METHOD 551

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

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1.0 SCOPE AND APPLICATION

1.1 This method[1-4] is applicable to the determination of the following analytes in finished drinking water, drinking water during intermediate stages of treatment, and raw source water:

Analyte	Chemical Abstract Services Registry Number
Bromochloroacetonitrile	83463-62-1
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Carbon Tetrachloride	56-23-5
Chloral Hydrate	75-87-6
Chloroform	67-66-3
Chloropicrin	76-06-2
Dibromoacetonitrile	3252-43-5
Dibromochloromethane	124-48-1
1,2-Dibromo-3-chloropropane [DBCP]	96-12-8
1,2-Dibromoethane [EDB]	106-93-4
Dichloroacetonitrile	3018-12-0
Trichloroacetonitrile	545-06-2
Tetrachloroethylene	127-18-4
1,1,1-Trichloroethane	71-55-6
Trichloroethylene	79-01-6
1,1,1-Trichloro-2-propanone	918-00-3
1,1-Dichloro-2-propanone	513-88-2

1.2 This analyte list includes 12 commonly observed chlorination disinfection byproducts[3,4] and six commonly used chlorinated organic solvents - carbon tetrachloride, 1,2-dibromo-3-chloropropane (DBCP), 1,2-dibromoethane (EDB), tetrachloroethylene, 1,1,1-tri-chloroethane and trichloroethylene.

1.3 This method is intended as a stand-alone procedure for the analysis of only the trihalomethanes (THMs) or as a procedure for the total analyte list. The dechlorination/preservation technique presented in Section 8.0 differs for the two modes of operation, with a simpler technique available for the THM analysis. The six solvents may be analyzed in the THM mode, since the same dechlorination reagents may be employed.

1.4 The experimentally determined method detection limits (MDLs)[5] for the above listed analytes are provided in Table 2. Actual MDL values will vary according to the particular matrix analyzed and the specific instrumentation employed.

2.0 SUMMARY OF METHOD

2.1 A 35 mL sample aliquot is extracted with 2 mL of methyl-tert-butyl ether (MTBE). 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. Aqueous calibration standards are also extracted and analyzed in order to compensate for any extraction losses. A typical sample can be extracted and analyzed in 40-50 minutes using the primary column chosen for this method (Section 6.8.2.1). Confirmation of the eluted compounds may be obtained using a dissimilar column (Section 6.8.2.2) or by the use of GC-MS.

3.0 DEFINITIONS

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

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

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

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

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

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

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

3.8 Laboratory Fortified Sample Matrix (LFM) -- An aliquot of an envi-ronmental 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 concen-trations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

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

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

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

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

4.0 INTERFERENCES

4.1 Impurities contained in the extracting solvent usually account for the majority of the analytical problems. Solvent blanks should be analyzed for each new bottle of solvent before use. An interference-free solvent is a solvent containing no peaks yielding data at greater than or equal to the MDL (Table 2) and 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 10.2). Whenever an interference is noted in the sample blank, the analyst should analyze another solvent blank. Low level interferences generally can be removed by distillation or column chromatography[2].

4.2 Commercial lots of the MTBE extraction solvent often contain observable amounts of chlorinated solvent impurities, e.g., chloroform, trichloroethylene, carbon tetrachloride. When present, these impurities can normally be removed by a double distillation of the MTBE.

4.3 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 6.8.2.2) is provided for this purpose. Alternatively, a more powerful technique is confirmation by GC-MS.

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[6-8] 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.

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 APPARATUS AND EQUIPMENT (All specifications in Sections 6.0 and 7.0 are suggested. Catalog numbers are included for illustration only.)

6.1 Sample Containers -- 40 mL screw cap vials (Pierce #13075) or equivalent each equipped with a PTFE-faced silicone septum (Pierce #12722, Fisher TFE-lined #02-883-3F or equivalent).

NOTE: Some commercial 40 mL vials do not have adequate volume when salt is added. (See Section 11.1.4). Prior to use, wash vials and septa with detergent and rinse with tap water, followed by distilled water. Allow the vials and septa to dry at room temperature, place 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.

6.2 Vials -- Autosampler, screw cap with septa, 1.8 mL, Varian #96-000099-00 or equivalent.

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

6.4 Pipettes -- 2.0 mL transfer, glass.

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

6.6 Disposable Pasteur Pipets -- Kimble No. 72050575 or equivalent.

6.7 Standard Solution Storage Containers -- 15 mL Boston round, amber glass bottles with TFE-lined caps. Wheaton Cat. No. 220092 or equivalent. TFE-lined caps must be purchased separately. Size 18-400, Fisher TFE-lined screw cap No. 02-883-3D or equivalent.

6.8 Gas Chromatography System

6.8.1 The GC must be capable of temperature programming and should be equipped with a linearized electron capture detector, fused silica capillary column, and splitless injector (splitless mode, 30 second delay). An auto-sampler/injector is desirable.

6.8.2 Two GC columns are recommended. Column A should be used as the primary analytical column unless routinely occurring analytes are not adequately resolved. Column B is recommended for use as a confirmatory column when GC/MS confirmation is unavailable.

6.8.2.1 Column A -- 0.32 mm ID x 30 m fused silica capillary with chemically bonded methyl polysiloxane phase (DB-1, 1.0 µm film thickness or equivalent). The linear velocity of the helium carrier is established at 23 cm/sec at 35°C. The oven is programmed to hold at 35°C for nine minutes, to increase to 40°C at 1°C/min, and held for three minutes, to increase to 120°C at 6°C/min and held at 120° until all expected compounds have eluted. A temperature of 150°C is then maintained for five minutes. Injector temperature: 200°C. Detector temperature: 290°C (See Table 1 for retention time data).

6.8.2.2 Column B -- 0.32 mm ID x 30 m with chemically bonded 50% trifluoropropyl phase (DB-210, SP-2401, 0.5 µm film thickness or equivalent). The linear velocity of the helium carrier gas is established at 27 cm/sec. The column temperature is programmed to hold at 30°C for 11 minutes, to increase to 120°C

at 10°C/min and held at 120°C until all expected compounds have eluted. A temperature of 150°C is then maintained for five minutes. (See Table 1 for retention data).

6.9 pH Meter -- Capable of accurate measurement of pH (±0.2 units) in the range, pH = 4-8. For laboratory or field measurement of sample pH.

6.10 pH Paper -- Narrow ranges, pH = 3-5.5 and pH = 6.0-8.0. For measurement of initial and adjusted sample pH in the field.

7.0 REAGENTS AND CONSUMABLE MATERIALS

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 Acetone -- High purity, demonstrated to be free of analytes.

7.1.3 Sodium chloride, NaCl -- ACS reagent grade. Before use pulverize a batch of NaCl and place in muffle furnace, increase temperature to 400°C and hold for 30 minutes. Store in a capped bottle.

7.2 Reagent Water -- Reagent water is defined as purified water which does not contain any measurable quantities of the analyte 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 11.2.

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

7.3.1 Prepare stock standard solutions (5 mg/mL) for the THM's and the six solvents by accurately weighing approximately 0.05 g of pure material. Dilute to volume with methanol in a 10 mL volumetric flask. Accurate standards for the more volatile analytes may be prepared in the following manner.

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

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

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

7.3.2 Prepare stock standard solutions (5.0 mg/mL) for the eight remaining chlorination byproducts (Section 1.1) by accurately weighing about 0.0500 g of pure material. Dissolve the material in acetone and dilute to volume in a 10 mL volumetric flask. Acetone is employed because decomposition has been observed during storage in methanol for the dihaloacetonitriles, chloropicrin and 1,1,1-trichloropropanone-2.

7.3.3 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. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

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

7.3.5 The stored THM stock standards in methanol are stable for up to six months. The solvent standards in methanol are stable at least four months. The other analytes stored in acetone are stable for at least four months except for chloral hydrate. Initially, fresh chloral hydrate standards should be prepared weekly, until the stability of this analyte is determined.

7.4 Primary Dilution Standards -- Prepare primary dilution standards by combining and diluting stock standards in methanol (THMs and solvents) or acetone (remaining disinfection byproducts). The primary dilution standards should be prepared at concentrations that can be easily diluted to prepare aqueous calibration standards (Section 9.1) that will bracket the working concentration range. Store the primary dilution standard solutions at 4°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 7.3.5 apply to primary dilution standards.

7.5 Method Analytes -- Known commercial sources of the analytes are given below.

ANALYTE	SOURCES
Bromodichloromethane	Columbia Chemicals Camden, S.C. Pfalz and Bauer Waterbury, Conn.
Bromochloroacetonitrile	Columbia
Bromoform	Aldrich Chemical Milwaukee, WI
Carbon Tetrachloride	Aldrich
Chloral Hydrate	Sigma Chemical St. Louis, MO
Chloroform	Aldrich Burdick and Jackson
Chloropicrin	Pfalz and Bauer Eastman
Dibromoacetonitrile	Aldrich Pfalz and Bauer
Dibromochloromethane	Pfalz and Bauer
1,2-Dibromoethane	Aldrich
1,2-Dibromo-3-chloropropane	Columbia
Dichloroacetonitrile	Pfalz and Bauer
1,1-Dichloropropanone-2	Aldrich
Tetrachloroethylene	Aldrich
Trichloroacetonitrile	Aldrich Columbia Pfalz and Bauer
1,1,1-Trichloroethane	Aldrich
Trichloroethylene	Aldrich
1,1,1-Trichloro-2-propanone	

7.6 Hydrochloric Acid Solutions, 0.2 and 1.0 N -- Prepare solutions for adjustment of sample pH by serial dilution of ACS reagent grade hydrochloric acid (HCl).

7.7 Stock Solution of Internal Standard(s) -- Prepare a solution of in-ternal standard(s) in methanol at concentration(s) of 0.5-1.0 mg/mL. Dilute an aliquot of the solution with methanol by an appropriate factor (e.g., 1:100) required for the internal standard fortification solution used in preparing calibration standards (Section 9.1.2) or for-tifying aqueous samples (Section 11.1.3).

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection, Dechlorination, and Preservation

8.1.1 The analyte list of Section 1.1 may be conveniently divided into three classes: the four THM's, the six halogenated solvents (Section 1.2) and the eight remaining organic disinfection by-products. The halogenated solvents are quite stable compounds by design and stability upon storage after collec-tion is not an issue. Likewise, the THM's are preserved by the addition of any of the following common dechlorination reagents, sodium sulfite or thiosulfate, ascorbic acid and ammonium chloride. If the sample assay is only for the THM's and/or solvents, the acidification step in Section 8.1.3 should be omitted and only dechlorination reagent added as specified in Section 8.1.2. Thiosulfate, sulfite and ascorbic acid promote the decomposition of some members of the third class of analytes, e.g., the dihaloacetonitriles and chloropicrin, and may not be used as dechlorination reagents in their analysis. In addition, many of these analytes require the acidification step in Section 8.1.3 for storage stability. Thus analysis for the total analyte list requires the use of ammonium chloride for dechlorination and sample acidification.

NOTE: However, the possible exception of a separate sampling requirement for chloral hydrate in Section 8.1.8.

8.1.2 Add the dechlorination reagent as the neat material to the 40 mL sample vials (Section 6.1) immediately before shipment to the field. The reagent amounts are 4 mg for sodium thiosulfate or sulfite and ammonium chloride and 25 mg for ascorbic acid. Alternatively, for the first three reagents, 100 µL of a freshly prepared solution at a concentration of 40 mg/mL may be added to the sample vial just before sample collection (Section 8.1.4). Any of these reagents may be used for the THM's, whereas ammonium chloride must be employed for the simultan-eous measurement in a single sample of all the analytes listed (Section 1.1). As described in Section 8.1.8, the measurement of chloral hydrate may require the collection of a separate sample dechlorinated with sodium sulfite or ascorbic acid.

8.1.3 Adjustment of sample pH -- Prior to sample collection, the amount of HCl required to reduce the sample pH to the range, 4.5-5.0 must be measured. Collect 40 mL samples and add to 100 mL beakers containing 10 mg ammonium chloride. Measure the initial pH with the narrow range pH paper, 6.0-8.0 (Section 6.10), or a pH meter. Initially, adjust the sample pH to the range 4.5-5.0 with the 0.2 N HCl solution by dropwise addition with a Pasteur pipet (Section 6.6). Measure the pH during addition with the narrow range pH paper, 3.0-5.5, or a pH meter. If greater than 10 drops are required (ca. 0.1 mL), measure the amount of 1.0 N HCl solution required and use this amount for sample

acidification. Care should be exercised not to adjust the sample pH below the carbonic acid endpoint, pH ≈ 4.2. Below the endpoint, the pH will decrease rapidly with dropwise acid addition. Some of the analytes may not be stable below pH = 4.0. Add the required volume of HCl solution to the 40 mL sample vials (Section 6.1) immediately before collection (Section 8.1.4).

8.1.4 Collect all samples in duplicate. Fill sample bottles to just overflowing but take care not to flush out the dechlorination and preservation 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.

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

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

8.1.7 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 suffi-cient ice to ensure that they will be at 4°C on arrival at the laboratory.

8.1.8 In some matrices dechlorinated with ammonium chloride, forti-fied matrix recoveries of chloral hydrate have been lower than expected by 50% or greater, when compared to the same sample dechlorinated with ascorbic acid or sodium sulfite. In other matrices, recoveries have been normal. The reason for these differences has not been determined. Any analyst employing this method must demonstrate that ammonium chloride is a suitable dechlorination agent for chloral hydrate in the matrix of concern by determining matrix recoveries as outlined in Section 10.6. If problems are encountered, a separate sample, dechlorinated with 100 mg/L sodium sulfite or 625 mg/L ascorbic acid, must be collected for the analysis of chloral hydrate. Limited field data obtained to date have indicated better precision for chloral hydrate analyses in samples dechlorinated with sodium sulfite than with ascorbic acid.

8.2 Sample Storage

8.2.1 Store samples at 4°C until analysis. The sample storage area must be free of organic solvent vapors.

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

9.0 CALIBRATION

9.1 Preparation of Calibration Standards

9.1.1 At least three calibration standards are needed. One should contain the analytes at a concentration near to but greater than the method detection limit (Table 2) for each compound; the other two should bracket the concentration range expected in samples. For example, if the MDL is 0.1 µg/L, and a sample expected to contain approximately 1.0 µg/L is to be analyzed, aqueous standards should be prepared at concentrations of 0.2 µg/L, 1.0 µg/L, and 2.0 µg/L.

9.1.2 To prepare a calibration standard, add an appropriate volume of a primary dilution standard to a 35-mL aliquot of reagent water in a 40 mL vial. Use a 25 µL micro syringe and rapidly inject the standard into the middle point of the water volume. Remove the needle as quickly as possible after injection. If required (Section 9.3), add an appropriate volume of the internal standard fortification solution (Section 7.7) in the same manner. The aqueous concentration of internal standard(s) should yield area counts or peak heights equivalent to the medium to upper ranges of analyte concentrations. Mix by inverting the sample vial three times without shaking. Aqueous standards must be prepared fresh daily and extracted immediately after preparation (Section 11.2).

9.1.3 Alternatively, add an appropriate volume of primary dilution standard and internal standard solution to reagent water in a 100 mL volumetric flask and fill to the mark. Mix by inverting three times as in Section 9.1.2. Weigh a 35 mL aliquot of this standard into a precalibrated 40 mL vial.

9.2 External Standard Calibration Procedure

9.2.1 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. Alternatively, if the ratio of response to concentration (response factor) is constant over the working range (≤10% relative standard deviation, [RSD]), linearity to the origin can be assumed, and the average ratio or response factor can be used in place of a calibration curve.

9.2.2 Single-point calibration is sometimes an acceptable alternative to a calibration curve. Prepare single point standards from the primary dilution standard solutions. The single point calibration standard should be prepared at a concentration that produces a response close (±20%) to that of the unknowns.

9.3 Internal Standard (IS) Calibration Procedure -- To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Specific internal standard are not recommended in this method. The method validation data reported in Section 13.0 were obtained by the external calibration procedure.

9.3.1 Extract and analyze each calibration standard according to Section 11.0. Tabulate peak height or area responses against concentration for each compound and internal standard. Calculate response factor (RF) for each compound using Equation 1.

Equation 1

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

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

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

9.4 The working calibration curve, calibration factor, or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any analyte varies from the predicted response by more than ±20%, the test must be repeated using fresh calibration standard. If the fresh calibration standard also deviates by more ±20%, a new calibration curve must be prepared for that compound.

9.4.1 Daily calibration requirements using the external standard calibration procedure are a minimum of two calibration check standards, one at the beginning and one at the end of the analysis day. These check standards should be at two diff-erent concentration levels to verify the calibration curve. For extended periods of analysis (greater than eight hours), it is strongly recommended that check standards be

interspersed with samples at regular intervals during the course of the analysis.

9.4.2 Minimum daily calibration requirements using the internal standard calibration procedure consist of initial analyses of a calibration check standard followed by verification of the internal standard response of each sample applying criterian described in Section 10.4.

10.0 QUALITY CONTROL

10.1 Each laboratory that uses this method is required to operate a formal quality control (QC) program. Minimum QC requirements are initial demonstration of laboratory capability, monitoring internal standard peak area or height in each sample and blank, analysis of laboratory reagent blanks, laboratory fortified blanks, laboratory fortified sample matrices, and QC samples. Additional quality control practices are recommended.

10.2 Laboratory Reagent Blanks (LRB) -- Before processing any samples, the analyst must analyze at least one LRB to demonstrate that all glass-ware 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 within the retention time window of any analyte (Section 11.3.5), the LRB produces a peak that would prevent the determination of that analyte, determine the source of contamination and eliminate the interference before processing samples.

10.3 Initial Demonstration of Capability

10.3.1 Select a representative fortified concentration for each of the target analytes. Concentrations near analyte levels in Table 4 are recommended. Prepare a laboratory control (LC) sample concentrate in acetone or methanol 1000 times more concentrated than the selected concentration. The LC sample concentrate must be prepared independently from the standards used to prepare the calibration curve (Section 9.1). With a syringe, add 100 µL of the LC sample concentrate to each of four to seven 100 mL aliquots of reagent water. Analyze the aliquots according to the method beginning in Section 11.0, but use calibration curves based upon non-extracted standards as called for in Section 10.3.2.

10.3.2 Calculate the mean percent recovery (R) and the standard deviation of the recovery (S_r). The recovery is determined as the ratio of the measured concentration to the actual fortified concentration. The measured concentration must be based upon absolute or non-extracted standards, rather than the extracted aqueous standards called for in Section 9.2.1 or 9.3.1. Prepare absolute calibration curves by injecting known standards in MTBE, which span the range of fortified concentrations measured. For each analyte, the mean recovery value

must fall in the range of R ±30% or within R ±3Sr, if broader, using the values for R and S for reagent water in Table 4. The standard deviation should be less than ±30% or $3S_r$, whichever is larger. 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 a minimum of five fresh samples until satisfactory performance has been demonstrated.

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

10.3.4 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 10.3.1.

10.4 Assessing the Internal Standard

10.4.1 When using the internal standard calibration procedure, the analyst is expected to monitor the IS response (peak area or peak height) of all samples during each analysis day. The IS response for any sample chromatogram should not deviate from daily calibration standard's IS response by more than 30%.

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

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

10.4.2.2 If a deviation of greater than 30% is obtained for the reinjected extract, analysis of the samples should be repeated beginning with Section 11.0, provided the sample is still available. Otherwise, report results obtained from the reinjected extract, but annotate as suspect.

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

10.4.3.1 If the check standard provides a response factor (RF) within 20% of the predicted value, then follow procedures itemized in Section 10.4.2 for each sample failing the IS response criterion.

10.4.3.2 If the check standard provides a response factor which deviates more than 20% of the predicted value, then the analyst must recalibrate, as specified in Section 9.0.

10.5 Laboratory Fortified Blank (LFB)

10.5.1 The laboratory must analyze at least one LFB sample with every 20 samples or one per sample set (all samples extracted within a 24-hour period), whichever is greater. Fortified concentrations near those in Table 4 are recommended. The LFB sample must be prepared from a standard mix, which is prepared separately and independently from the standards used to prepare the calibration curve. Calculate the mean accuracy (R), based upon extracted standards as called for in Sections 9.2.1 and 9.3.1. If the accuracy for any analyte falls outside the control limits (see Section 10.5.2), that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

10.5.2 Prepare control charts based on mean upper and lower control limits, $R \pm 3\ S_r$, from accuracy and precision data collected over a period of time. The initial demonstration of capability (Section 10.3) may be used to estimate the initial limits, after correction of recovery data to an accuracy basis. After each four to six new accuracy measurements, recalculate R and S_r using all the data, and construct new control limits. When the total number of data points reach 20, update the control limits by calculating R and S_r using only the most recent 20 data points. At least quarterly, replicates of LFBs should be analyzed to determine the precision of the laboratory measurements. Add these results to the ongoing control charts to document data quality.

10.6 Laboratory Fortified Sample Matrix

10.6.1 The laboratory must add known fortified concentrations of analytes to a minimum of 10% of the routine samples or one fortified sample per sample set, whichever is greater. The concentrations should be equal to or greater than the background concentrations in the sample selected for fortification. Ideally, the concentration should be the same as that used for the laboratory fortified blank (Section 10.5). Over time, samples from all routine sample sources should be fortified.

10.6.2 Calculate the mean percent accuracy, R, of the concentration for each analyte, after correcting the total mean measured concentration, A, from the fortified sample for the back-ground concentration, B, measured in the unfortified sample, i.e.:

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

where C is the fortifying concentration. Compare these values to control limits appropriate for reagent water data collected in the same fashion (Section 10.5).

10.6.3 If the analysis of the unfortified sample reveals the absence of measurable background concentrations, and the added concentrations are those specified in Section 10.5, then the appropriate control limits would be the acceptance limits in Section 10.5.

10.6.4 If the sample contains measurable background concentrations of analytes, calculate mean accuracy of the fortified con-centration, R, for each such analyte after correcting for the background concentration.

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

Compare these values to reagent water accuracy data, R*, at comparable fortified concentrations from Tables 3-5. Results are considered comparable if the measured accuracies fall within the range,

$$R^* \pm 3S_c,$$

where S_c is the estimated percent relative standard devi-ation in the measurement of the fortified concentration. By contrast to the measurement of accuracies in reagent water (Section 10.5.2) or matrix samples without background (Section 10.6.3), the relative standard deviation, S_c, must be expressed as the statistical sum of variation from two sources, the measurement of the total concentration as well as the measurement of background concentration. In this case, variances defined as S^2, are additive and S_c can be expressed as

$$S_c^2 = S_a^2 + S_b^2$$

$$\text{or} \quad S_c = (S_a^2 + S_b^2)^{1/2},$$

where S_a and S_b are the percent relative standard deviations of the total measured concentration and the background concentration respectively. The value of S_a may be esti-mated from the mean measurement of A above or from data at comparable concentrations from Tables 3-5. Likewise, S_b can be measured from repetitive measurements of the background concentration or estimated from comparable concentration data from Tables 3-5.

10.6.5 If the accuracy of any such analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control (Section 10.5), the accuracy problem encountered with the fortified sample is judged to be matrix related, not system related. The result for that analyte in the unfortified sample is labeled

suspect/matrix to inform the data user that the results are suspect due to matrix effects.

10.7 Quality Control Sample (QCS) -- At least quarterly, analyze a QCS from an external source. If measured analyte concentrations are not of acceptable accuracy, check the entire analytical procedure to locate and correct the problem source.

10.8 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 or laboratory duplicates may be analyzed to assess the precision of the environmental measurements or field reagent blanks may be used to assess contamination of samples under site conditions, transportation and storage.

11.0 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. Discard a 5 mL volume of the sample. 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 35 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 an aliquot of the internal standard fortification solution (Section 7.7) into the sample. The aqueous concentration of internal standard(s) must be the same as that used in preparing calibration standards (Section 9.1.2).

11.1.4 Remove the vial cap of each sample and add 8 g NaCl (Section 7.1.3) to the sample vial. Recap and dissolve the NaCl by inverting and shaking the vial vigorously (approximately 20 seconds).

11.2 Sample Extraction

11.2.1 Remove the vial cap and add 2 mL of MTBE with a transfer or automatic dispensing pipet. Recap and shake by hand for one minute. Invert the vial and allow the water and MTBE phases to separate (approximately two minutes).

11.2.2 By using a disposable Pasteur pipet (Section 6.6), transfer a portion of the solvent phase from the 40 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 by using a Pasteur pipet. The remaining MTBE phase may be transferred to a second autosampler vial for a subsequent analysis. Approximately 1.5 mL of the solvent phase can be conveniently transferred from the original 2 mL volume.

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 at 4°C for a maximum of seven days before chromatographic analysis if required.

11.3 Sample Analysis and Identification

11.3.1 The recommended GC operating conditions are described in Sections 6.8.2.1 and 6.8.2.2 along with recommended primary and confirmation columns. Retention data for the primary and confirmation columns are given in Table 1 and examples of separations attained with the primary column are shown in Figures 1 and 2. Other GC columns, chromatographic conditions, or detectors may be used if the requirements of Section 10.0 are met.

11.3.2 Calibrate the system daily as described in Section 9.0. The standards and extracts must be in MTBE.

11.3.3 Inject 1-2 µL of the sample extract and record the resulting peak size in area units. For optimum performance and precision, an autosampler for sample injection and a data system for signal processing are strongly recommended.

11.3.4 Identify sample components by comparison of retention times to retention data from a reference chromatogram. If the retention time of an unknown compound corresponds, within limits (Section 11.3.5), to the retention time of a standard compound, then identification is considered positive.

11.3.5 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested

window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.3.6 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 required by the use of a dissimilar column or by GC-MS.

11.3.7 If the peak area exceeds the linear range of the calibration curve, the final extract should be diluted with MTBE and reanalyzed.

12.0 CALCULATIONS

12.1 Calculate the uncorrected concentrations (Ci) of each analyte in the sample from the response factors or calibration curves generated in Section 9.2.1 or 9.3.1.

12.2 Calculate the corrected sample concentration as:

$$\text{Concentration, } \mu g/L = Ci \times \frac{35}{Vs},$$

where the sample volume, Vs in mL, is equivalent to the net sample weight in grams determined in Sections 11.1.2 and 11.2.4.

13.0 METHOD PERFORMANCE

13.1 Single laboratory (EMSL-Cincinnati) recovery and precision data at three concentrations in a reagent water matrix are presented in Tables 3-5. Accuracy and precision data based on extracted standards for fortified tap water, raw source water and groundwater are presented in Tables 6-8.

14.0 REFERENCES

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6. "Carcinogens-Working with Carcinogens", Publication No. 77-206, Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute of Occupational Safety and Health, Atlanta, Georgia, August 1977.

7. "OSHA Safety and Health Standards, General Industry", (29 CFR 1910), OSHA 2206, Occupational Safety and Health Administration, Washington, D.C. Revised January 1976.

8. "Safety in Academic Chemistry Laboratories", 3rd Edition, American Chemical Society Publication, Committee on Chemical Safety, Washington, D.C., 1979.

TABLE 1. RETENTION DATA

Analyte	Column A Retention Time (min)	Column B Time (min)
Chloroform	5.25	3.09
1,1,1-Trichloroethane	6.37	2.04
Carbon Tetrachloride	7.29	3.41
Trichloroacetonitrile	7.59	5.03
Dichloroacetonitrile	8.72	9.09
Bromodichloromethane	9.02	4.21
Trichloroethylene	9.13	4.38
Chloral Hydrate	9.70	6.56
1,1,-dichloropropanone-2	10.73	11.19
Chloropicrin	15.80	39.94
Dibromochloromethane	16.40	6.40
Bromochloroacetonitrile	16.77	14.43
1,2-Dibromoethane (EDB)	17.40	9.71
Tetrachloroethylene	19.57	6.94
1,1,1-Trichloropropanone	21.36	15.66
Bromoform	23.54	10.73
Dibromoacetonitrile	24.03	17.45
1,2-Dibromo-3-Chloropropane (DBCP)	32.32	20.35

Column A: DB-1, 0.32 mm x 30 m, 1 micron film thickness
Column B: DB-210, 0.32 mm x 30 m, 0.5 micron film thickness

TABLE 2. METHOD DETECTION LIMITS

Analyte	Fortified Conc. (µg/L)	Mean Meas. Conc. (µg/L)	Std. Dev. (µg/L)	Rel. Std. Dev. (%)	Method Detection Limit (µg/L)
Bromochloroacetonitrile	.029	.027	.0030	11.1	.011
Bromodichloromethane	.023	.023	.0018	7.9	.006
Bromoform	.029	.028	.0035	12.7	.012
Carbon Tetrachloride	.020	.019	.0014	7.2	.004
Chloral Hydrate	.035	.037	.0091	24.8	.026
Chloroform	.005	.005	.00063	12.7	.002
Chloropicrin	.029	.030	.0033	11.2	.012
Dibromoacetonitrile	.080	.072	.0097	13.5	.034
Dibromochloromethane	.023	.023	.0034	14.8	.012
1,2-Dibromoethane	.028	.028	.0017	6.0	.006
1,2-Dibromo-3-chloropropane	.043	.041	.0027	6.6	.009
Dichloroacetonitrile	.032	.036	.0063	17.6	.019
1,1-Dichloropropanone-2	.021	.020	.0013	6.7	.005
Tetrachloroethylene	.022	.022	.0013	5.9	.004
Trichloroacetonitrile	.143	.135	.0307	22.7	.092
1,1,1-Trichloroethane	.032	.033	.0025	7.7	.008
Trichloroethylene	.018	.023	.00076	3.4	.002
1,1,1-Trichloropropanone	.043	.044	.0033	7.6	.012

TABLE 3. ANALYTE RECOVERY AND PRECISION DATA FROM SEVEN ANALYSES OF FORTIFIED REAGENT WATER

Analyte	True Conc. (µg/L)	Mean Meas. Conc. (µg/L)	Relative Accuracy (Recovery) (%)	Relative Standard Deviation (%)
Bromochloroacetonitrile	0.14	0.134	96	3.7
Bromodichloromethane	0.86	0.852	99	2.7
Bromoform	0.20	0.218	109	0.7
Chloral Hydrate	1.60	1.03	64	4.6
Chloroform	2.00	1.60	80	2.4
Chloropicrin	0.16	0.132	83	3.8
Dibromoacetonitrile	0.14	0.134	96	5.8
Dibromochloromethane	0.77	0.804	104	1.5
Dichloroacetonitrile	0.21	0.185	88	3.1
1,1-Dichloropropanone-2	0.10	0.082	82	3.0
Trichloroacetonitrile	0.25	0.179	72	5.3
1,1,1-Trichloropropanone-2	0.18	0.150	83	2.8

TABLE 4. ANALYTE RECOVERY AND PRECISION DATA FROM SEVEN ANALYSES OF FORTIFIED REAGENT WATER

Analyte	True Conc. (µg/L)	Mean Meas. Conc. (µg/L)	Relative Accuracy (Recovery) (%)	Relative Standard Deviation (%)
Bromochloroacetonitrile	1.5	1.67	111	2.7
Bromodichloromethane	11.6	12.4	107	2.7
Bromoform	1.9	2.19	115	0.9
Carbon Tetrachloride	2.3	1.98	86	6.9
Chloral Hydrate	23.4	17.1	73	1.6
Chloroform	15.0	15.5	103	3.2
Chloropicrin	1.8	1.62	90	8.9
Dibromoacetonitrile	1.5	1.62	108	5.6
Dibromochloromethane	10.7	12.2	114	2.0
1,2-Dibromoethane	5.0	5.15	103	4.8
1,2-Dibromo-3-chloropropane	5.0	5.60	112	4.7
Dichloroacetonitrile	2.7	2.56	95	1.5
1,1-Dichloropropanone-2	0.92	0.74	80	1.7
Tetrachloroethylene	2.3	1.99	87	6.6
Trichloroacetonitrile	3.6	2.50	69	6.8
1,1,1-Trichloroethane	2.3	2.18	95	8.3
Trichloroethylene	2.3	2.07	90	10
1,1,1-Trichloropropanone-2	2.3	1.95	85	1.9

TABLE 5. ANALYTE RECOVERY AND PRECISION DATA FROM SEVEN ANALYSES OF FORTIFIED REAGENT WATER

Analyte	True Conc. (µg/L)	Mean Meas. Conc. (µg/L)	Relative Accuracy (Recovery) (%)	Relative Standard Deviation (%)
Bromochloroacetonitrile	7.7	7.83	102	5.5
Bromodichloromethane	27	27.0	100	5.4
Bromoform	7.6	7.99	105	1.4
Carbon Tetrachloride	11	9.13	83	13
Chloral Hydrate	42	36.1	86	4.6
Chloroform	54	49.4	91	1.5
Chloropicrin	10	8.37	84	11
Dibromoacetonitrile	7.9	7.60	96	7.9
Dibromochloromethane	42	42.2	100	3.5
1,2-Dibromoethane	10	10.1	101	7.5
1,2-Dibromo-3-chloropropane	10	11.3	113	7.5
Dichloroacetonitrile	11	9.7	88	4.5
1,1-Dichloropropanone-2	4.3	3.19	74	2.7
Tetrachloroethylene	11	9.46	86	12
Trichloroacetonitrile	16	12.1	76	3.7
1,1,1-Trichloroethane	11	8.80	80	11
Trichloroethylene	11	9.24	84	11
1,1,1-Trichloropropanone-2	11	8.5	77	1.6

TABLE 6. ANALYTE RECOVERY AND PRECISION DATA FROM SEVEN ANALYSES OF FORTIFIED TAP WATER

Analyte	Back-ground Conc. (µg/L)	Fortified Conc. (µg/L)	Total Meas. Conc. (µg/L)	Net Conc. (µg/L)	Accuracy (%)	Rel. Std. Dev. (%)
Bromochloroacetonitrile	1.26	4.0	6.31	5.05	126	2.8
Bromodichloromethane	12.5	20.0	23.5	11.0	55	5.2
Bromoform	5.83	8.0	13.41	7.58	95	2.5
Chloral Hydrate	2.72	10.0	9.09	6.37	44	7.2
Chloroform	19.4	15.0	30.3	10.9	70	2.2
Chloropicrin	0.26	4.0	5.23	4.97	124	2.6
Dibromoacetonitrile	2.18	6.0	10.35	8.17	136	1.6
Dibromochloromethane	8.69	20	30.9	22.2	111	3.8
Dichloroacetonitrile	5.35	6.0	11.90	6.55	109	2.7
1,1-Dichloropropanone-2	0.43	2.0	2.36	1.93	98	5.3
Trichloroacetonitrile	0.02	4.0	4.10	4.08	102	3.8
1,1,1-Trichloropropanone-2	1.61	4.0	5.82	4.21	105	3.0

TABLE 7. ANALYTE RECOVERY AND PRECISION DATA FROM SEVEN ANALYSES OF FORTIFIED RAW SOURCE WATER

Analyte	Back-ground Conc. (µg/L)	Fortified Conc. (µg/L)	Total Meas. Conc. (µg/L)	Net Conc. (µg/L)	Accuracy (%)	Rel. Std. Dev. (%)
Bromochloroacetonitrile		4.0	3.67	3.67	92	4.2
Bromodichloromethane	0.06	20.0	20.03	19.97	100	2.1
Bromoform	0.13	8.0	9.14	9.01	111	1.7
Chloral Hydrate		10.0	11.72	11.72	117	1.6
Chloroform	2.08	15.0	19.34	17.26	109	2.7
Chloropicrin		4.0	4.60	4.60	116	4.8
Dibromoacetonitrile		6.0	5.66	5.66	94	4.8
Dibromochloromethane	0.04	20.0	23.18	23.14	111	2.2
Dichloroacetonitrile	0.04	6.0	6.28	6.24	103	1.5
1,1-Dichloropropanone-2		2.0	1.88	1.88	94	1.3
Trichloroacetonitrile		4.0	4.55	4.55	114	6.9
1,1,1-Trichloropropanone-2	0.03	4.0	3.96	3.93	98	2.2

TABLE 8. ANALYTE RECOVERY AND PRECISION DATA FROM SEVEN ANALYSES OF FORTIFIED GROUND WATER

Analyte	Fortified Conc. (µg/L)	Mean Meas. Conc. (µg/L)	Accuracy (%)	Relative Standard Deviation (%)
Bromochloroacetonitrile	2.0	1.55	78	4.8
Bromodichloromethane	12	13.2	110	1.9
Bromoform	2.0	2.03	102	1.9
Chloral Hydrate	12	14.3	119	5.5
Chloroform	16	18.6	116	1.3
Chloropicrin	2.0	1.29	65	7.7
Dibromoacetonitrile	2.0	1.53	77	1.0
Dibromochloromethane	5.0	4.75	95	3.0
Dichloroacetonitrile	3.0	2.68	89	1.8
1,1-Dichloropropanone-2	1.0	0.90	90	2.1
Trichloroacetonitrile	4.0	5.58	140	2.6
1,1,1-Trichloropropanone-2	2.0	1.82	91	2.5

FIGURE 1

Chlorination Byproducts -- DB-1 Primary Column

		Concentration (µg/L)
1.	Chloroform	13.8
2.	TCAN	10.8
3.	DCAN	2.4
4.	BDCM	2.4
5.	MTBE Contaminant	----
6.	CH	17.5
7.	DCP	----
8.	CP	10.0
9.	DBCM	3.2
10.	BCAN	9.9
11.	EDB	4.7
12.	TCP	18.7
13.	Bromoform	11.9
14.	DBAN	5.3
15.	DBCP	2.2

1. Chloroform
2. TCAN
3. DCAN
4. BDCM
5. MTBE Contaminant
6. Chloral hydrate
7. 1,1-Dichloro-2-propanone
8. Chloropicrin
9. DBCM
10. BCAN
11. CNB
12. 1,1,1-TCP
13. Bromoform
14. DBAN
15. DBCP

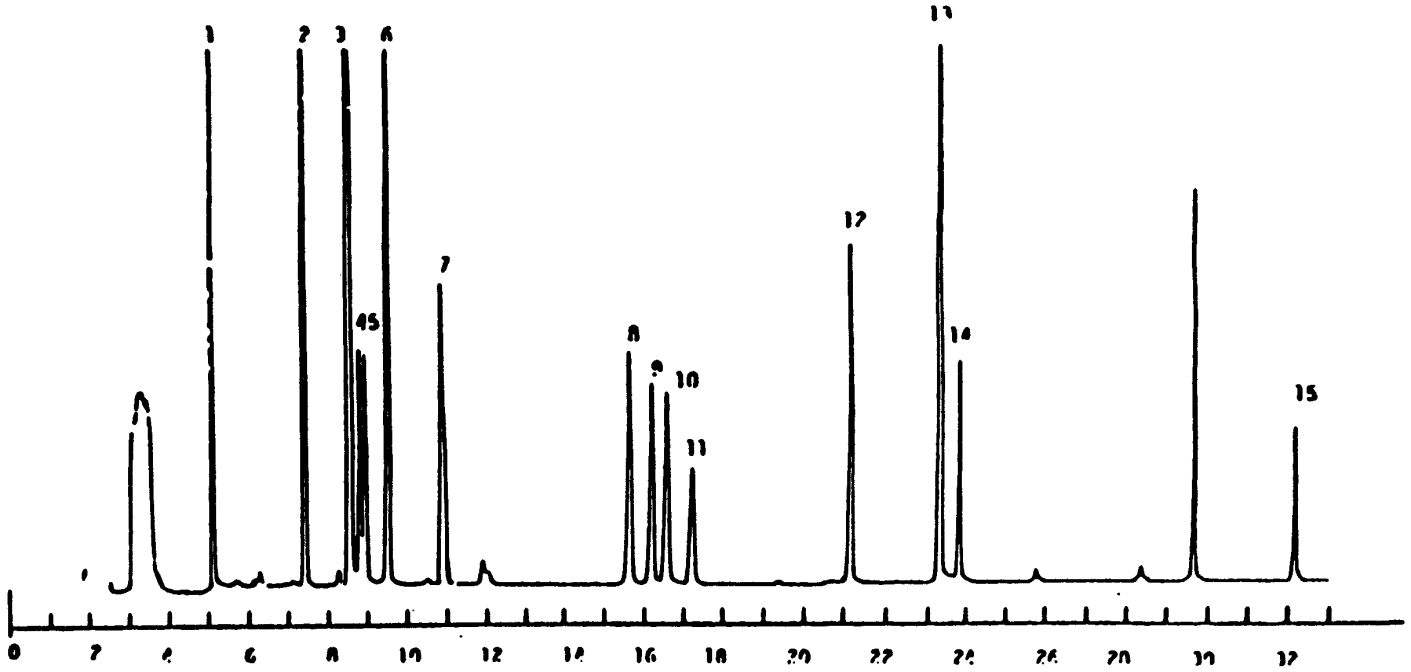
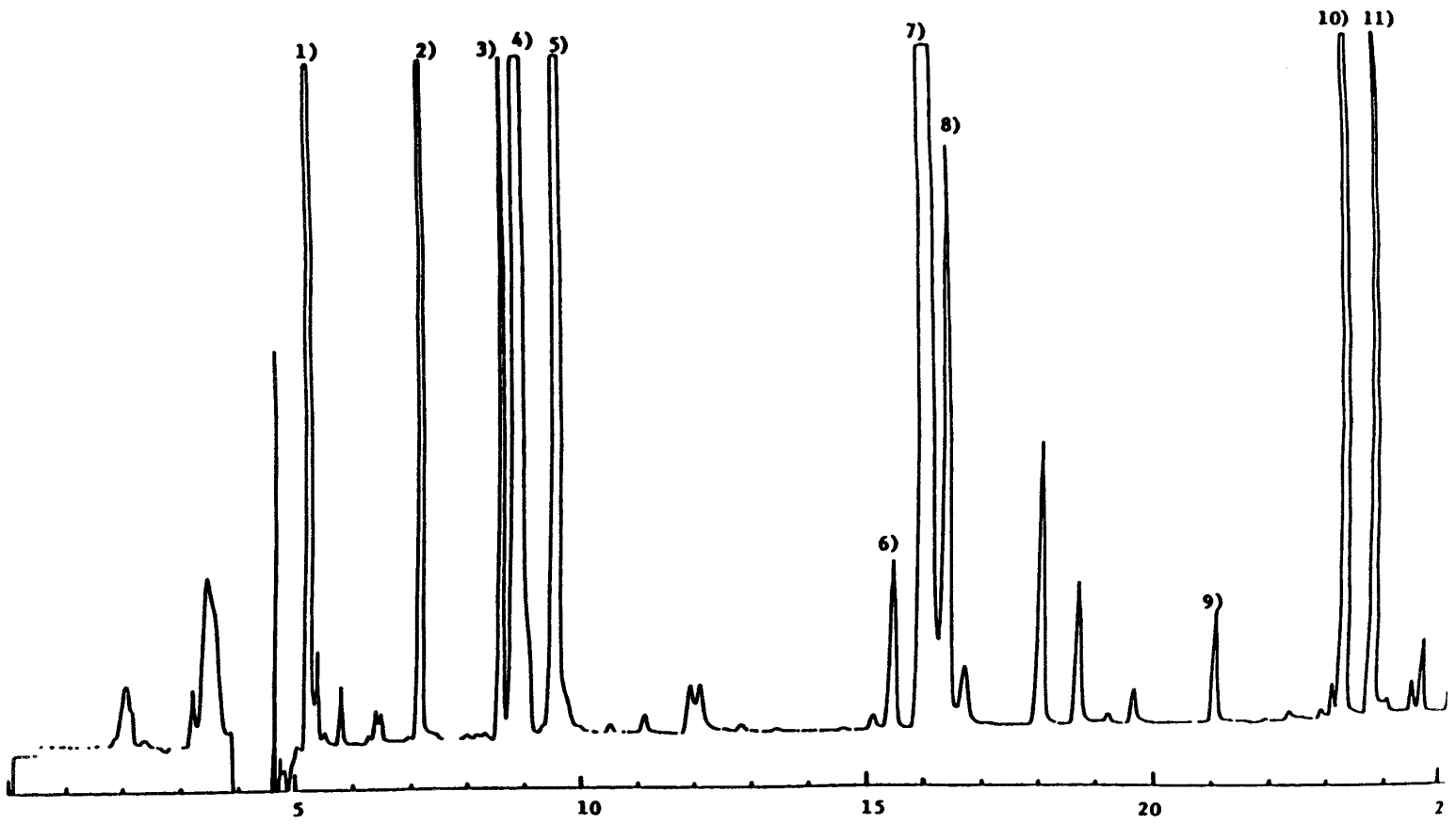


Figure 1

FIGURE 2. TAP WATER CHROMATOGRAM



1) Chloroform - 12.3 µg/L
2) MTBE Impurity - CCl_4
3) Dichloroacetonitrile - 0.5 µg/L
4) Bromodichloromethane - 30.1 µg/L
5) Chloral Hydrate - 20.0 µg/L
6) Chloropicrin - 1.2 µg/L
7) Dibromochloromethane - 30.3 µg/L
8) Bromochloroacetonitrile - 3.6 µg/L
9) 1,1,1-Trichloroacetone - 0.8 µg
10) Bromoform - 7.3 µg/L
11) Dibromoacetonitrile - 2.9 µg/L