetonitrile	32.77	5.00
19	1,2-Dibromo-3-chloropropane (DBCP)	36.11	5.00
20	Surrogate: Decafluorobiphenyl	36.28	10.0
21	Hexachlorocyclopentadiene	39.53	28.0
22	Trifluralin	45.43	7.04
23	Hexachlorobenzene	46.47	1.98
24	Atrazine/Simazine	48.56	400
25	Lindane (gamma-BHC)	49.68	30.1
26	Heptachlor	53.15	5.00
27	Metribuzin	53.92	19.9
28	Alachlor	54.38	34.9
29	Metolachlor	57.07	70.0
30	Heptachlor Epoxide	59.05	14.0
31	Bromacil	59.60	30.1
32	Cyanazine	59.89	60.4
33	Endrin	65.24	5.00
34	Endrin Aldehyde	71.56	7.00

TABLE 11. ANALYTE PEAK IDENTIFICATION, RETENTION TIMES, CONCENTRATIONS AND CONDITIONS USING MTBE FOR FIGURE 2 NH_4Cl PRESERVED FORTIFIED REAGENT WATER ON THE CONFIRMATION Rtx-1301

Peak #	Analyte	Retention Time[a] minutes	Conc. µg/L
35	Methoxychlor	76.73	20.1
36	Endrin Ketone	81.28	4.96

Note: Bromofluorobenzene (ret. time 31.30 min.) as the internal standard was not included in this chromatogram.

[a]Column B - 0.25 mm ID x 30 m with chemically bonded 6% cyanopropylphenyl/ 94% dimethyl polysiloxane phase (Restek, Rtx-1301, 1.0 µm film thickness or equivalent). The linear velocity of the helium carrier gas is established at 25 cm/sec. at 35°C.

The column oven is temperature programmed as follows:

[1] HOLD at 35°C for 22 minutes
[2] INCREASE to 145°C at 10°C/min. and hold at 145°C for two minutes
[3] INCREASE to 225°C at 20°C/min. and hold at 225°C for 15 minutes
[4] INCREASE to 260°C at 10°C/min. and hold at 260°C for 30 minutes or until all expected compounds have eluted.

Injector temperature: 200°C
Detector temperature: 290°C

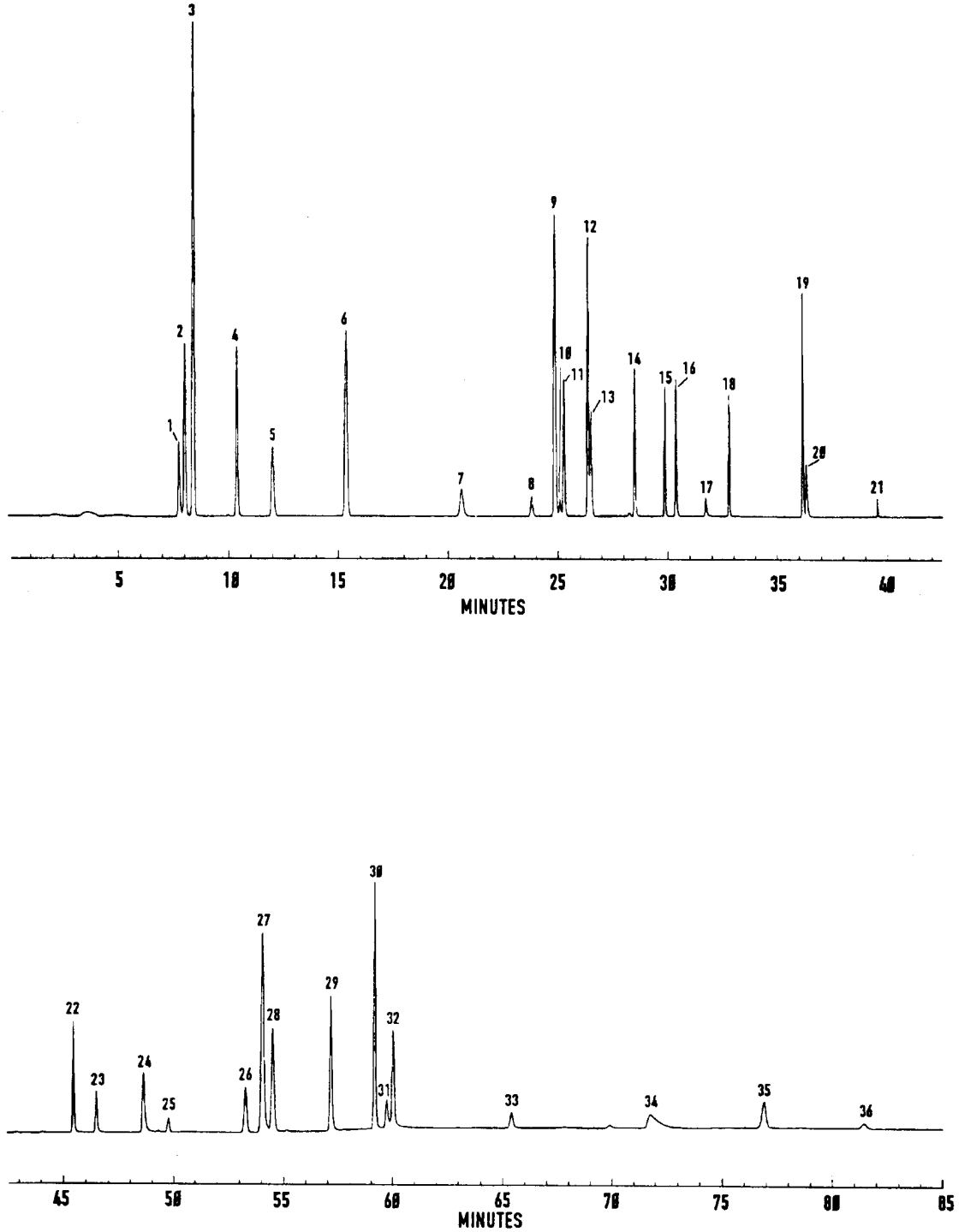

Figure 2. Fortified reagent water extract using MTBE on confirmation Rtx-1301 column

TABLE 12. ANALYTE PEAK IDENTIFICATION, RETENTION TIMES, CONCENTRATIONS AND CONDITIONS USING PENTANE FOR FIGURE 3 NH_4Cl PRESERVED FORTIFIED REAGENT WATER ON THE PRIMARY DB-1 COLUMN

Peak #	Analyte	Retention Time[a] minutes	Conc. µg/L
1	Chloroform	8.41	5.00
2	1,1,1-Trichloroethane	10.26	5.00
3	Carbon Tetrachloride	11.56	5.00
4	Trichloroacetonitrile	12.03	5.00
5	Dichloroacetonitrile	13.53	5.00
6	Bromodichloromethane	13.73	5.00
7	Trichloroethylene	13.89	5.00
8	1,1-Dichloro-2-Propanone	15.60	5.00
9	1,1,2-Trichloroethane	18.57	44.8
10	Chloropicrin	20.49	5.00
11	Dibromochloromethane	21.03	5.00
12	Bromochloroacetonitrile	21.25	5.00
13	1,2-Dibromoethane (EDB)	22.03	5.00
14	Tetrachloroethylene	24.75	5.00
15	1,1,1-Trichloropropanone	27.94	5.00
16	Bromoform	30.97	5.00
17	Dibromoacetonitrile	31.45	5.00
18	1,2,3-Trichloropropane	32.82	50.0
19	Internal Standard: Bromofluorobenzene	33.60	1.00 µg/mL in pentane extract
20	1,2-Dibromo-3-Chloropropane (DBCP)	38.34	5.00
21	Surrogate: Decafluorobiphenyl	39.48	10.0
22	Hexachlorocyclopentadiene	43.92	28.0
23	Trifluralin	49.04	7.04
24	Simazine	50.08	200
25	Atrazine	50.37	200
26	Hexachlorobenzene	51.11	1.98
27	Lindane (gamma-BHC)	51.66	30.1
28	Metribuzin	53.95	19.9
29	Bromacil	55.72	30.1
30	Alachlor	55.87	34.9
31	Cyanazine	57.04	60.4
32	Heptachlor	57.21	5.00
33	Metolachlor	59.13	70.0
34	Heptachlor Epoxide	62.50	14.0
35	Endrin	68.00	5.00
36	Endrin Aldehyde	69.25	7.00

TABLE 12. ANALYTE PEAK IDENTIFICATION, RETENTION TIMES, CONCENTRATIONS AND CONDITIONS USING PENTANE FOR FIGURE 3 NH_4Cl PRESERVED FORTIFIED REAGENT WATER ON THE PRIMARY DB-1 COLUMN

Peak #	Analyte	Retention Time[a] minutes	Conc. µg/L
37	Endrin Ketone	75.74	4.96
38	Methoxychlor	76.98	20.1

[a]Column A - 0.25 mm ID x 30 m fused silica capillary with chemically bonded methyl polysiloxane phase (J&W, DB-1, 1.0 µm film thickness or equivalent). The linear velocity of the helium carrier is established at 25 cm/sec. at 35°C.

The column oven is temperature programmed as follows:

[1] HOLD at 15°C for 0 minutes
[2] INCREASE to 50°C at 2°C/min. and hold at 50°C for 10 minutes
[3] INCREASE to 225°C at 10°C/min. and hold at 225°C for 15 minutes
[4] INCREASE to 260°C at 10°C/min. and hold at 260°C for 30 minutes or until all expected compounds have eluted.

Injector temperature: 200°C
Detector temperature: 290°C

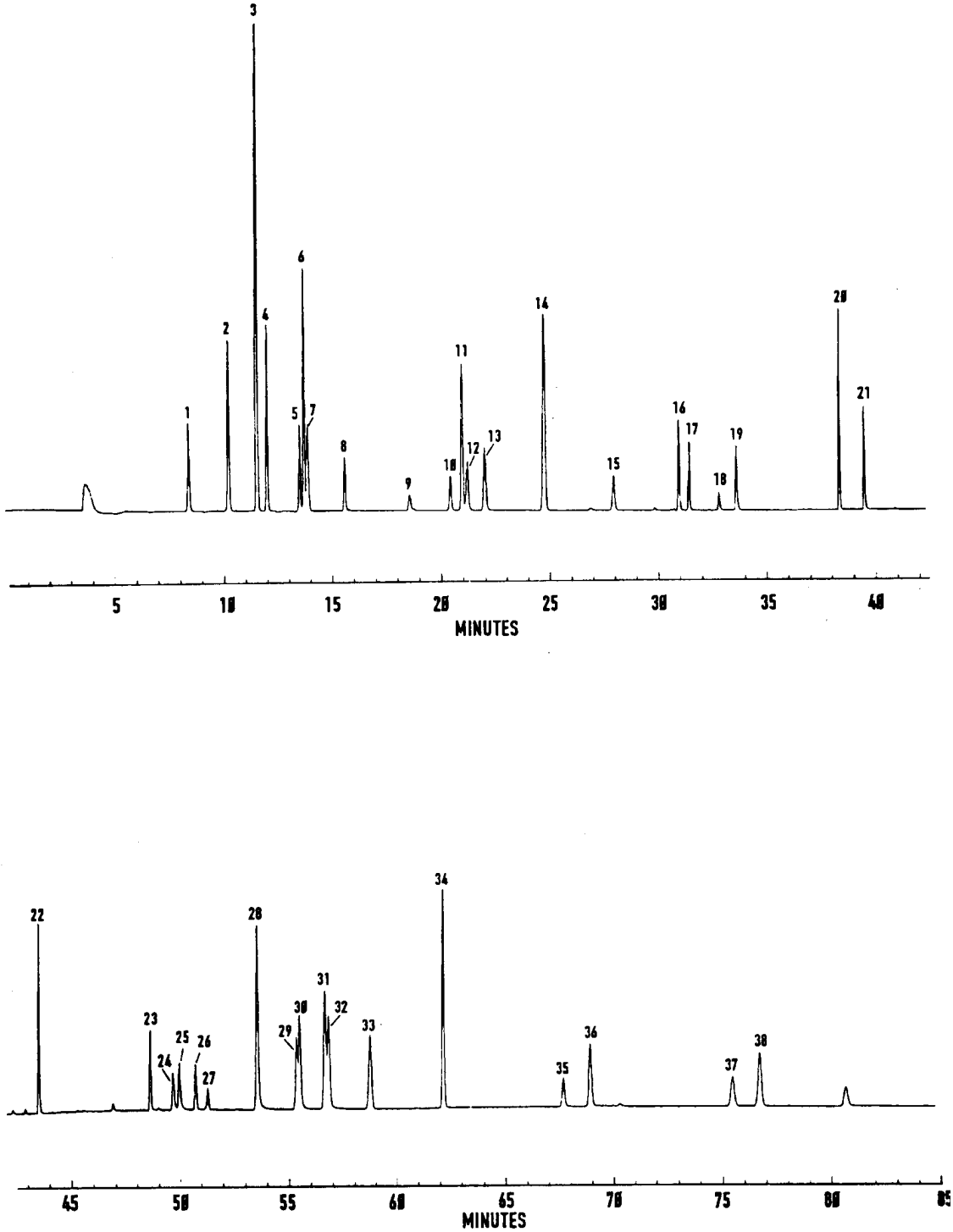

Figure 3. Fortified reagent water extract using pentane on primary DB-1 column