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APPENDIX A

Standard method 4500-Cl G. DPD Colorimetric Method

Standard method 5310 C. Persulfate-Ultraviolet Oxidation Method

Standard method 5710 B. Trihalomethane Formation Potential (THMFP)

EPA method 300.1 Determination of inorganic anions in drinking water by ion chromatography

EPA method 551.1 Determination of chlorination disinfection by product, Chlorinated solvents, and halogenated pesticides/herbicides in Drinking water by liquid-liquid extraction and gas chromatography with electron-capture detection

Standard method 4500-Cl G. DPD Colorimetric Method

1. General Discussion

a. Principle: This is a colorimetric version of the DPD method and is based on the same principles. Instread of titration with standard ferrous ammonium sulfate (FAS) solution as in the titrimetric method, a colorimetric procedure is used.

b. Interference: See A.3 and F.1d. Compensate for color and turbidity by using sample to zero photometer. Minimize chromate interference by using the thioacetamide blank correction.

c. Minimum detectable concentration: Approximately 10 μg Cl as Cl_2/L. This detection limit is achievable under ideal conditions; normal working detection limits typically are higher.

2. Apparatus

a. Photometric equipment: One of the following is required:

1) Spectrophotometer, for use at a wavelength of 515 nm and providing a light path of 1 cm or longer.

2) Filter photometer, equipped with a filter having maximum transmission in the wavelength range of 490 to 530 nm and providing a light path of 1 cm or longer.

b. Glassware: Use separate glassware, including separate spectrophotometer cells, for free and combined (dichloramine) measurements, to avoid iodide contamination in free chlorine measurement.

3. Reagents

See F.2a, b, c, d, e, h, I, and j.

4. Procedure

a. Calibration of photometric equipment: Calibrate instrument with chlorine or potassium permanganate solutions.

1) Chlorine solution – Prepare chlorine standards in the range of 0.05 to 4.0 mg/L from about 100 mg/L chlorine water standardized as follows: Place 2 mL acetic acid and 10 to 25 mL chlorine-demand-free water in a flask. Add about 1 g KI. Measure into the flask a suitable volume of chlorine solution. In choosing a convenient volume, note that 1 mL 0.025 *N* $Na_2S_2O_3$ titrant (see

B.2d) is equivalent to about 0.9 mg chlorine. Titrate with standardized 0.025 *N* $Na_2S_2O_3$ titrant until the yellow iodide color almost disappears. Add 1 to 2 mL starch indicator solution and continue titrating to disappearance of blue color.

Determine the blank by adding identical quantities of acid, KI, and starch indicator to a volume of chlorine-demand-free water corresponding to the sample used for titration. Perform blank titration A or B, Whichever applies, according to B.3d.

$$\text{mg Cl as } Cl_2/\text{mL} = \frac{(A+B) \times N \times 35.45}{\text{mL sample}}$$

Where:

N = normality of $Na_2S_2O_3$

A = mL of titrant for sample,

B = mL titrant for blank (to be added or substracted according to required blank titration. See B.3d).

Use chlorine-demand-free water and glassware to prepare these standards. Develop color by first placing 5 mL phosphate buffer solution and 5 mL DPD indicator reagent in flask and adding 100 mL chlorine standard with through mixing as described in b and c below. Fill photometer or colorimeter cell from flask and read color at 515 nm. Return cell contents to flask and titrate with standard FAS titrant as a check on chlorine concentration.

2) Potassium Permanganate solutions – Prepare a stock solution containing 891 mg $KMnO_4$/100mL. Dilute 10.00 mL stock solution to 100 mL with distilled water in a volumetric flask. When 1 mL of this solution is diluted to 100 mL with distilled water, a chlorine equivalent of 1.00 mg/L will be produced in the DPD reaction. Prepare a series of $KMnO_4$ standards covering the chlorine equivalent range of 0.05 to 4 mg/L. Develop color by first placing 5 mL phosphate buffer and 5 mL DPD indicator reagent in flask and adding 100 mL standard with thorough mixing as described in b and c below. Fill photometer or colorimeter cell from flask and read color at 515 nm. Return cell contents to flask and titrate with FAS titrant as a check on any absorption of permanganate by distilled water.

b. Volume of sample: Use a sample volume appropriate to the photometer or colorimeter. The following procedure is based on using 10-mL volumes; adjust reagent quantities proportionately for other sample volumes. Dilute sample with chlorine-demand-free water when total chlorine exceeds 4 mg/L.

c. Free chlorine: Place 0.5 mL each of buffer reagent and DPD indicator reagent in a test tube or photometer cell. Add 10-mL sample and mix. Read color immediately (Reading A).

d. Monochloramine: Continue by adding one very small crystal of KI (about 0.1 mg) and mix. If dichloramine concentration is expected to be high, instead of small crystal add 0.1 mL (2 drops) freshly prepared KI solution (0.1 g/ 100 mL). Read color immediately (Reading B).

e. Dichloramine: Continue by adding several crystals of KI (about 0.1 g) and mix to dissolve. Let stand about 2 min and read color (Reading C).

f. Nitrogen trichloride: Place a very small crystal of KI (about 0.1 mg) in a clean test tube or photometer cell. Add 10 mL sample and mix. To a second tube or cell add 0.5 mL each of buffer and indicator reagents; mix. Add contents to first tube or cell and mix. Read color immediately (Reading N).

g. Chromate correction using thioacetamide: Add 0.5 mL thioacetamide solution (F2i) to 100 mL of sample. After mixing, add buffer and DPD reagent. Read color immediately. Add several crystals of KI (about 0.1 g) and mix to dissolve. Let stand about 2 min and read color. Subtract the first reading from Reading A and the second reading from Reading C and use in calculations.

h. Simplified procedure for total chlorine: Omit step d above to obtain monochloramine and dichloramine together as combined chlorine. To obtain total chlorine in one reading, add the full amount of KI at the start, with the specified amounts of buffer reagent and DPD indicator. Read color after 2 min.

5. Calculation

Reading	NCl_3 Absent	NCl_3 Present
A	Free Cl	Free Cl
B-A	NH_2Cl	NH_2Cl
C-B	$NHCl_2$	$NHCl_2 + ½ NCl_3$
N	-	Free Cl + ½ NCl_3
2(N-A)	-	NCl_3
C-N	-	$NHCl_2$

In the event that monochloramine is present with NCl_3, it will be included in Reading N, in which case obtain NCl_3 from 2 (N-B)

6. Bibliography

See F.6.

5310 C. Persulfate-Ultraviolet Oxidation Method

1. General Discussion

Many instruments utilizing persulfate oxidation of organic carbon are available. They depend either on heat or ultraviolet irradiation activation of the reagents. The persulfate-ultraviolet oxidation method is a rapid, precise method for the measurement of trace levels of organic carbon in water and is of particular interest to the electronic, pharmaceutical, and stream-power-generation industries where even trace concentrations of organic compounds may degrade ion-exchange capacity, serve as a nutrient source for biological growth, or be detrimental to the process for which the water is being utilized.

a. Principle: Organic carbon is oxidized to carbon dioxide, CO_2, by persulfate in the presence of ultraviolet light. The CO_2 produced may be measured directly by a nondispersive infrared analyzer, be reduced to methane and measured by a flame ionization detector, or be chemically titrated.

Instruments are available that utilize an ultraviolet lamp submerged in a continuously gas-purged reactor that is filled with a constant-feed persulfate solution. The samples are introduced serially into the reactor by an autosampler or they are injected manually. The CO_2 produced is sparged continuously from the solution and is carried in the gas stream to an infrared analyzer that is specifically turned to the absorptive wavelength of CO_2. The intrument's microprocessor calculates the area of the peaks produce by analyzer, compares them to the peak area of the calibration standard stored in its memory, and prints out a calibrated organic carbon value in milligrams per liter.

b. Interference: See Section 5310B.1. Excessive acidification of sample, producing a reduction in pH of the persulfate solution to 1 or less, can result in sluggish and incomplete oxidation of organic carbon.

The intensity of the ultraviolet light reaching the sample matrix may be reduced by highly turbid samples or with aging of the ultraviolet source, resulting in sluggish or incomplete oxidation. Large organic particles or very large or complex organic molecules such as tannins, lignins, and humic acid may be oxidized slowly slowly because persulfate oxidation is rate-limited. Because the efficiency of conversion of organic carbon to CO_2 may be affected by many factors, check efficiency of oxidation with selected model compounds representative of the sample matrix.

Persulfate oxidation of organic molecules is slowed in samples containing significant concentrations of chloride by the preferential oxidation of chloride; at a concentration of 0.1% chloride, oxidation of organic matter may be inhibited completely. To remove this interference add mercuric nitrate to the persulfate solution.

With any organic carbon measurement, contamination during sample handling and treatment is a likely source of interference. This is especially true of trace analysis. Take extreme care in sampling, handling, and analysis of samples below 1 mg TOC/L.

c. Minimum detectable concentration: Concentration of 0.05 mg organic carbon/L can be measured if scrupulous attention is given to minimizing sample contamination and method background. More typical blank concentrations are 0.2 to 0.3 mg/L; a reporting level of 0.5 mg/L or greater is usual. Use the combustion-infrared method (B) for high concentrations of TOC.

d. Sampling and storage: See Section 5310B.1d.

2. Apparatus

a. Total organic carbon analyzer

b. Syringes: 0 to 50 μL, 0 to 250 μL, and 0 to 1 μL capacity, fitted with a blunt-tipped needle.

3. Reagents

See Section 5310B.3.

4. Procedure

a. Instrument operation: Follow manufacturer's instructions for assembly, testing, calibration, and operation.

b. Sample preparation: If a sample contains gross particulates or insoluble matter, homogenize until a representative portion can be withdrawn through the syringe needle or autosampler tubing.

If dissolved organic carbon is to be determined, filter sample and a reagent water blank through 0.7 μm glass fiber filter with vacuum. Pretreat filter by submerging overnight in a 1:1 solution of HNO_3 and reagent water and collect in an acid-washed, baked flask. Use a clean filter and flask for each sample.

To determine NPOC, transfer 15 to μL sample to a flask or test tube and acidify to a pH of 2. Purge according to manufacturer's recommendations.

c. Sample injection: See Section 5310B.4c.

d. Standard curve preparation: Prepare an organic carbon standard series over the range of organic carbon concentrations in the samples. Inject standards and blanks and record analyzer's response. Determine peak area for each standard and blank. Determinations based on peak height may be inadequate because of differences in the rate of oxidation of standards and samples. Correct peak area of standards by subtracting reagent water blank and plot organic carbon concentration in milligrams per liter against corrected peak area. For instruments providing a digital readout of concentration, this is not necessary. Inject samples, treatment blanks, if applicable, and instrument blank. Subtract appropriate blank's peak area from each sample's peak area and determine organic carbon from the standard curve.

Characteristic of analysis	Spring water	Spring water + 0.15 mg/L KHP	Tap water	Tap water+ 10 mg/L KHP*	Municipal Wastewater Effluent
Concentration determined, mg/L:					
Replicate 1	0.402	0.559	2.47	11.70	5.88
Replicate 2	0.336	0.491	2.49	11.53	5.31
Replicate 3	0.340	0.505	2.47	11.70	5.21
Replicate 4	0.341	0.523	2.47	11.64	5.17
Replicate 5	0.355	0.542	2.46	11.55	5.10
Replicate 6	0.366	0.546	2.46	11.68	5.33
Replicate 7	0.361	0.548	2.42	11.55	5.35
Mean, mg/L	0.35	0.53	2.46	11.53	5.32
Standard deviation: mg/L					
%	0.02	0.03	0.02	0.21	0.23
Actual value,	6	6	1	2	4
mg/L	-	0.50	-	12.46	-
Recovery, %	-	106	-	93	-
Error, %	-	6	-	7	-

* KHP = potassium acid phthalate.

5. Calculation

See section 5310B.5, but use peak area rather than peak height.

6. Precision and Bias

See Table 5310:I

7. Bibliography

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5710 B. Trihalomethane Formation Potential (THMFP)

1. General Discussion

a. Principle: Under standard conditions, sample are buffered at pH 7.0±0.2, chlorinated with an excess of free chlorine, and stored at 25 ±2 °C for 7 d to allow the reaction to approach completion. As a minimum, pH is buffered at a defined value and a free chlorine residual of 3 to 5 mg Cl_2/L exists at the end of the reaction time. THM concentration is determined by using liquid-liquid extraction (see Section 6232B) or purge and trap (see Section 6230C or D).

b. Interference: If the water was exposed to free chlorine before sample collection (e.g., in a water treatment plant), a fraction of precursor material may have been converted to THM. Take special precautions to avoid loss of volatile THMs by minimizing turbulence and filling sample bottle completely. Interference will be caused by any organic THM-precursor materials present in the reagents or adsorbed on glassware. Heat nonvolumetric glassware to 400 °C for 1 h, unless routine analysis of blanks demonstrates that this precaution is unnecessary. Reagent impurity is unnecessary. Reagent water containing bromide ion or organic impurities. Use high-grade reagent water as free of organic contamination and chlorine demand as possible. If anion exchange is used to remove bromide or organic ions, follow such treatment by activated carbon adsorption (see Section 1080).

Other interferences include volatile organic compounds (VOCs), including THMs and chlorine-demanding substances. VOCs may co-elute with THMs during analysis. THMs or other interfering substances that are present as the result of a chemical spill, etc., will bias the results.

Nitrogenous species and other constituents may interfere in the determination of free residual chlorine. Add enough free chlorine to oxidize chlorine-demanding substances and leave a free chlorine residual of at least 3 mg/L, but not more than 5 mg/L, at the end of the incubation period. A free chlorine residual of at least 3 mg/L decreases the likelihood that a combined residual will be mistaken for a free residual and assures that THM formation occurs under conditions that are reasonably independent of variations in chlorine residual concentrations.

c. Minimum detectable quantity: The sensitivity of the method is determined by the analytical procedure used for THM.

2. Apparatus

a. Incubator, to maintain temperature of 25 ± 2 °C.

b. Bottles, glass, with TFE-lined screw caps to contain 245 to 255 mL, 1-L, 4-L.

c. Vials, glass, 25- or 40-mL with TFE ± 0.1 unit.

d. pH meter, accurate to within ±0.1 unit.

3. Reagents

Prepare aqueous reagents in organic-free water (π 3e below) unless chlorine-demand-free water (π 3f below) is specified.

a. Standardized stock hypochlorite solution: Dilute 1 mL, using a 1-mL volumetric pipet, 5% aqueous soldium hypochlorite (NaOCl, to be referred to as stock hypochlorite) solution to approximately 25 mL with chlorine-demand-free water(see π 3f below), mix well, and titrate to a starch-iodide end point using 0.100 N sodium thiosulfate titrant (see Section 4500-Cl.B). Calculate chlorine concentration of the stock hypochlorite solution as:

$$\text{Stock hypochlorite, mg } Cl_2\text{/mL} = \frac{N \times 35.45 \times \text{mL titrant}}{\text{mL stock hypochlorite added}}$$

Where N is the normality of the titrant (= 0.100). Use at least 10 mL titrant; if less is required, standardize 2 mL stock hypochlorite solution. Measure chlorine concentration each time a dosing solution (π 3b below) is made; discard stock hypochlorite solution if its chlorine concentration is less than 20 mg Cl_2/mL.

b. Chlorine dosing solution, 5 mg Cl_2/mL: Calculate volume of stock hypochlorite solution required to produce a chlorine concentration of 5 mg Cl_2/mL:

$$\text{mL required} = \frac{1250}{\text{stock hypochlorite conc. mg } Cl_2\text{/mL}}$$

c. Phosphate buffer: Dissolve 68.1 g potassium dihydrogen phosphate (anhydrous), KH_2PO_4, and 11.7 g sodium hydroxide, NaOH, in 1 L water. Refrigerate when not in use. If a precipitate develops, filter through a glass fiber filter. After buffer is added to a sample, a pH of 7.0 should result. Check before use with a sample portion that can be discarded.

d. Sodium sulfite solution: Dissolve 10 g sodium sulfite, Na_2SO_3, in 100 mL water. Use for dechlorination: 0.1 mL will destroy about 5 mg residual chlorine. Make fresh every 2 weeks.

e. Organic-free water: Pass distilled or deionized water through granular-activated-carbon columns. A commercial system may be used. Special techniques such as preoxidation, activated carbon adsorption (perhaps accompanied by acidification and subsequent reneutralization), or purging with an inert gas to remove THMs may be necessary.

f. Chlorine-demand-free water: Follow the procedure outlined in 4500-Cl.C.3m, starting with organic-free water. After residual chlorine has been destroyed completely, purge by passing a clean, inert gas through the water until all THMs have been removed.

g. DHBA solution: Dissolve 0.078 g anhydrous 3,5-dihydroxy-benzoic acid (DHBA) in 2 L chlorine-demand-free water. This solution is not stable; make fresh before each use.

h. Nitric or hydrochloric acid, HNO_3 or HCl, concentrations of 1:1, 1:0 N, and 0.1 N.

i. Sodium hydroxide, NaOH, 1.0 N and 0.1 N.

j. Borate buffer (optional): Dissolve 30.9 g anhydrous boric acid, H_3BO_3, and 10.8 g sodium hydroxide, NaOH, in 1 L water. Filter any precipitate that may form with a glass fiber filter. This solution will keep sample pH at 9.2; check before using. Note: waters containing significant amounts of calcium may precipitate calcium phosphate (or carbonate) at high pH values.

k. Mixed buffer (optional): Mix equal amounts of phosphate and borate buffer solutions, then adjust pH as desired before using with samples. Determine the amount of acid or base needed on a separate sample that can be discarded. This mixed buffer is reasonably effective in the pH range of 6 to 11.

4. Procedure

a. Chlorine demand determination: Determine or accurately estimate the 7-d sample chlorine demand. A high chlorine dose is specified below to drive the reaction close to completion quickly. The following procedure yields only a rough estimate of chlorine demand; other techniques may be used.

Pipet 5 mL chlorine dosing solution into a 250-mL bottle, fill completely with chlorine-demand-free water, and cap with a TFE-lined screw cap. Shake well. Titrate 100 mL with 0.025 N sodium thiosulfate to determine the initial chlorine concentration (Ci). This should be about 100 mg Cl_2/L. Pipet 5 mL phosphate buffer and 5 mL chlorine dosing solution into a second 250 mL bottle, fill completely with sample, and seal with a TFE-lined screw cap. Store in the dark for at least 4 h at 25 °C. Calculate chlorine demand as follows:

$$D_{Cl} = C_i - C_R$$

Where:

D_{Cl} = chlorine demand, mg Cl_2/L,

C_R = chlorine residual of sample after at least 4 h storage, mg Cl_2/L, and

C_i = initial (dosed) chlorine concentration, mg Cl_2/L

b. Sample chlorination: If sample contains more than 200 mg/L alkalinity or acidity, adjust pH to 7.0 ± 0.2 using 0.1 or 1.0 N HNO_3, HCl, or NaOH and a pH meter. With a graduated pipet, transfer appropriate volume of the 5 mg Cl_2/ml chlorine dosing solution, V_D, into sample bottle:

$$V_D = \frac{D_{Cl} + 3}{5} \times \frac{V_S}{1000}$$

where:

V_S = volume of sample bottle, mL, and

V_D = volume of dosing solution required, mL.

Add 5 mL phosphate buffer solution if using a 250-mL sample bottle (or 1 mL buffer/50 mL sample) and fill completely with sample. Immediately seal with

a TFE-lined screw cap, shake well, and store in the dark at 25± 2° C for 7 d. Analyze a reagent blank (π 4d) with each batch of samples. To increase the likelihood of achieving the desired chlorine residual concentration (3 to 5 mg/L) at the end of the 7-d reaction period, dose interval sample portions to provide a range of chlorine concentrations, with each chlorine dose differing in increments of 2 mg Cl_2/L.

c. Sample analysis: After the 7-d reaction period, place 0.1 mL sulfite reducing solution in a 25-mL vial and gently and completely fill vial with sample. If free chlorine residual has not been determined previously, measure it using a method accurate to 0.1 mg/L and able to distinguish free and combined chlorine (see Section 4500-Cl). Adjust pH to the value required by the method chosen for chlorine analysis. [Note: If other by-products are to be measured, a different quenching agent may be needed (see 5710D.4). Also, if sample portions have been dosed with different chlorine concentrations, first determine the free chlorine residual and select only that portion having the required chlorine residual concentration of 3 to 5 mg/L for further processing.] If THMs will not be analyzed immediately, lower the pH to < 2 by adding 1 or 2 drops of 1:1 HCl to the reduced sample in the vial. Seal vial with TFE-lined screw cap. /store samples at 4 °C until ready for THM analysis (preferably no longer than 7 d). Let sample reach room temperature before beginning analysis.

d. Reagent blank: Add 1 mL chlorine dosing solution to 50 mL phosphate buffer, mix, and completely fill a 25-mL vial, seal with a TFE-lined screw cap, and store with samples. (Note: This reagent blank is for quality control of reagent solutions only and is not a true blank, because the reagent concentrations in this blank are considerably higher than those in samples THM concentrations in the reagent blank will be biased high and cannot be subtracted from sample values. Make no further dilutions before the reaction because the reagent water itself might contribute to THM formation.) After reaction for 7 d, pipet 1 mL sulfite reducing solution into a 250-mL bottle and add, without stirring, 5.0 mL reacted reagent mixture. Immediately fill bottle with organic-free water that has been purged free of THMs and seal with a TFE-lined screw cap. Mix. Analyze a portion of this reagent blank for THMs using the same method used

for samples. The sum of all THM compounds in the reagent blank should be less than 5 μg TTHM as $CHCl_3$/L.

The reagent blank is a rough measure of THMs contributed by reagents added to the samples, but it cannot be used as a correction factor. If the reagent blank is greater than 5% of the sample value or greater than 5μg TTHM/L, whichever is larger, additional treatment for reagent water is necessary. See Section 1080. It also may be necessary to obtain reagents of higher purity. Analyze a reagent blank each time samples are analyzed and each time fresh reagents are prepared.

5. Calculation

Report concentration of each of the four common THM compounds separately because it is desirable to know their relative concentrations. Larger amounts of bromine-substituted compounds, relative to chlorine-substituted compounds, indicate a higher concentration of dissolved bromide in the water (see Figure 5710:1). Also report free chlorine concentration at end of reaction time along with the incubation time, temperature, and pH.

THM concentrations may be reported as a single value as micrograms $CHCl_3$ per liter (μg $CHCl_3$/L), or micromoles per liter (μM). Do not use the simple sum of mass units micrograms per liter except when required for regulatory reporting. Compute TTHM concentration using one of the following equations:

To report TTHM in units of μg $CHCl_3$/L:

$$TTHM = A + 0.728B + 0.574C + 0.472D$$

Where:

A = μg $CHCl_3$/L

B = μg $CHBrCl_2$/L,

C = μg $CHBr_2Cl$/L, and

D = μg $CHBr_3$/L

To report TTHM in units of μM as $CHCl_3$:

$$TTHM = \frac{TTHM, \mu g\ CHCl_3/L}{119}$$

To report TTHM on a weight basis as μg/L (not used except for regulatory purposes):

$$TTHM = A + B + C + D$$

To report a change of TTHM concentration over 7 d:

$$\Delta THMFP = TTHM_7 - TTHM_0$$

Finally, if $TTHM_0 = 0$, then:

$$THMFP = TTHM_7 = \Delta\ THMFP$$

Do not make blank correction or a correction for sample dilution resulting from addition of reagents. If conditions differ from pH of 7, 25 °C, 7-d reaction time, and 3-5 mg/L chlorine residual, report these nonstandard test conditions with the results. Nonstandard test conditions may mimic water quality conditions in a specific distribution system or may be relevant to other investigations (see Section 5710C).

6. Quality Control

a. Use dihydroxy-benzoic acid solution (DHBA) as a quality-control check, especially for the presence of interfering bromides in reagents or reagents water.

   Dilute 1.0 mL chlorine dosing solution to 1000 mL with chlorine-demand-free water (diluted chlorine dosing solution). Pipet 5 mL phosphate buffer solution (pH = 7.0) into each of two 250-mL bottles; add 1.00 mL DHBA solution to one bottle and fill both bottles completely with diluted chlorine dosing solution; seal with TFE-lined screw caps. Store in the dark for 7 d at 25 ± 2°C, and analyze as directly in π 4c.

b. The THMs concentration of the solution containing the added DHBA minus the THM concentration of the blank (i.e., the bottle that does not contain added DHBA, which is a true blank for this application only and differs from

the reagent blank discussed in π 4b above) should be about 119 μg/L THM as $CHCl_3$, with essentially no contribution from bromide-containing THMs. If there is a significant contribution from brominated THMs, 10 % or more of the total THM, it may be necessary to remove bromide from the reagent water or to obtain higher-purity reagents containing less bromide. Determine source of bromide and correct the problem. If the THM concentration of water blank exceeds 20 μg/L, treat reagent water to reduce contamination.

7. Precision and Bias

The precision of this method is determined by the analytical precision and bias of the method used for measuring THM as well as the control of variables such as pH, chlorine residual, temperature, sample homogeneity, etc. Method bias can be determined only for synthetic solutions (e.g., the DHBA solution), because THM formation potential is not an intrinsic property of the sample but rather a quantity defined by this method.

Table 5710:I presents single-operator precision and bias data for samples processed under standard conditions. The values were obtained by analyzing DHBA solutions and blanks. The expected value for the samples listed is 116 μg/L TTHM (as $CHCl_3$), rather than 119, because the DHBA reagent used was only 97% pure. Percent recovery was calculated by the formula:

$$\% \text{ recovery} = \frac{\text{DHBA sample} - \text{average blank}}{116} \times 100$$

Table 5710:II presents the same data set, except that the pH of samples and blanks was adjusted to 9.2 with borate buffer. Also included are results for single-operator precision with filtered river-water samples that had been diluted with 2 parts organic-free water to 1 part filtrate, again using borate-buffered samples at a pH of 9.2.

Table 5710:I SINGLE-OPERATOR PRECISION AND BIAS DATA FOR THMFP*

	THM (µg/L)					
Sample	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	THMFP µg/L as $CHCl_3$	Recovery %
Blank 1	0.8	-	-	-	0.8	-
Blank 2	1.9	-	-	-	1.9	-
Blank 3	0.1	0.1	-	-	0.2	-
Blank 4	0.7	-	-	-	0.7	-
Blank 5	0.5	-	-	-	0.5	-
Blank 6	0.7	-	-	-	0.7	-
Average					0.8	-
Standard deviation					±0.6	-
DHBA 1	114.1	0.1	-	-	114.2	97.8
DHBA 2	113.2	-	-	-	113.2	96.9
DHBA 3	107.8	-	-	-	107.8	92.2
DHBA 4	108.3	-	-	-	108.3	92.7
DHBA 5	109.6	0.1	-	-	109.7	93.9
DHBA 6	111.8	0.1	-	-	111.9	95.8
DHBA 7	112.6	-	-	-	112.6	96.4
Average					111.1	95.1
Standard deviation					±2.5	2.2

Source: MOORE, L., Unpublished data. U.S. Environmental Protection Agency, Cincinnati, Ohio.

Expected value = 116

Table 5710:II SINGLE-OPERATOR PRECISION AND BIAS DATA FOR TTHM (pH = 9.2)*

THM µg/L						
Sample	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	TTHM µg/L as $CHCl_3$	Recovery %
Blank 1	3.0	0.3	-	-	3.2	-
Blank 2	1.7	0.1	-	-	1.8	-
Blank 3	1.3	0.1	-	-	1.4	-
Blank 4	1.6	0.1	-	-	1.7	-
Blank 5	2.3	0.2	-	-	2.4	-
Blank 6	2.6	0.1	-	-	2.7	-
Average	2.5	0.2			2.6	-
Standard deviation					2.3	
					± 0.6(± 26.1%)	
					47.9	98.3
DHBA 1	45.4	3.3	3.3	-	53.9	111.2
DHBA 2	51.0	3.9	3.9	-	41.4	84.3
DHBA 3	39.2	3.0	3.0	-	51.0	105.0
DHBA 4	48.3	3.6	3.6	-	50.4	103.7
DHBA 5	47.6	3.7	3.7	-	45.8	93.8
DHBA 6	43.4	3.2	3.2	-	48.7	100.0
DHBA 7	46.0	3.6	3.6	-	48.4	99.5
Average					± 0.6(± 26.1%)	
Standard deviation						
					52.3	
RWS 1	33.1	17.2	11.3	0.5	49.7	
RWS 2	31.7	16.1	10.6	0.5	59.1	
RWS 3	38.7	18.4	11.7	0.6	55.3	
RWS 4	35.1	18.0	11.7	0.8	56.0	
RWS 5	36.0	17.9	11.7	0.6	59.3	
RWS 6	38.7	18.7	11.7	0.6	57.6	
RWS 7	37.7	18.1	11.2	0.6	55.6	

METHOD 300.1

DETERMINATION OF INORGANIC ANIONS IN DRINKING WATER BY ION CHROMATOGRAPHY

Revision 1.0

John D. Pfaff (USEPA, ORD, NERL) - Method 300.0, (1993)

Daniel P. Hautman (USEPA, Office of Water) and David J. Munch (USEPA, Office of Water) - Method 300.1, (1997)

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ERRATA COVER SHEET TO U.S.EPA METHOD 300.1
April 27, 1999

The following were editorial changes which have been incorporated into U.S.EPA Method 300.1. These minor clarifications are incorporated into the body of this text as follows:

ERRATA #1 -
An additional sentence was added to Section 4.1.1 reiterating the analyst's responsibilities when incorporating any method change, including modifying eluent strength, or any other method parameter. The additional sentence states,

> "*...The analyst must verify that these changes do not negatively affect performance by repeating and passing all the QC criteria in Section 9.*"

On this same theme, section 11.9, was also further clarified and specific precautions were added as follows,

> "*...The analysts must verify that this dilution does not negatively affect performance by repeating and passing all the QC criteria in Section 9. As a specific precaution, upon dilution of the carbonate eluent, a peak for bicarbonate may be observed within the retention time window for bromate which will negatively impact the analysis.*"

ERRATA #2 -
An acronym in Section 9.3.2.2 for Laboratory Fortified Blank (LFB) was incorrectly identified as LRB. This typographical error was corrected.

ERRATA #3 -
Clarifications and corrections were made to Section 9.4.1.5, 9.4.3.2 and 9.4.3.3. These clarifications pertain to data reportability for Laboratory Fortified Sample Matrices (LFM) as well as to analysis continuation when Duplicate Sample QC acceptance criteria are not met.

Section 9.4.1.5 clarifies and now specifies how to report data when the LFM recovery falls outside the established control criteria by stating,

> "*...the recovery problem encountered with the LFM is judged to be matrix induced and the results for that sample and the LFM are reported with a "matrix induced bias" qualifier.*"

Section 9.4.3.2 required the correction of a typographical reference by removing "%Diff" in the duplicate sample acceptance criteria and replacing it with the defined RPD, indicating "relative percent difference".

Section 9.4.3.3, also had a "%Diff" reference corrected with RPD and included clarification regarding continuation of an analysis set when a duplicate analysis fails to meet the acceptance criteria. This section now reads,

> "*If the RPD fails to meet these criteria, the samples must be reported with a qualifier identifying the sample analysis result as yielding a poor duplicate analysis RPD. This should not be a chronic problem and if it frequently recurs, (>20% of duplicate analysis) it indicates a problem with the instrument or individual technique.*"

METHOD 300.1

DETERMINATION OF INORGANIC ANIONS IN DRINKING WATER BY ION CHROMATOGRAPHY

1. SCOPE AND APPLICATION

1.1 This method covers the determination of the following inorganic anions in reagent water, surface water, ground water, and finished drinking water. As a result of different specified injection volumes (See conditions in Tables 1A and 1B), these anions are divided between the common anions listed in Part A and the inorganic disinfection by-products listed in Part B. These different injection volumes are required in order to compensate for the relative concentrations of these anions in drinking water and maintain good chromatographic peak shape throughout the expected dynamic range of the detector. Bromide is included in both Part A, due to its importance as a common anion, as well as Part B due to its critical role as a disinfection by-product precursor.

PART A.-- Common Anions

Bromide	Nitrite
Chloride	ortho-Phosphate-P
Fluoride	Sulfate
Nitrate	

PART B.-- Inorganic Disinfection By-products

Bromate	Chlorite
Bromide	Chlorate

1.2 The single laboratory Method Detection Limits (MDL, defined in Sect. 3.11) for the above analytes are listed in Tables 1A, 1B and 1C. The MDL for a specific matrix may differ from those listed, depending upon the nature of the sample and the specific instrumentation employed.

1.2.1 In order to achieve comparable detection limits, an ion chromatographic system must utilize suppressed conductivity detection, be properly maintained and must be capable of yielding a baseline with no more than 5 nS noise/drift per minute of monitored response over the background conductivity.

1.3 This method is recommended for use only by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatograms.

1.4 When this method is used to analyze unfamiliar samples for any of the above anions, anion identification should be supported by the use of a fortified sample matrix covering the anions of interest. The fortification procedure is described in Sect. 9.4.1.

1.5 Users of the method data should state the data-quality objectives prior to analysis. Users of the method must demonstrate the ability to generate acceptable results with this method, using the procedures described in Sect. 9.0.

1.6 Bromide and nitrite react with most oxidants employed as disinfectants. The utility of measuring these anions in treated water should be considered prior to conducting the analysis.

2. SUMMARY OF METHOD

2.1 A small volume of sample, 10 uL for Part A and 50 uL for Part B, is introduced into an ion chromatograph. The anions of interest are separated and measured, using a system comprised of a guard column, analytical column, suppressor device, and conductivity detector.

2.2 The ONLY difference between Parts A and B is the volume of sample analyzed by the ion chromatographic system. The separator columns and guard columns as well as eluent conditions are identical.

3. DEFINITIONS

3.1 ANALYSIS BATCH -- A group of no more than 20 field samples (Field sample analyses include only those samples derived from a field sample matrix. These include the initial and duplicate field samples as well as all Laboratory Fortified Sample Matrices). The analysis batch must include an Initial Calibration Check Standard, an End Calibration Check Standard, Laboratory Reagent Blank, and a Laboratory Fortified Blank. Within an ANALYSIS BATCH, for every group of ten field samples, at least one Laboratory Fortified Matrix (LFM) and either a Field Duplicate, a Laboratory Duplicate or a duplicate of the LFM must be analyzed. When more than 10 field samples are analyzed, a Continuing Calibration Check Standard must be analyzed after the tenth field sample analysis.

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

3.2.1 INITIAL CALIBRATION STANDARDS -- A series of CAL solutions used to initially establish instrument calibration and develop calibration curves for individual target anions.

3.2.2 INITIAL CALIBRATION CHECK STANDARD -- An individual CAL solution, analyzed initially, prior to any sample analysis, which verifies previously established calibration curves.

3.2.3 CONTINUING CALIBRATION CHECK STANDARD -- An individual CAL solution which is analyzed after every tenth field sample analyses

which verifies the previously established calibration curves and confirms accurate analyte quantitation for the previous ten field samples analyzed.

3.2.4 END CALIBRATION CHECK STANDARD -- An individual CAL solution which is analyzed after the last field sample analyses which verifies the previously established calibration curves and confirms accurate analyte quantitation for all field samples analyzed since the last continuing calibration check.

3.3 FIELD DUPLICATES -- 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 field duplicates indicate the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

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

3.5 LABORATORY DUPLICATE -- 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 specifically with the laboratory procedures, removing any associated variables attributed by sample collection, preservation, or storage procedures.

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

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

3.8 LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, 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.

3.9 LINEAR CALIBRATION RANGE (LCR) -- The concentration range over which the instrument response is linear.

3.10 MATERIAL SAFETY DATA SHEET (MSDS) -- Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

3.11 METHOD DETECTION LIMIT (MDL) -- The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

3.12 MINIMUM REPORTING LEVEL (MRL) -- The minimum concentration that can be reported for an anion in a sample following analysis. This defined concentration can be no lower than the concentration of the lowest calibration standard and can only be used if acceptable quality control criteria for this standard are met.

3.13 PERFORMANCE EVALUATION SAMPLE (PE) -- A certified solution of method analytes whose concentration is unknown to the analyst. Often, an aliquot of this solution is added to a known volume of reagent water and analyzed with procedures used for samples. Results of analyses are used to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst.

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

3.15 SURROGATE ANALYTE -- An analyte added to a sample, which is unlikely to be found in any sample at significant concentration, and which is added directly to a sample aliquot in known amounts before any sample processing procedures are conducted. It is measured with the same procedures used to measure other sample components. The purpose of the surrogate analyte is to monitor method performance with each sample.

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

4. INTERFERENCES

4.1 Interferences can be divided into three different categories: direct chromatographic coelution, where an analyte response is observed at very nearly the same retention time as the target anion; concentration dependant coelution, which is observed when the response of higher than typical concentrations of the

neighboring peak overlap into the retention window of the target anion; and, ionic character displacement, where retention times may significantly shift due to the influence of high ionic strength matrices (high mineral content or hardness) overloading the exchange sites in the column and significantly shortening target analyte's retention times.

4.1.1 A direct chromatographic coelution may be solved by changing columns, eluent strength, modifying the eluent with organic solvents (if compatible with IC columns), changing the detection systems, or selective removal of the interference with pretreatment. Sample dilution will have little to no effect. The analyst must verify that these changes do not negatively affect performance by repeating and passing all the QC criteria in Section 9.

4.1.2 Sample dilution may resolve some of the difficulties if the interference is the result of either concentration dependant coelution or ionic character displacement, but it must be clarified that **sample dilution will alter your Minimum Reporting Limit (MRL)** by a proportion equivalent to that of the dilution. Therefore, careful consideration of project objectives should be given prior to performing such a dilution. An alternative to sample dilution, may be dilution of the eluent as outlined in 11.9.

4.1.3 Pretreatment cartridges can be effective as a means to eliminate certain matrix interferences. Prior to using any pretreatment, the analyst should be aware that all instrument calibration standards must be pretreated in exactly the same manner as the pretreated unknown field samples. The need for these cartridges have been greatly reduced with recent advances in high capacity anion exchange columns.

4.1.3.1 Extreme caution should be exercised in using these pretreatment cartridges. Artifacts are known to leach from certain cartridges which can foul the guard and analytical columns causing loss of column capacity indicated by shortened retention times and irreproducible results. Frequently compare your calibration standard chromatograms to those of the column test chromatogram (received when the column was purchased) to insure proper separation and similar response ratios between the target analytes is observed.

4.2 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baselines in an ion chromatogram. These interferences can lead to false positive results for target analytes as well as reduced detection limits as a consequence of elevated baseline noise.

4.3 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

4.4 Any anion that is only weakly retained by the column may elute in the retention time window of fluoride and potentially interfere. At concentrations of fluoride above 1.5 mg/L, this interference may not be significant, however, it is the responsibility of the user to generate precision and accuracy information in each sample matrix.

4.5 Close attention should be given to the potential for carry over peaks from one analysis which will effect the proper detection of analytes of interest in a second, subsequent analysis. Normally, the elution of sulfate (retention time of 13.8 min.) indicates the end of a chromatographic run, but, in the ozonated and chlorine dioxide matrices, which were included as part of the single operator accuracy and bias study (See Table 2B), a small response (200 nS baseline rise) was observed for a very late eluting unknown peak at approximately 23 minutes. Consequently, a run time of 25 minutes is recommended to allow for the proper elution of any potentially interferant late peaks. It is the responsibility of the user to confirm that no late eluting peaks have carried over into a subsequent analysis thereby compromising the integrity of the analytical results.

4.6 Any residual chlorine dioxide present in the sample will result in the formation of additional chlorite prior to analysis. If any concentration of chlorine dioxide is suspected in the sample, the sample must be purged with an inert gas (helium, argon or nitrogen) for approximately five minutes or until no chlorine dioxide remains. This sparging must be conducted prior to ethylenediamine preservation and at time of sample collection.

5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials or procedures.

5.2 Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) should be made available to all personnel involved in the chemical analysis. The preparation of a formal safety plan is also advisable.

5.3 The following chemicals have the potential to be highly toxic or hazardous, consult MSDS.

5.3.1 Sulfuric acid -- When used to prepared a 25 mN sulfuric acid regenerant solution for chemical suppression using a Dionex Anion Micro Membrane Suppressor (AMMS).

6. EQUIPMENT AND SUPPLIES

6.1 Ion chromatograph -- Analytical system complete with ion chromatograph and all required accessories including syringes, analytical columns, compressed gasses and a conductivity detector.

6.1.1 Anion guard column: Dionex AG9-HC, 2 mm (P/N 52248), or equivalent. This column functions as a protector of the separator column. If omitted from the system the retention times will be shorter.

6.1.2 Anion separator column: Dionex AS9-HC column, 2 mm (P/N 52244), or equivalent. The microbore (2 mm) was selected in the development of this method as a means to tighten the bromate elution band and thus reduce the detection limit. An optional column (2 mm or 4 mm) may be used if comparable resolution of peaks is obtained, and the requirements of Sect. 9.0 can be met. The AS9-HC, 2 mm column using the conditions outlined in Table 1A and 1B produced the separation shown in Figures 1 through 4.

6.1.2.1 If a 4 mm column is employed, the injection volume should be raised by a factor of four to 40 uL for Part A anions and 200 uL for Part B anions in order to attain comparable detection limits. A four fold increase in injection volume compensates for the four fold increase in cross sectional surface area of the 4 mm standard bore column over the 2 mm microbore column.

6.1.2.2 Comparable results can be attained using the Dionex, AS9-HC, 4 mm column. MDLs for the part B, inorganic disinfection by-products using this 4 mm column are displayed along with analysis conditions in Table 1C.

6.1.3 Anion suppressor device: The data presented in this method were generated using a Dionex Anion Self Regenerating Suppressor (ASRS, P/N 43187). An equivalent suppressor device may be utilized provided comparable detection limits are achieved and adequate baseline stability is attained as measured by a combined baseline drift/noise of no more than 5 nS per minute over the background conductivity.

6.1.3.1 The ASRS was set to perform electrolytic suppression at a current setting of 100 mA using an external source DI water mode. Insufficient baseline stability was observed using the ASRS in recycle mode.

6.1.4 Detector -- Conductivity cell (Dionex CD20, or equivalent) capable of providing data as required in Sect. 9.2.

6.2 The Dionex Peaknet Data Chromatography Software was used to generate all the data in the attached tables. Systems using a strip chart recorder and integrator or other computer based data system may achieve approximately the same MDL's but the user should demonstrate this by the procedure outlined in Sect. 9.2.

6.3 Analytical balance, ±0.1 mg sensitivity. Used to accurately weigh target analyte salts for stock standard preparation.

6.4 Top loading balance, ±10 mg sensitivity. Used to accurately weigh reagents to prepare eluents.

6.5 Weigh boats, plastic, disposable - for weighing eluent reagents.

6.6 Syringes, plastic, disposable, 10 mL - used during sample preparation.

6.7 Pipets, Pasteur, plastic or glass, disposable, graduated, 5 mL and 10 mL.

6.8 Bottles, high density polyethylene (HDPE), opaque or glass, amber, 30 mL, 125 mL, 250 mL. For sampling and storage of calibration solutions. Opaque or amber due to the photoreactivity of chlorite anion.

6.9 Micro beakers, plastic, disposable - used during sample preparation.

7. REAGENTS AND STANDARDS

7.1 Reagent water: Distilled or deionized water, free of the anions of interest. Water should contain particles no larger than 0.20 microns.

7.2 Eluent solution : Sodium carbonate (CASRN 497-19-8) 9.0 mM. Dissolve 1.91 g sodium carbonate (Na_2CO_3) in reagent water and dilute to 2 L.

7.2.1 This eluent solution must be purged for 10 minutes with helium prior to use to remove dissolved gases which may form micro bubbles in the IC compromising system performance and adversely effecting the integrity of the data.

7.3 Stock standard solutions, 1000 mg/L (1 mg/mL): Stock standard solutions may be purchased as certified solutions or prepared from ACS reagent grade, potassium or sodium salts as listed below, for most analytes. Chlorite requires careful consideration as outline below in 7.3.5.1.

7.3.1 Bromide (Br^-) 1000 mg/L: Dissolve 0.1288 g sodium bromide (NaBr, CASRN 7647-15-6) in reagent water and dilute to 100 mL in a volumetric flask.

7.3.2 Bromate (BrO_3^-) 1000 mg/L: Dissolve 0.1180 g of sodium bromate ($NaBrO_3$, CASRN 7789-38-0) in reagent water and dilute to 100 mL in a volumetric flask.

7.3.3 Chlorate (ClO_3^-) 1000 mg/L: Dissolve 0.1275 g of sodium chlorate ($NaClO_3$, CASRN 7775-09-9) in reagent water and dilute to 100 mL in a volumetric flask.

7.3.4 Chloride (Cl^-) 1000 mg/L: Dissolve 0.1649 g sodium chloride (NaCl, CASRN 7647-14-5) in reagent water and dilute to 100 mL in a volumetric flask.

7.3.5 Chlorite (ClO_2^-) 1000 mg/L: Assuming an exact 80.0 % $NaClO_2$ is amperometrically titrated from technical grade $NaClO_2$ (See Sect. 7.3.5.1). Dissolve 0.1676 g of sodium chlorite ($NaClO_2$, CASRN 7758-19-2) in reagent water and dilute to 100 mL in a volumetric flask.

7.3.5.1 High purity sodium chlorite ($NaClO_2$) is not currently commercially available due to potential explosive instability. Recrystallization of the technical grade (approx. 80%) can be performed but it is labor intensive and time consuming. The simplest approach is to determine the exact % $NaClO_2$ using the iodometric titration procedure (Standard Methods, 19th Ed., 4500-ClO_2.C). Following titration, an individual component standard of chlorite must be analyzed to determine if there is any significant contamination (greater than 1% of the chlorite weight) in the technical grade chlorite standard from any of the Part B components. These contaminants will place a high bias on the calibration of the other anions if all four Part B components are mixed in an combined calibration solution. If these other anions are present as contaminants, a separate chlorite calibration needs to be performed.

7.3.6 Fluoride (F^-) 1000 mg/L: Dissolve 0.2210 g sodium fluoride (NaF, CASRN 7681-49-4) in reagent water and dilute to 100 mL in a volumetric flask.

7.3.7 Nitrate (NO_3^--N) 1000 mg/L: Dissolve 0.6068 g sodium nitrate ($NaNO_3$, CASRN 7631-99-4) in reagent water and dilute to 100 mL in a volumetric flask.

7.3.8 Nitrite (NO_2^--N) 1000 mg/L: Dissolve 0.4926 g sodium nitrite ($NaNO_2$, CASRN 7632-00-0) in reagent water and dilute to 100 mL in a volumetric flask.

7.3.9 Phosphate (PO_4^{3-}-P) 1000 mg/L: Dissolve 0.4394 g potassium dihydrogenphosphate (KH_2PO_4, CASRN 7778-77-0) in reagent water and dilute to 100 mL in a volumetric flask.

7.3.10 Sulfate (SO_4^{2-}) 1000 mg/L: Dissolve 0.1814 g potassium sulfate (K_2SO_4, CASRN 7778-80-5) in reagent water and dilute to 100 mL in a volumetric flask.

NOTE: Stability of standards: Stock standards (7.3) for most anions are stable for at least 6 months when stored at 4°C. Except for the chlorite standard which is only stable for two weeks when stored protected from light at 4°C, and nitrite and phosphate which are only stable for 1 month when stored at 4°C. Dilute working standards should be prepared monthly, except those that contain chlorite, or nitrite and phosphate which should be prepared fresh daily.

7.4 Ethylenediamine (EDA) preservation solution, 100 mg/mL: Dilute 2.8 mL of ethylenediamine (99%) (CASRN 107-15-3) to 25 mL with reagent water. Prepare fresh monthly.

7.5 Surrogate Solution: 0.50 mg/mL dichloroacetate (DCA) prepared by dissolving 0.065 g dichloroacetic acid, potassium salt (Cl_2CHCO_2K, CASRN 19559-59-2) in reagent water and dilute to 100 mL in a volumetric flask.

7.5.1 Dichloroacetate is potentially present in treated drinking waters as the acetate of the organic disinfection by product, dichloroacetic acid (DCAA). Typical concentrations of DCAA rarely exceed 50 ug/L, which, for this worst case example, would represent only a five percent increase in the observed response over the fortified concentration of 1.00 mg/L. Consequently, the criteria for acceptable recovery (90% to 115%) for the surrogate is weighted to 115% to allow for this potential background.

7.5.2 Prepare this solution fresh every 3 months or sooner if signs of degradation are present.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. Volume collected should be sufficient to insure a representative sample, allow for replicate analysis, if required, and minimize waste disposal.

8.2 Special sampling requirements and precautions for chlorite.

8.2.1 Sample bottles used for chlorite analysis must be opaque to protect the sample from light.

8.2.2 When preparing the LFM, be aware that chlorite is an oxidant and may react with the natural organic matter in an untreated drinking water matrix as a result of oxidative demand. If untreated water is collected for chlorite analysis, and subsequently used for the LFM, EDA preservation will not control this demand and reduced chlorite recoveries may be observed.

8.3 Sample preservation and holding times for the anions that can be determined by this method are as follows:

PART A : Common Anions

Analyte	Preservation	Holding Time
Bromide	None required	28 days
Chloride	None required	28 days
Fluoride	None required	28 days
Nitrate-N	Cool to 4°C	48 hours
Nitrite-N	Cool to 4°C	48 hours
ortho-Phosphate-P	Cool to 4°C	48 hours
Sulfate	Cool to 4°C	28 days

PART B : Inorganic Disinfection By-products

Analyte	Preservation	Holding Time
Bromate	50 mg/L EDA	28 days
Bromide	None required	28 days
Chlorate	50 mg/L EDA	28 days
Chlorite	50 mg/L EDA, Cool to 4°C	14 days

8.4 When collecting a sample from a treatment plant employing chlorine dioxide, the sample must be sparged with an inert gas (helium, argon, nitrogen) prior to addition of the EDA preservative at time of sample collection.

8.5 All four anions, in Part B, can be analyzed in a sample matrix which has been preserved with EDA. Add a sufficient volume of the EDA preservation solution (Sect. 7.4) such that the final concentration is 50 mg/L in the sample. This would be equivalent to adding 0.5 mL of the EDA preservation solution to 1 L of sample.

8.6 EDA is primarily used as a preservative for chlorite. Chlorite is susceptible to degradation both through catalytic reactions with dissolved iron salts and reactivity towards free chlorine which exists as hypochlorous acid/hypochlorite ion in most drinking water as a residual disinfectant. EDA serves a dual purpose as a preservative for chlorite by chelating iron as well as any other catalytically destructive metal cations and removing hypochlorous acid/hypochlorite ion by forming an organochloroamine. EDA preservation of chlorite also preserves the integrity of chlorate which can increase in unpreserved samples as a result of chlorite degradation. EDA also preserves the integrity of bromate concentrations by binding with hypobromous acid/hypobromite which is an intermediate formed

as by-product of the reaction of either ozone or hypochlorous acid/hypochlorite with bromide ion. If hypobromous acid/hypobromite is not removed from the matrix further reactions may form bromate ion.

8.7 Degradation of ortho-phosphate has been observed in samples held at room temperature for over 16 hrs (see table 3A). Therefore, samples to be analyzed for ortho-phosphate must not be held at room temperature for more than 12 cumulative hours.

9. QUALITY CONTROL

9.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The requirements of this program consist of an initial demonstration of laboratory performance, and subsequent analysis in each analysis batch (Sect. 3.1) of a Laboratory Reagent Blank, Laboratory Fortified Blank, Instrument Performance Check Standard, calibration check standards, Laboratory Fortified Sample Matrices (LFM) and either Field, Laboratory or LFM duplicate sample analyses. This section details the specific requirements for each of these QC parameters. The laboratory is required to maintain performance records that define the quality of the data that are generated.

9.2 INITIAL DEMONSTRATION OF PERFORMANCE

9.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of accuracy through the analysis of the QCS) and laboratory performance (determination of MDLs) prior to performing analyses by this method.

9.2.2 Quality Control Sample (QCS) -- When beginning the use of this method, on a quarterly basis or as required to meet data-quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a QCS. If the determined concentrations are not within ± 15% of the stated values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding with the initial determination of MDLs or continuing with on-going analyses.

9.2.3 Method Detection Limit (MDL) -- MDLs must be established for all analytes, using reagent water (blank) fortified at a concentration of three to five times the estimated instrument detection limit.[6] To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method over at least three separate days. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = (t) \times (S)$$

where, t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates].
S = standard deviation of the replicate analyses.

9.2.3.1 MDLs should be determined every 6 months, when a new operator begins work or whenever there is a significant change in the background, or instrument response.

9.3 ASSESSING LABORATORY PERFORMANCE

9.3.1 Laboratory Reagent Blank (LRB) -- The laboratory must analyze at least one LRB with each analysis batch (defined Sect 3.1). Data produced are used to assess contamination from the laboratory environment. Values that exceed the MDL indicate laboratory or reagent contamination should be suspected and corrective actions must be taken before continuing the analysis.

9.3.1.1 If conducting analysis for the Part B anions, EDA must be added to the LRB at 50 mg/L. By including EDA in the LRB, any bias as a consequence of the EDA which may be observed in the field samples, particularly in terms of background contamination, will be identified.

9.3.2 Laboratory Fortified Blank (LFB) -- The LFB should be prepared at concentrations similar to those expected in the field samples and ideally at the same concentration used to prepare the LFM. Calculate accuracy as percent recovery (Sect. 9.4.1.3). If the recovery of any analyte falls outside the required concentration dependant control limits (Sect. 9.3.2.2), that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

9.3.2.1 If conducting analysis for the Part B anions, EDA must be added to the LFB at 50 mg/L. The addition of EDA to all reagent water prepared calibration and quality control samples is required not as a preservative but rather as a means to normalize any bias attributed by the presence of EDA in the field samples.

9.3.2.2 Control Limits for the LFB

Concentration range	Percent Recovery Limits
MRL to 10xMRL	75 - 125 %
10xMRL to highest calibration level	85 - 115 %

9.3.2.2.1 These control limits only apply if the MRL is established within a factor of 10 times the MDL. Otherwise, the limits are set at 85% to 115%.

9.3.2.3 The laboratory must use the LFB to assess laboratory performance against the required control limits listed in 9.3.2.2. When sufficient internal performance data become available (usually a minimum of 20-30 analyses), optional control limits can be developed from the percent mean recovery (x) and the standard deviation (S) of the mean recovery. These data can be used to establish the upper and lower control limits as follows:

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

The optional control limits must be equal to or better than those listed in 9.3.2.2. After each five to ten new recovery measurements, new control limits can be calculated using only the most recent 20-30 data points. Also, the standard deviation (S) data should be used to establish an on-going precision statement for the level of concentrations monitored. These data must be kept on file and be available for review.

9.3.3 Instrument Performance Check Solution (IPC) -- The Initial Calibration Check Standard is to be evaluated as the instrument performance check solution in order to confirm proper instrument performance. Proper chromatographic performance must be demonstrated by calculating the Peak Gaussian Factor (PGF), which is a means to measure peak symmetry and monitoring retention time drift in the surrogate peak over time. Critically evaluate the surrogate peak in the initial calibration check standard, and calculate the PGF as follows,

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

where: W(1/2) is the peak width at half height
W(1/10) is the peak width at tenth height

9.3.3.1 The PGF must fall between 0.80 and 1.15 in order to demonstrate proper instrument performance.

9.3.3.2 The retention time for the surrogate in the IPC must be closely monitored on each day of analysis and throughout the lifetime of the analytical column. Small variations in retention time can be anticipated when a new solution of eluent is prepared but if shifts of more than 2% are observed in the surrogate retention time, some type of instrument problem is present. Potential

problems include improperly prepared eluent, erroneous method parameters programmed such as flow rate or some other system problem. The chromatographic profile (elution order) of the target anions following an ion chromatographic analysis should closely replicate the profile displayed in the test chromatogram that was shipped when the column was purchased. As a column ages, it is normal to see a gradual shift and shortening of retention times, but if after several years of use, extensive use over less than a year, or use with harsh samples, this retention time has noticeably shifted to any less than 80% of the original recorded value, the column may require cleaning or replacement. Particularly if resolution problems are beginning to become common between previously resolved peaks. A laboratory must retain a historic record of retention times for the surrogate and all the target anions to provide evidence of an analytical columns vitality.

9.4 ASSESSING ANALYTE RECOVERY AND DATA QUALITY

9.4.1 Laboratory Fortified Sample Matrix (LFM) -- The laboratory must add a known amount of analyte to a minimum of 10% of the field samples within an analysis batch. The LFM sample must be prepared from a sample matrix which has been analyzed prior to fortification. The analyte concentration must be high enough to be detected above the original sample and should adhere to the requirement of 9.4.1.2. It is recommended that the solutions used to fortify the LFM be prepared from the same stocks used to prepare the calibration standards and not from external source stocks. This will remove the bias contributed by an externally prepared stock and focus on any potential bias introduced by the field sample matrix.

9.4.1.1 If the fortified concentration is less than the observed background concentration of the unfortified matrix, the recovery should not be calculated. This is due to the difficulty in calculating accurate recoveries of the fortified concentration when the native sample concentration is so high.

9.4.1.2 The LFM should be prepared at concentrations no greater than five times the highest concentration observed in any field sample. If no analyte is observed in any field sample, the LFM must be fortified no greater than five times the lowest calibration level which as outlined in 12.2 is the minimum reported level (MRL). For example, if bromate is not detected in any field samples above the lowest calibrations standard concentration of 5.00 ug/L, the highest LFM fortified concentration allowed is 25.0 ug/L.

9.4.1.3 Calculate the percent recovery for each analyte, corrected for concentrations measured in the unfortified sample. Percent recovery should be calculated using the following equation: 126

$$R = \frac{C_s - C}{s} \times 100$$

where, R = percent recovery.
C_s = fortified sample concentration
C = sample background concentration
s = concentration equivalent of analyte added to sample.

9.4.1.4 Until sufficient data becomes available (usually a minimum of 20 to 30 analysis), assess laboratory performance against recovery limits of 75 to 125%. When sufficient internal performance data becomes available develop control limits from percent mean recovery and the standard deviation of the mean recovery. The optional control limits must be equal to or better than the required control limits of 75-125%.

9.4.1.5 If the recovery of any analyte falls outside the designated LFM recovery range and the laboratory performance for that analyte is shown to be in control (Sect. 9.3), the recovery problem encountered with the LFM is judged to be matrix induced and the results for that sample and the LFM are reported with a "matrix induced bias" qualifier.

9.4.2 SURROGATE RECOVERY -- Calculate the surrogate recovery from all analyses using the following formula

$$R = \frac{SRC}{SFC} \times 100$$

where, R = percent recovery.
SRC = Surrogate Recovered Concentration
SFC = Surrogate Fortified Concentration

9.4.2.1 Surrogate recoveries must fall between 90-115% for proper instrument performance and analyst technique to be verified. The recovery of the surrogate is slightly bias to 115% to allow for the potential contribution of trace levels of dichloroacetate as the halogenated organic disinfection by-product (DBP) dichloroacetic acid (DCAA) Background levels of this organic DBP are rarely observed above 50 ug/L (0.05 mg/L) which constitutes only 5% of the 1.00 mg/L recommended fortified concentration.

9.4.2.2 If the surrogate recovery falls outside the 90-115% recovery window, a analysis error is evident and sample reanalysis is

required. Poor recoveries could be the result of imprecise sample injection or analyst fortification errors.

9.4.3 FIELD OR LABORATORY DUPLICATES -- The laboratory must analyze either a field or a laboratory duplicate for a minimum of 10% of the collected field samples or at least one with every analysis batch, whichever is greater. The sample matrix selected for this duplicate analysis must contain measurable concentrations of the target anions in order to establish the precision of the analysis set and insure the quality of the data. If none of the samples within an analysis batch have measurable concentrations, the LFM should be employed as a laboratory duplicate.

9.4.3.1 Calculate the relative percent difference (RPD) of the initial quantitated concentration (I_C) and duplicate quantitated concentration (D_c) using the following formula,

$$RPD = \frac{(I_C - D_c)}{([I_C + D_c]/2)} \times 100$$

9.4.3.2 Duplicate analysis acceptance criteria

Concentration range	RPD Limits
MRL to 10xMRL	+/- 20 %
10xMRL to highest calibration level	+/- 10 %

9.4.3.3 If the RPD fails to meet these criteria, the samples must be reported with a qualifier identifying the sample analysis result as yielding a poor duplicate analysis RPD. This should not be a chronic problem and if it frequently recurs (>20% of duplicate analyses) it indicates a problem with the instrument or individual technique.

9.4.4 Where reference materials are available, they should be analyzed to provide additional performance data. The analysis of reference samples is a valuable tool for demonstrating the ability to perform the method acceptably.

9.4.5 In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options, such as the use of different columns, injection volumes, and/or eluents, to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Sect. 9.2 and adhere to the condition of baseline stability found in Sect. 1.2.1.

9.4.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most

productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should perform analysis of quality control check samples and participate in relevant performance evaluation sample studies.

10. CALIBRATION AND STANDARDIZATION

10.1 Establish ion chromatographic operating parameters equivalent to those indicated in Tables 1A or 1B if employing a 2 mm column, Table 1C if employing a 4 mm column.

10.2 Estimate the Linear Calibration Range (LCR) -- The LCR should cover the expected concentration range of the field samples and should not extend over more than 2 orders of magnitude in concentration (For example, if quantitating nitrate in the expected range of 1.0 mg/L to 10 mg/L, 2 orders of magnitude would permit the minimum and maximum calibration standards of 0.20 mg/L and 20 mg/L, respectively.) The restriction of 2 orders of magnitude is prescribed since beyond this it is difficult to maintain linearity throughout the entire calibration range.

10.2.1 If quantification is desired over a larger range, then two separate calibration curves should be prepared.

10.2.2 For an individual calibration curve, a minimum of three calibration standards are required for a curve that extends over a single order of magnitude and a minimum of five calibration standards are required if the curve covers two orders of magnitude. (For example, using the nitrate example cited above in section 10.2, but in this case limit the curve to extend only from 1.0 mg/L to 10 mg/L or a single order of magnitude. A third standard is required somewhere in the middle of the range. For the calibration range of 0.20 mg/L to 20 mg/L, over two orders of magnitude, five calibrations standards should be employed, one each at the lower and upper concentration ranges and the other three proportionally divided throughout the middle of the curve.)

10.3 Prepare the calibration standards by carefully adding measured volumes of one or more stock standards (7.3) to a volumetric flask and diluting to volume with reagent water.

10.3.1 For the Part B anions, EDA must be added to the calibration standards at 50 mg/L. The addition of EDA to all reagent water prepared calibration and quality control samples is required not as a preservative but rather as a means to normalize any bias attributed by the presence of EDA in the field samples.

10.3.2 Prepare a 10.0 mL aliquot of surrogate fortified calibration solution which can be held for direct manual injection or used to fill an autosampler vial. Add 20 uL of the surrogate solution (7.5) to a 20 mL disposable plastic micro beaker. Using a 10.0 mL disposable pipet, place

exactly 10.0 mL of calibration standard into the micro beaker and mix. The calibration standard is now ready for analysis. The same surrogate solution that has been employed for the standards should also be used in the section 11.3.2 for the field samples.

10.4 Using a 2 mm column, inject 10 uL (Part A) or 50 uL (Part B) of each calibration standard. Using a 4 mm column, inject 50 uL (Part A) or 200 uL (Part B) of each calibration standard. Tabulate peak area responses against the concentration. The results are used to prepare calibration curves using a linear least squares fit for each analyte. Acceptable calibration curves are confirmed after reviewing the curves for linearity and passing the criteria for the initial calibration check standard in section 10.5.1. Alternately, if the ratio of response to concentration (response factor) is constant over the LCR (indicated by < 15% 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,

10.4.1 Peak areas are strongly recommended since they have been found to be more consistent, in terms of quantitation, than peak heights. Peak height can tend to be suppressed as a result of high levels of common anions in a given matrix which can compete for exchange sites. Using peak areas, it is the analyst responsibility to review all chromatograms to insure accurate baseline integration of target analyte peaks since poorly drawn baselines will more significantly influence peak areas than peak heights.

10.5 Once the calibration curves have been established they must be verified prior to conducting any sample analysis using an initial calibration check standard (3.2.2). This verification must be performed on each analysis day or whenever fresh eluent has been prepared. A continuing calibration check standard (3.2.3) must be analyzed after every tenth sample and at the end of the analysis set as an end calibration check standard (3.2.4). The response for the initial, continuing and end calibration check must satisfy the criteria listed in 10.5.1. If during the analysis set, the response differs by more than the calibration verification criteria shown in 10.5.1., or the retention times shift more than ± 5% from the expected values for any analyte, the test must be repeated, using fresh calibration standards. If the results are still outside these criteria, sample analysis must be discontinued, the cause determined and/or in the case of drift, the instrument recalibrated. All samples following the last acceptable calibration check standard must be reanalyzed.

10.5.1 Control limits for calibration verification

Concentration range	Percent Recovery Limits
MRL to 10xMRL	75 - 125 %
10xMRL to highest calibration level	85 - 115 %

10.5.1.1 These control limits only apply if the MRL is established within a factor of 10 times the MDL. Otherwise, the limits are set at 85% to 115%.

10.5.2 CALIBRATION VERIFICATION REQUIREMENT FOR PART B
As a mandatory requirement of calibration verification, the laboratory MUST verify calibration using the lowest calibration standard as the initial calibration check standard.

10.5.3 After satisfying the requirement of 10.5.2, the levels selected for the other calibration check standards should be varied between a middle calibration level and the highest calibration level.

11. PROCEDURE

11.1 Tables 1A and 1B summarize the recommended operating conditions for the ion chromatograph. Included in these tables are estimated retention times that can be achieved by this method. Other columns, chromatographic conditions, or detectors may be used if the requirements of Sect. 9.2 are met.

11.2 Check system calibration daily and, if required, recalibrate as described in Sect. 10.

11.3 Sample Preparation

11.3.1 For refrigerated or samples arriving to the laboratory cold, ensure the samples have come to room temperature prior to conducting sample analysis by allowing the samples to warm on the bench for at least 1 hour.

11.3.2 Prepare a 10.0 mL aliquot of surrogate fortified sample which can be held for direct manual injection or used to fill an autosampler vial. Add 20 uL of the surrogate solution (7.5) to a 20 mL disposable plastic micro beaker. Using a 10.0 mL disposable pipet, place exactly 10.0 mL of sample into the micro beaker and mix. Sample is now ready for analysis.

11.3.2.1 The less than 1% dilution error introduced by the addition of the surrogate is considered insignificant.

11.4 Using a Luer lock, plastic 10 mL syringe, withdraw the sample from the micro beaker and attach a 0.45 um particulate filter (demonstrated to be free of ionic contaminants) directly to the syringe. Filter the sample into an autosampler vial (If vial is not designed to automatically filter) or manually load the injection loop injecting a fixed amount of well mixed sample. If using a manually loaded injection loop, flush the loop thoroughly between sample analysis using sufficient volumes of each new sample matrix.

11.5 Using a 2 mm column, inject 10 uL (Part A) or 50 uL (Part B) of each sample. Using a 4 mm column, inject 40 uL (Part A) or 200 uL (Part B) of each sample. Tabulate peak area responses against the concentration. During this procedure, retention times must be recorded. Use the same size loop for standards and

samples. Record the resulting peak size in area units. An automated constant volume injection system may also be used.

11.6 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 each analyte. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.7 If the response of a sample analyte exceeds the calibration range, the sample may be diluted with an appropriate amount of reagent water and reanalyzed. If this is not possible then three new calibration concentrations must be employed to create a separate high concentration curve, one standard near the estimated concentration and the other two bracketing around an interval equivalent to ± 25% the estimated concentration. The latter procedure involves significantly more time than a simple sample dilution therefore, it is advisable to collect sufficient sample to allow for sample dilution or sample reanalysis, if required.

11.8 Shifts in retention time are inversely proportional to concentration. Nitrate, phosphate and sulfate will exhibit the greatest degree of change, although all anions can be affected. In some cases this peak migration may produce poor resolution or make peak identification difficult.

11.9 Should more complete resolution be needed between any two coeluting peaks, the eluent (7.2) can be diluted. This will spread out the run, however, and will cause late eluting anions to be retained even longer. The analysts must verify that this dilution does not negatively affect performance by repeating and passing all the QC criteria in Section 9. As a specific precaution, upon dilution of the carbonate eluent, a peak for bicarbonate may be observed within the retention time window for bromate which will negatively impact the analysis.

11.9.1 Eluent dilution will reduce the overall response of an anion due to chromatographic band broadening which will be evident by shortened and broadened peaks. This will adversely effect the MDLs for each analyte.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Prepare a calibration curve for each analyte by plotting instrument response, as peak area, against standard concentration. Compute sample concentration by comparing sample response with the standard curve. If a sample has been diluted, multiply the response by the appropriate dilution factor.

12.2 Report ONLY those values that fall between the lowest and the highest calibration standards. Samples with target analyte responses exceeding the highest standard should be diluted and reanalyzed. Samples with target analytes identified but quantitated below the concentration established by the lowest

calibration standard should be reported as below the minimum reporting limit (MRL).

12.3 Report results for Part A anions in mg/L and for Part B anions in ug/L.

12.4 Report NO_2^- as N
NO_3^- as N
$HPO_4^=$ as P
Br^- in mg/L when reported with Part A
Br^- in ug/L when reported with Part B

13. METHODS PERFORMANCE

13.1 Tables 1A, 1B, and 1C give the single laboratory (OW OGWDW TSC-Cincinnati) retention times, standard conditions and MDL determined for each anion included in the method. MDLs for the Part A anions were determined in reagent water on the 2 mm column (Table 1A). MDLs for the Part B anions were conducted not only in reagent water but also a simulated high ionic strength water (HIW) on the 2 mm column (Table 1B) and in reagent water on the 4 mm column (Table 1C). HIW is designed to simulate a high ionic strength field sample. It was prepared from reagent water which was fortified with the common anions of chloride at 100 mg/L, carbonate at 100 mg/L, nitrate at 10.0 mg/L as nitrogen, phosphate at 10.0 mg/L as phosphorous, and sulfate at 100 mg/L.

13.2 Tables 2A and 2B give the single laboratory (OW OGWDW TSC-Cincinnati) standard deviation for each anion included in the method in a variety of waters for the standard conditions identified in Table 1A and 1B, respectively.

13.3 Tables 3A and 3B shown stability data for the Part A and B anions, respectively. Each data point in these tables represent the mean percent recovery following triplicate analysis. These data were used to formulate the holding times shown in Sect. 8.3.

14. POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 Quantity of the chemicals purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction," available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N.W., Washington D.C. 20036, (202) 872-4477.

15. WASTE MANAGEMENT

15.1 The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes should be characterized and disposed of in an acceptable manner. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any waste discharge permit and regulations, and by complying with all solid and hazardous waste 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," available from the American Chemical Society at the address listed in Sect. 14.3.

16. REFERENCES

1. "Determination of Inorganic Disinfection By-Products by Ion Chromatography", J. Pfaff, C. Brockhoff. J. Am. Water Works Assoc., Vol 82, No. 4, pg 192.

2. Standard Methods for the Examination of Water and Wastewater, Method 4110B, "Anions by Ion Chromatography", 18th Edition of Standard Methods (1992).

3. Dionex, System DX500 Operation and Maintenance Manual, Dionex Corp., Sunnyvale, California 94086, 1996.

4. Method Detection Limit (MDL) as described in "Trace Analyses for Wastewater," J. Glaser, D. Foerst, G. McKee, S. Quave, W. Budde, Environmental Science and Technology, Vol. 15, Number 12, page 1426, December, 1981.

5. American Society for Testing and Materials. Test Method for Anions in Water by Chemically-Suppressed Ion Chromatography D4327-91. Annual Book of Standards, Vol 11.01 (1993).

6. Code of Federal Regulations 40, Ch. 1, Pt. 136, Appendix B.

7. Hautman, D.P. & Bolyard, M. Analysis of Oxyhalide Disinfection By-products and other Anions of Interest in Drinking Water by Ion Chromatography. Jour. of Chromatog., 602, (1992), 65-74.

8. Standard Methods for the Examination of Water and Wastewater, Method 4500-ClO_2,C "Amperometric Method I" (for the determination of Chlorine Dioxide), 19th Edition of Standard Methods (1995).

17. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

TABLE 1A. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS IN REAGENT WATER FOR THE COMMON ANIONS (PART A).

ANALYTE	PEAK # [1]	RETENTION TIME (MIN.)	MDL DETERMINATION Fort Conc, mg/L	Number of Replicates	DI MDL mg/L
Fluoride	1	2.53	0.020	7	0.009
Chloride	2	4.67	0.020	7	0.004
Nitrite-N	3	6.01	0.010	7	0.001
Surrogate: DCA	4	7.03			
Bromide	5	8.21	0.040	7	0.014
Nitrate-N	6	9.84	0.010	7	0.008
ortho-Phosphate-P	7	11.98	0.040	7	0.019
Sulfate	8	13.49	0.040	7	0.019

Standard Conditions:

Ion Chromatograph: Dionex DX500
Columns : Dionex AG9-HC / AS9-HC, 2 mm
Detector: Suppressed Conductivity Detector, Dionex CD20
Suppressor: ASRS-I, external source electrolytic mode, 100 mA current
Eluent: 9.0 mM Na_2CO_3
Eluent Flow: 0.40 mL/min
Sample Loop: 10 uL

System Backpressure: 2800 psi
Background Conductivity: 22 uS

Recommended method total analysis time: 25 minutes

(1) See Figure 1

TABLE 1B. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS IN BOTH REAGENT WATER AND HIGH IONIC STRENGTH WATER FOR THE INORGANIC DISINFECTION BY-PRODUCTS (PART B).

			MDL DETERMINATION			
ANALYTE	PEAK # [1]	RETENTION TIME (MIN.)	Fort Conc, ug/L	Number of Replicates	DI MDL ug/L	HIW[2] MDL ug/L
Chlorite	1	3.63	2.00	7	0.89	0.45
Bromate	2	4.19	2.00	7	1.44	1.28
Surrogate: DCA	4	7.28				
Bromide	5	8.48	2.00	7	1.44	2.51
Chlorate	6	9.28	2.00	7	1.31	0.78

Standard Conditions:

Ion Chromatograph: Dionex DX500
Columns : Dionex AG9-HC / AS9-HC, 2 mm
Detector: Suppressed Conductivity Detector, Dionex CD20
Suppressor: ASRS-I, external source electrolytic mode, 100 mA current
Eluent: 9.0 mM Na_2CO_3
Eluent Flow: 0.40 mL/min
Sample Loop: 50 uL

System Backpressure: 2800 psi
Background Conductivity: 22 uS

Recommended method total analysis time: 25 minutes

(1) See Figure 2 and 3

(2) HIW indicates High Ionic Strength Water which is a simulated drinking water prepared from reagent water and fortified with chloride at 100 mg/L, carbonate at 100 mg/L, nitrate at 10.0 mg/L as nitrogen, phosphate at 10.0 mg/L as phosphorous, and sulfate at 100 mg/L.

TABLE 1C. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS IN REAGENT WATER FOR THE INORGANIC DISINFECTION BY-PRODUCTS USING AN ALTERNATE 4 mm AS9-HC COLUMN (PART B).

			MDL DETERMINATION		
ANALYTE	PEAK #	RETENTION TIME (MIN.)	Fort Conc, ug/L	Number of Replicates	DI MDL ug/L
Chlorite	1	4.43	2.00	7	1.44
Bromate	2	5.10	2.00	7	1.32
Surrogate: DCA	4	8.82			
Bromide	5	10.11	2.00	7	0.98
Chlorate	6	10.94	2.00	7	2.55

Standard Conditions:

Ion Chromatograph: Dionex DX500
Columns : Dionex AG9-HC / AS9-HC, 4 mm
Detector: Suppressed Conductivity Detector, Dionex CD20
Suppressor: ASRS-I, external source electrolytic mode, 300 mA current
Eluent: 9.0 mM Na_2CO_3
Eluent Flow: 1.25 mL/min
Sample Loop: 200 uL

System Backpressure: 1900 psi
Background Conductivity: 21 uS

Recommended method total analysis time: 25 minutes

TABLE 2A. SINGLE-OPERATOR PRECISION AND RECOVERY FOR THE COMMON ANIONS (PART A).

ANALYTE	MATRIX	UNFORT MATRIX CONC., mg/L	FORT CONC mg/L	# OF REPLC	MEAN mg/L	MEAN %REC	SD(n-1)	%RSD
Fluoride	RW	<MDL[1]	2.00	9	1.79	89.7	0.02	1.18
	SW	0.139	2.00	9	1.75	80.4	0.01	0.56
	GW	0.280	2.00	9	1.97	84.3	0.02	0.85
	CDW	0.807	2.00	9	2.59	89.0	0.01	0.46
Chloride	RW	0.029	50.0	9	49.4	98.7	0.03	0.10
	SW	12.1	50.0	9	58.7	93.3	0.04	0.10
	GW	56.6	50.0	9	100.	---[2]	0.22	0.22
	CDW	16.0	50.0	9	64.9	97.8	0.11	0.16
Nitrite-N	RW	<MDL	1.00	9	0.851	85.1	0.00	0.51
	SW	<MDL	1.00	9	0.780	78.0	0.00	0.40
	GW	0.013	1.00	9	0.879	86.6	0.01	0.77
	CDW	<MDL	1.00	9	0.720	72.0	0.00	0.55
Bromide	RW	<MDL	0.500	9	0.480	96.1	0.00	0.92
	SW	0.028	0.500	9	0.469	88.1	0.00	0.94
	GW	0.153	0.500	9	0.634	96.3	0.00	0.52
	CDW	<MDL	0.500	9	0.431	86.2	0.01	1.28
Nitrate-N	RW	<MDL	10.0	9	9.50	95.0	0.01	0.14
	SW	2.12	10.0	9	10.9	87.7	0.03	0.30
	GW	0.016	10.0	9	9.64	96.3	0.03	0.27
	CDW	1.64	10.0	9	10.9	92.4	0.04	0.41
Phosphate-P	RW	<MDL	10.0	9	9.62	96.2	0.01	0.14
	SW	<MDL	10.0	9	8.70	87.0	0.02	0.18
	GW	<MDL	10.0	9	6.12	61.2	0.28	4.66
	CDW	<MDL	10.0	9	9.15	91.5	0.04	0.42
Sulfate	RW	<MDL	50.0	9	44.8	89.5	0.05	0.11
	SW	47.8	50.0	9	92.1	88.6	0.21	0.23
	GW	105	50.0	9	154	---[2]	0.60	0.39
	CDW	57.8	50.0	9	105	---[2]	0.33	0.32
Surrogate:	RW	----	5.00	9	5.12	102.3	0.50	0.49
	SW	----	5.00	9	5.09	102.3	1.12	1.09
	GW	----	5.00	9	5.16	101.8	0.67	0.66
	CDW	----	5.00	9	5.17	103.1	1.36	1.32

RW = Reagent Water GW = Ground Water
SW = Surface Water CDW = chlorine dioxide treated finished drinking water

(1) <MDL indicates less than method detection limit.
(2) Not calculated since amount fortified was less than unfortified native matrix concentration (See 9.4.1.1.).

TABLE 2B. SINGLE-OPERATOR PRECISION AND RECOVERY FOR THE INORGANIC DISINFECTION BY-PRODUCTS (PART B).

ANALYTE	MATRIX	UNFORT CONC. ug/L	FORT CONC ug/L	# OF REPLC	MEAN ug/L	MEAN %REC	SD(n-1)	%RSD
Chlorite	RW	<MDL[1]	100	9	96.2	96.2	0.95	0.99
			500	9	523	105	3.13	0.60
	HIW	<MDL	100	9	102	102	2.19	2.15
			500	9	520	104	3.64	0.70
	SW	<MDL	100	9	91.4	91.4	1.22	1.33
			500	9	495	99.0	7.54	1.52
	GW	<MDL	100	9	92.9	92.9	1.65	1.77
			500	9	490	98.1	3.40	0.69
	ClW	<MDL	100	9	87.4	87.4	0.59	0.68
			500	9	485	97.1	6.36	1.31
	CDW	292	100	9	396	---[2]	1.64	0.41
			500	9	811	104	4.00	0.49
	O3W	<MDL	100	9	84.4	84.4	0.46	0.54
			500	9	481	96.1	3.24	0.67
Bromate	RW	<MDL	5.00	9	5.04	101	0.45	8.86
			25.0	9	26.5	106	1.71	6.47
	HIW	<MDL	5.00	9	4.88	97.5	0.95	19.5
			25.0	9	25.6	102	1.37	5.37
	SW	<MDL	5.00	9	4.46	89.2	0.58	13.0
			25.0	9	26.3	105	1.10	4.18
	GW	<MDL	5.00	9	5.10	102	0.50	9.75
			25.0	9	22.2	88.9	1.29	5.81
	ClW	<MDL	5.00	9	4.63	92.6	0.77	16.7
			25.0	9	25.1	100	1.64	6.55
	CDW	<MDL	5.00	9	4.14	82.7	0.62	15.1
			25.0	9	25.1	101	1.28	5.09
	O3W	1.45	5.00	9	5.49	80.9	0.61	11.1
			25.0	9	24.1	90.6	1.13	4.69

RW = Reagent Water
HIW = High Ionic strength Water [see note (2) in Table 1B]
SW = Surface Water
GW = Groundwater
ClW = Chlorinated drinking water
CDW = Chlorine dioxide treated drinking water
O3W = Ozonated drinking water

(1) <MDL indicates less than method detection limit.
(2) Not calculated since amount fortified was less than unfortified native matrix concentration (See 9.4.1.1.).

TABLE 2B. SINGLE-OPERATOR PRECISION AND RECOVERY FOR THE INORGANIC DISINFECTION BY-PRODUCTS (PART B) (contd.).

ANALYTE	MATRIX	UNFORT CONC. ug/L	FORT CONC ug/L	# OF REPLC	MEAN ug/L	MEAN %REC	SD(n-1)	%RSD
Bromide	RW	<MDL[1]	20.0	9	20.9	104	0.80	3.82
			100	9	107	107	0.60	0.56
	HIW	3.24	20.0	9	21.8	92.5	0.79	3.63
			100	9	105	102	1.05	1
	SW	31.0	20.0	9	51.3	---[2]	0.97	1.9
			100	9	140.	109	1.88	1.35
	GW	151	20.0	9	172	---[2]	0.78	0.45
			100	9	265	---[2]	2.18	0.82
	ClW	16.3	20.0	9	39.3	115	0.64	1.62
			100	9	125	109	2.00	1.6
	CDW	11.5	20.0	9	34.4	115	0.76	2.22
			100	9	125	113	1.24	0.99
	O3W	39.8	20.0	9	65.4	---[2]	3.67	5.61
			100	9	153	113	1.00	0.65
Chlorate	RW	<MDL	100	9	98.3	98.3	0.80	0.82
			500	9	520	104	4.15	0.8
	HIW	<MDL	100	9	86.1	86.1	1.47	1.7
			500	9	502	100.	4.52	0.9
	SW	3.18	100	9	102	98.3	1.57	1.55
			500	9	513	102	7.11	1.39
	GW	<MDL	100	9	93.5	93.5	2.00	2.14
			500	9	510	102	3.84	0.75
	ClW	34.4	100	9	136	102	1.01	0.74
			500	9	549	103	3.11	0.57
	CDW	121	100	9	223	---[2]	3.20	1.44
			500	9	651	106	3.50	0.54
	O3W	6.15	100	9	106	100	1.20	1.13
			500	9	523	103	2.45	0.47

RW = Reagent Water
HIW = High Ionic strength Water [see note (2) in Table 1B]
SW = Surface Water
GW = Groundwater
ClW = Chlorinated drinking water
CDW = Chlorine dioxide treated drinking water
O3W = Ozonated drinking water

(1) <MDL indicates less than method detection limit.
(2) Not calculated since amount fortified was less than unfortified native matrix concentration (See 9.4.1.1.).

TABLE 2B. SINGLE-OPERATOR PRECISION AND RECOVERY FOR THE INORGANIC DISINFECTION BY-PRODUCTS (PART B)(contd.).

ANALYTE	MATRIX	FORT CONC mg/L	# OF REPLC	MEAN mg/L	MEAN %REC	SD(n-1)	%RSD
Surrogate: DCA	RW	5.00	9	5.11	102	0.93	0.91
(see NOTE below)				4.98	99.5	0.69	0.69
	HIW	5.00	9	5.00	100	0.79	0.79
				4.96	99.2	1.76	1.78
	SW	5.00	9	4.95	98.9	0.70	0.7
				4.99	99.8	1.60	1.61
	GW	5.00	9	5.12	102	0.50	0.49
				5.13	103	0.50	0.49
	ClW	5.00	9	5.15	103	1.73	1.68
				5.13	103	1.12	1.09
	CDW	5.00	9	5.01	100	1.02	1.02
				5.04	101	1.08	1.07
	O3W	5.00	9	4.99	99.8	0.70	0.7
				5.11	101	0.53	0.52

RW = Reagent Water
HIW = High Ionic strength Water [see note (2) in Table 1B]
SW = Surface Water
GW = Groundwater
ClW = Chlorinated drinking water
CDW = Chlorine dioxide treated drinking water
O3W = Ozonated drinking water

NOTE: The surrogate DCA was fortified at 5 mg/L but due to concerns about measuring trace concentrations of bromide with such high concentration of the neighboring surrogate peak, the recommended fortified concentration for the surrogate has been reduced to 1.00 mg/L.

TABLE 3A. STABILITY STUDY RESULTS FOR THE COMMON ANIONS (PART A). 142

ANALYTE	Preservative	Matrix	UNFORT CONC. mg/L	FORT CONC mg/L	Analyte % Recovery Day 0	Day 14	Day 28	See Note
Fluoride	None	RW	<MDL	2.00	89.8	88.3	88.4	
		SW	0.140	2.00	79.9	80.2	80.0	
		GW	0.280	2.00	84.7	87.8	87.0	
		CDW	0.929	2.00	82.9	83.6	81.6	
Chloride	None	RW	<MDL	50.0	98.8	99.1	98.1	
		SW	12.0	50.0	93.4	93.5	92.8	
		GW	56.6	50.0	87.6	87.6	86.5	
		CDW	16.0	50.0	97.9	98.4	97.8	
Nitrite-N	None	RW	<MDL	1.00	85.2	85.5	83.6	
		SW	<MDL	1.00	77.8	76.6	11.9	(1)
		GW	<MDL	1.00	88.2	85.4	56.1	(1)
		CDW	<MDL	1.00	71.9	71.7	73.9	(2)
Bromide	None	RW	<MDL	0.500	95.5	97.0	96.2	
		SW	0.028	0.500	87.5	88.3	86.7	
		GW	0.153	0.500	96.9	96.0	96.1	
		CDW	<MDL	0.500	85.7	87.1	89.2	(2)
Nitrate-N	None	RW	<MDL	10.0	94.9	94.7	94.2	
		SW	2.12	10.0	87.6	87.0	88.7	
		GW	<MDL	10.0	96.5	96.5	95.5	
		CDW	1.64	10.0	92.3	93.3	91.9	
Phosphate-P	None	RW	<MDL	10.0	96.3	95.8	95.2	
		SW	<MDL	10.0	86.9	86.4	85.1	
		GW	<MDL	10.0	62.8	93.1	89.5	(3)
		CDW	<MDL	10.0	91.6	91.4	90.8	
Sulfate	None	RW	<MDL	50.0	89.6	89.3	89.1	
		SW	47.8	50.0	89.0	89.0	88.1	
		GW	105	50.0	97.5	97.3	96.5	
		CDW	57.8	50.0	94.3	94.9	93.8	

NOTES:

(1) Degradation apparent.

(2) Analyte recovery will be adversely effected by reactions with free chlorine.

(3) Phosphate recovery on day 0 is believed to have been adversely effected by biological degradation since the sample sat in the autosampler for 18 hrs prior to analysis

TABLE 3B STABILITY STUDY RESULTS FOR THE INORGANIC DISINFECTION BY-PRODUCTS (PART B).

ANALYTE	Preservative	Matrix	UNFORT CONC. ug/L	FORT CONC ug/L	Analyte % Recovery Day 0	Day 3	Day 10	Day 30	See Note
Chlorite	None	RW	<MDL	500	99.8	100	104	94.3	
		HIW	<MDL	500	99.3	98.5	106	89.3	
		SW	<MDL	500	92	88.5	82.	75.1	(1)
		GW	<MDL	500	93.9	94.5	96.	91.7	
		ClW	<MDL	500	93.7	NA[(1)]	90.	84.7	(2,3)
		CDW	286	500	98.6	101	91.	77.5	(1,3)
		O3W	<MDL	500	10	NA	82.	90.5	(2)
Chlorite	EDA	RW	<MDL	500	101	101	104	95.3	
		HIW	<MDL	500	98.4	98.7	104	95.4	
		SW	<MDL	500	98.3	97.3	97.	92.7	
		GW	<MDL	500	97.7	97.1	97.	92.6	
		ClW	<MDL	500	98.9	NA	96.	92.6	(2)
		CDW	297	500	103	107	102	94.5	
		O3W	<MDL	500	105	NA	96.	91.9	(2)
Bromate	None	RW	<MDL	25.0	93.6	94.1	110	96.1	
		HIW	<MDL	25.0	100	86.0	105	87.7	
		SW	<MDL	25.0	98.7	95.1	105	102	
		GW	<MDL	25.0	79.4	92.4	77.	82.2	
		ClW	<MDL	25.0	102	NA	101	103	(2)
		CDW	<MDL	25.0	104	96.8	98.	92.1	
		O3W	2.27	25.0	87.3	NA	84.	99.9	(2)
Bromate	EDA	RW	<MDL	25.0	97.3	95.3	99.	102	
		HIW	<MDL	25.0	86.9	86.1	107	91.2	
		SW	<MDL	25.0	100	104	103	94.9	
		GW	<MDL	25.0	83.2	101	88.	88.3	
		ClW	<MDL	25.0	105	NA	101	102	(2)
		CDW	<MDL	25.0	117	97.3	98.	83.9	
		O3W	2.32	25.0	92.6	NA	84.	88.9	(2)

See bottom of next page for explanation of notes

TABLE 3B. STABILITY STUDY RESULTS FOR THE INORGANIC DISINFECTION BY-PRODUCTS (PART B)(contd.)

ANALYTE	Preservative	Matrix	UNFORT CONC. ug/L	FORT CONC ug/L	Analyte % Recovery Day 0	Day 3	Day 10	Day 30	See Note
Bromide	None	RW	<MDL	100	99.4	97.2	107	101	
		HIW	<MDL	100	102	103	105	105	
		SW	30.6	100	102	97.1	107	99.1	
		GW	149	100	97.7	95.3	109	100	
		ClW	4.73	100	8.9	NA(1)	37.	11.4	(2,3)
		CDW	<MDL	100	5.78	23.1	38.	51.3	(3)
		O3W	30.4	100	98.3	NA	120	108	(2)
Bromide	EDA	RW	<MDL	100	98.4	98.6	107	100	
		HIW	<MDL	100	104	103	106	105	
		SW	30.5	100	99.5	98.2	107	100	
		GW	149	100	100	97	114	97.7	
		ClW	11.9	100	101	NA	115	97.4	(2,3)
		CDW	6.14	100	101	96.5	119	110	(3)
		O3W	31.0	100	97.3	NA	122	102	(2)
Chlorate	None	RW	<MDL	500	102	102	105	97.4	
		HIW	<MDL	500	96.5	97.8	101	95.4	
		SW	5.84	500	99.8	97.8	100	96	
		GW	<MDL	500	99.5	98.7	101	99.8	
		ClW	37.8	500	102	NA	104	98.2	(2)
		CDW	125	500	102	99.9	104	99.6	
		O3W	8.34	500	100	NA	103	97.3	(2)
Chlorate	EDA	RW	<MDL	500	104	98.6	103	97.3	
		HIW	<MDL	500	97.3	103	100	95	
		SW	6.70	500	99.7	98.2	99.	95.6	
		GW	<MDL	500	102	97	101	99.3	
		ClW	38.2	500	101	NA	102	96.1	(2)
		CDW	123	500	102	96.5	105	97.7	
		O3W	8.62	500	98.4	NA	103	96.4	(2)

NOTES:

(1) Degradation in the unpreserved matrix is apparent.

(2) NA indicates "NOT ANALYZED"

(3) Analyte recovery will be adversely effected by reactions with free chlorine.

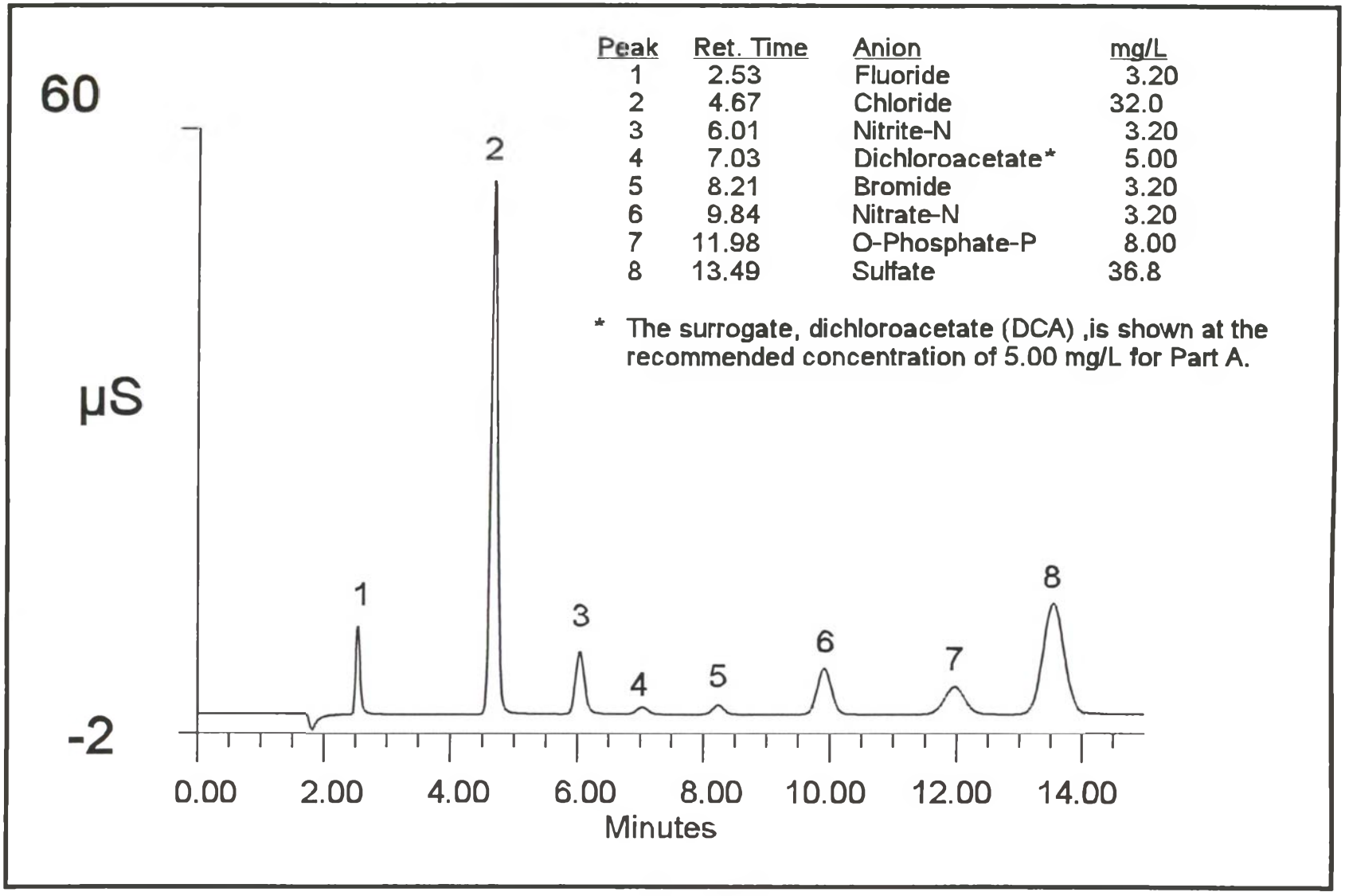

Figure 1. Chromatogram showing separation of the Part A common anions on the AS9-HC column. See Table 1A for analysis conditions.

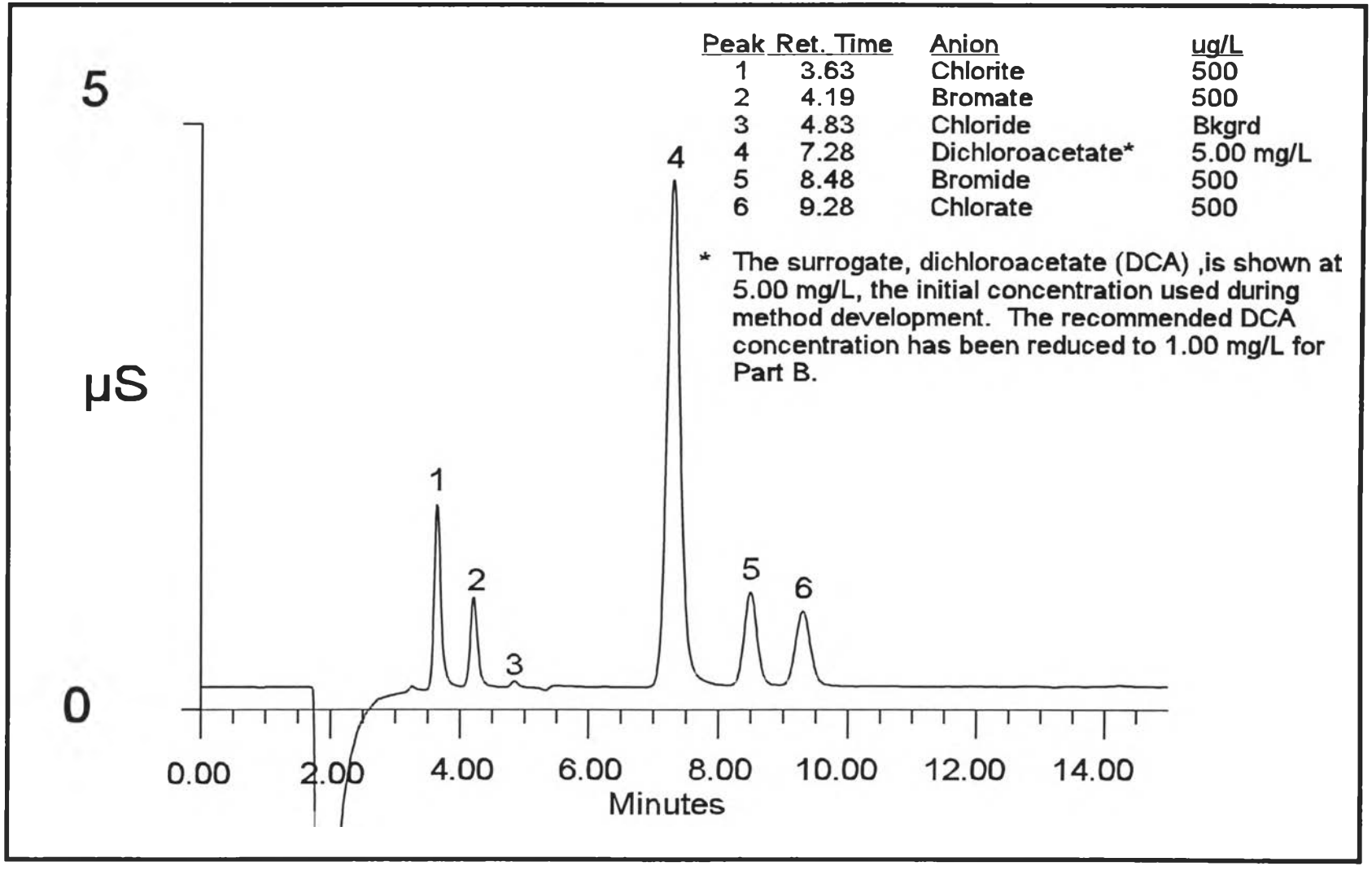

Figure 2 Chromatogram showing separation of the Part B inorganic DBPs and bromide on the AS9-HC column. See Table 1B for analysis conditions.

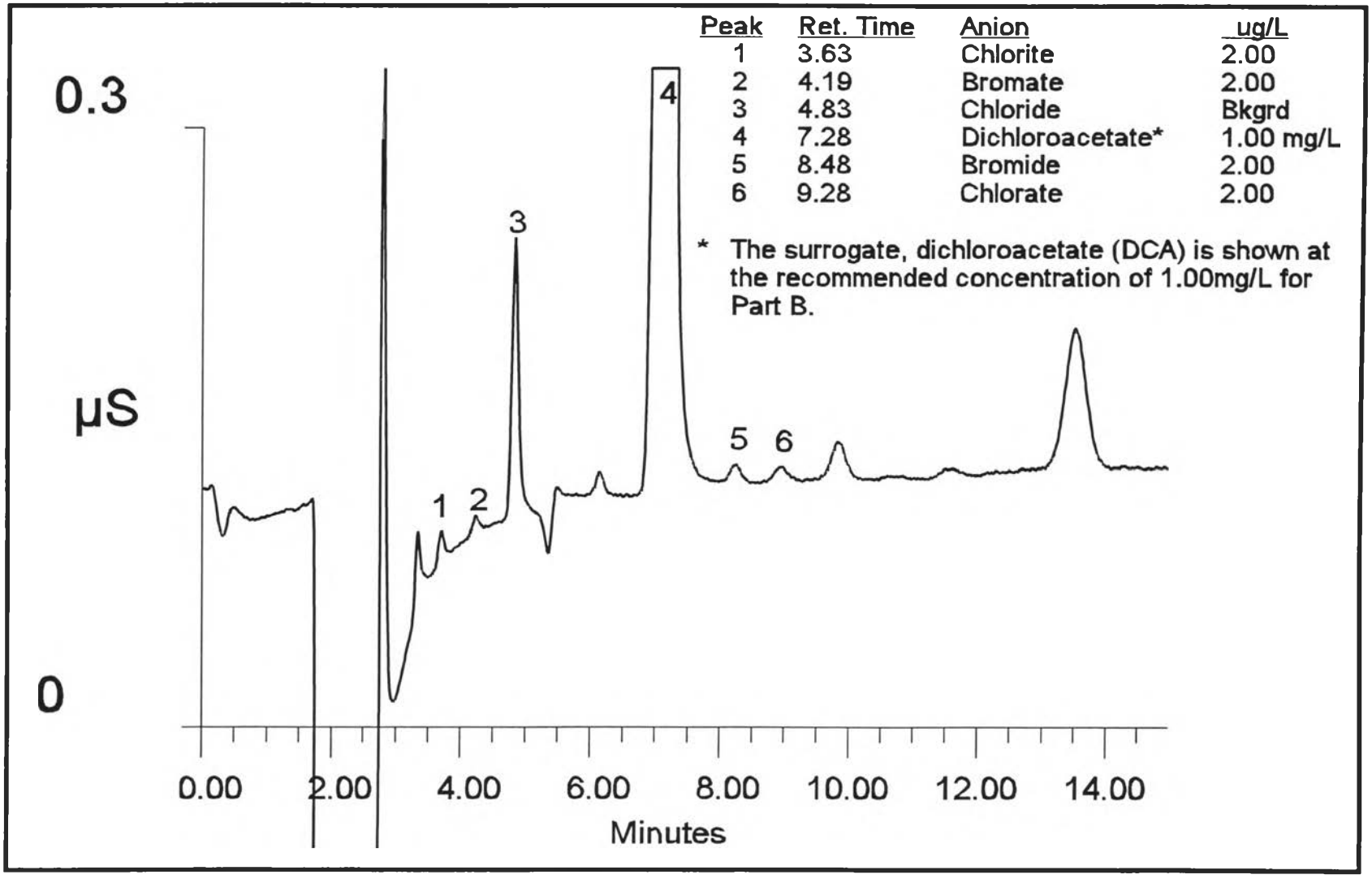

Figure 3. Chromatogram of the inorganic DBPs and bromide (Part B) during the MDL determination in reagent water. See Table 1B for analysis conditions.

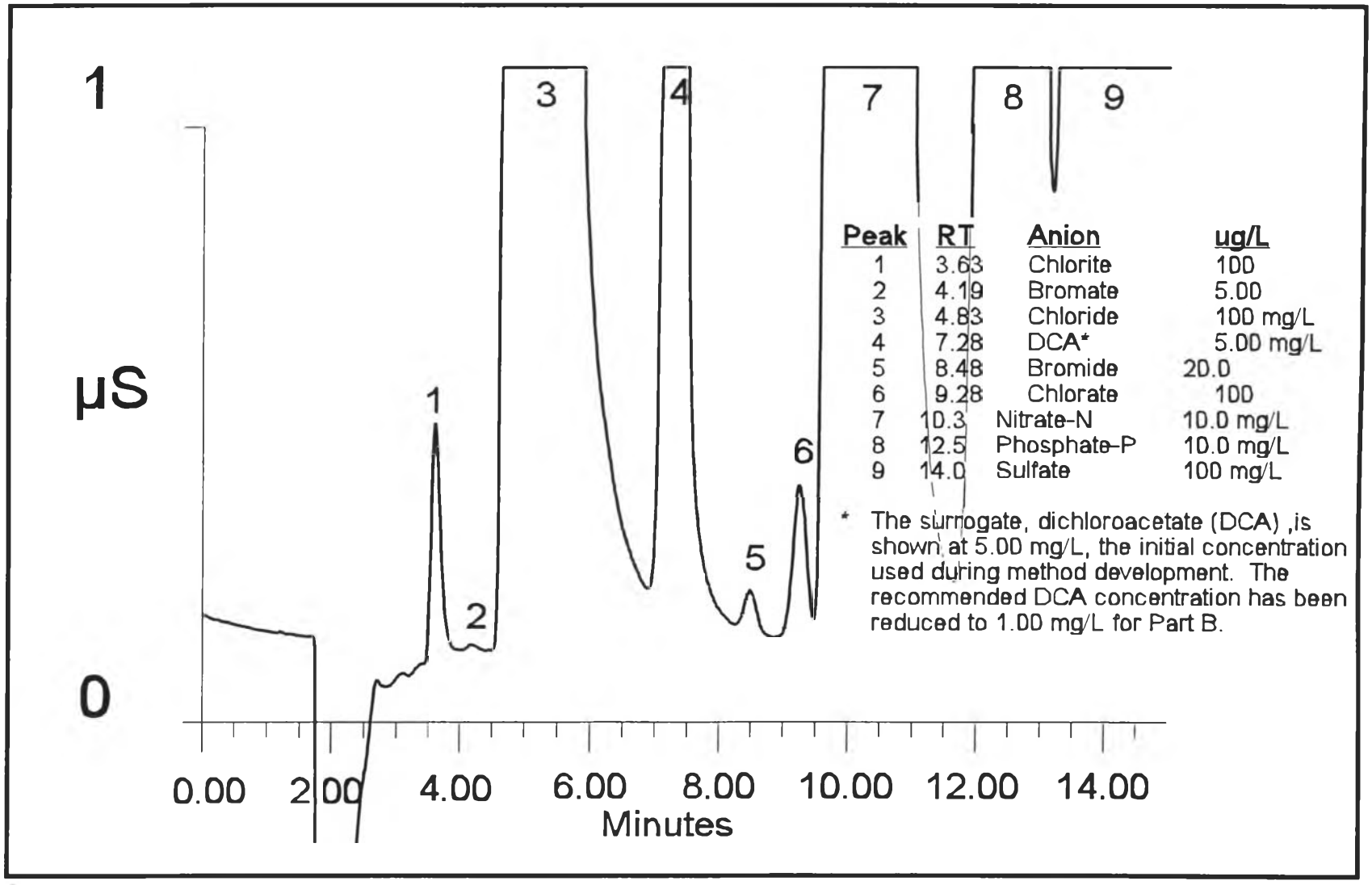

Figure 4. Chromatogram of the inorganic DBPs and bromide (Part B) in high ionic strength water (HIW). See Table 1B for analysis conditions.

METHOD 551.1

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

Revision 1.0

J.W. Hodgeson, A.L. Cohen - Method 551, (1990)

D.J. Munch (USEPA, Office of Water) and D.P. Hautman (International Consultants, Inc.) - Method 551.1, (1995)

NATIONAL EXPOSURE RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
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METHOD 551.1

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

1.0 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

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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 EQUIPMENT AND SUPPLIES (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.

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

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

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

7.3.6 Stock Solution of Internal Standard (IS) -- Use of an IS is optional when MTBE is the extraction solvent but mandatory if pentane is used. This is due to the high volatility of pentane when compared to MTBE (see boiling points, 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.

$$\% \text{ REC}_s = \frac{Sam_{SR}}{Cal_{SR}} \times 100$$

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.

16.0 REFERENCES

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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* 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

*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

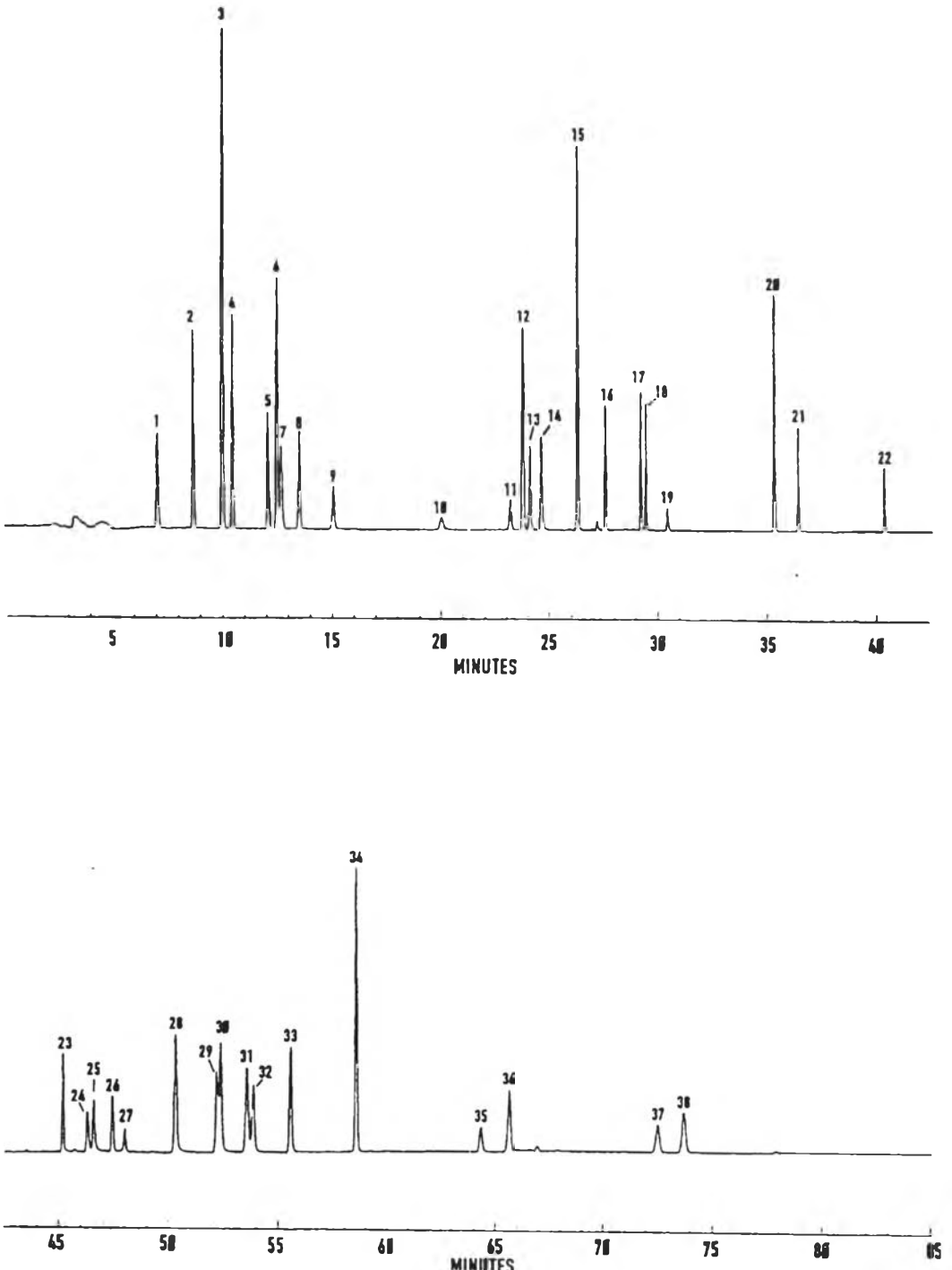

Figure 1. Fortified reagent water extract using MTBE on primary DB-1 column

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

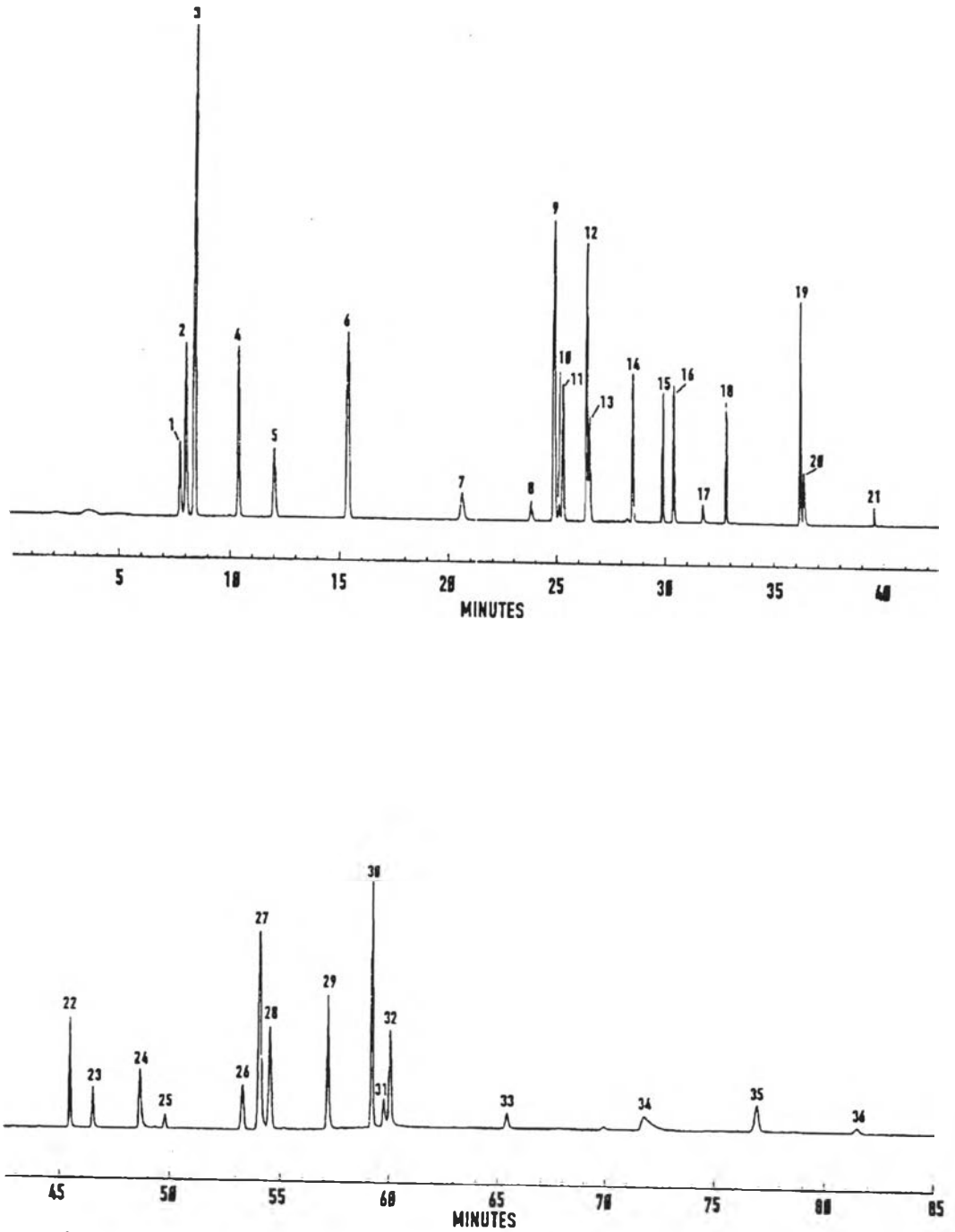

Figure 2. Fortified reagent water extract using MTBE on confirmation Rtx-1301 column

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

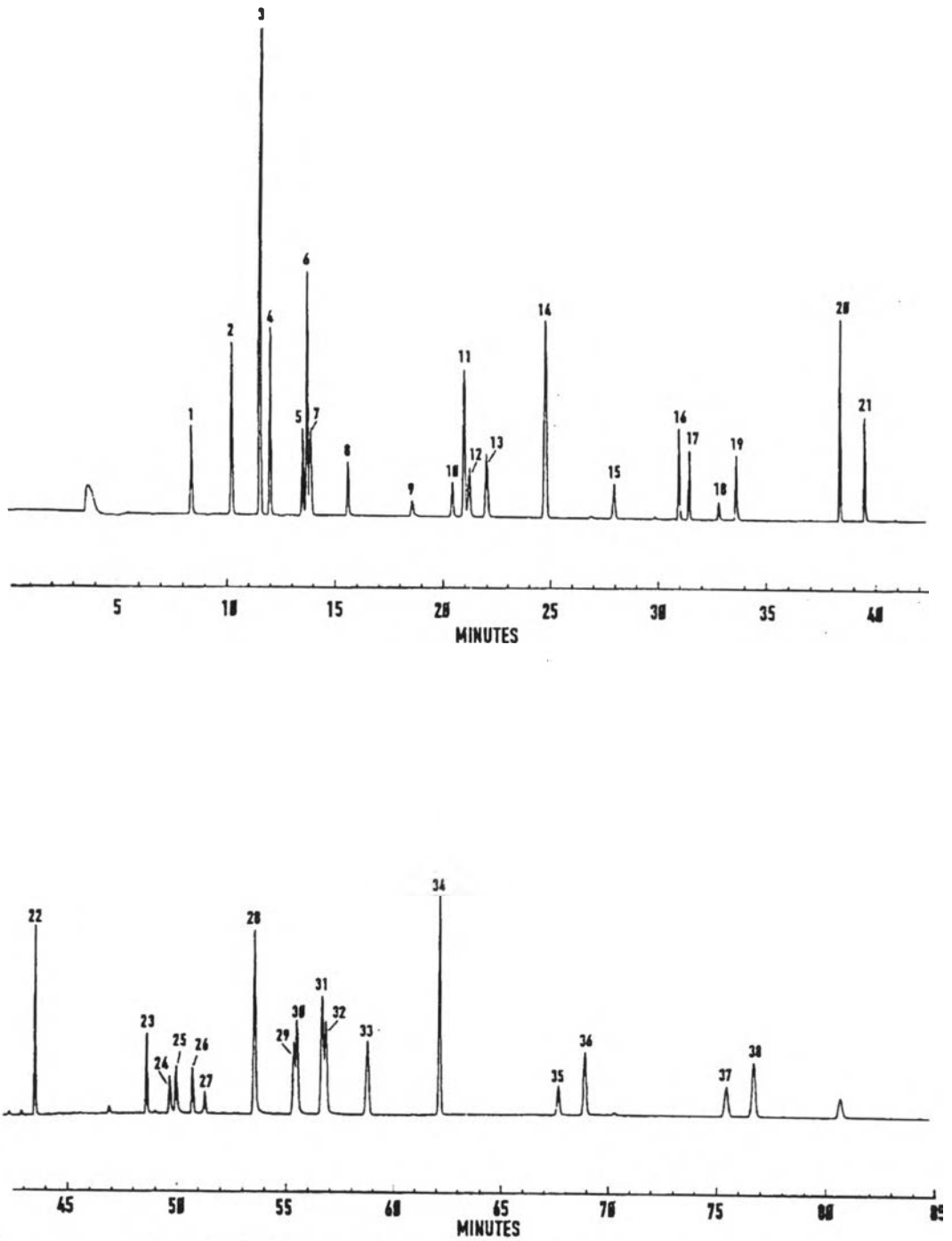

Figure 3. Fortified reagent water extract using pentane on primary DB-1 column

APPENDIX B

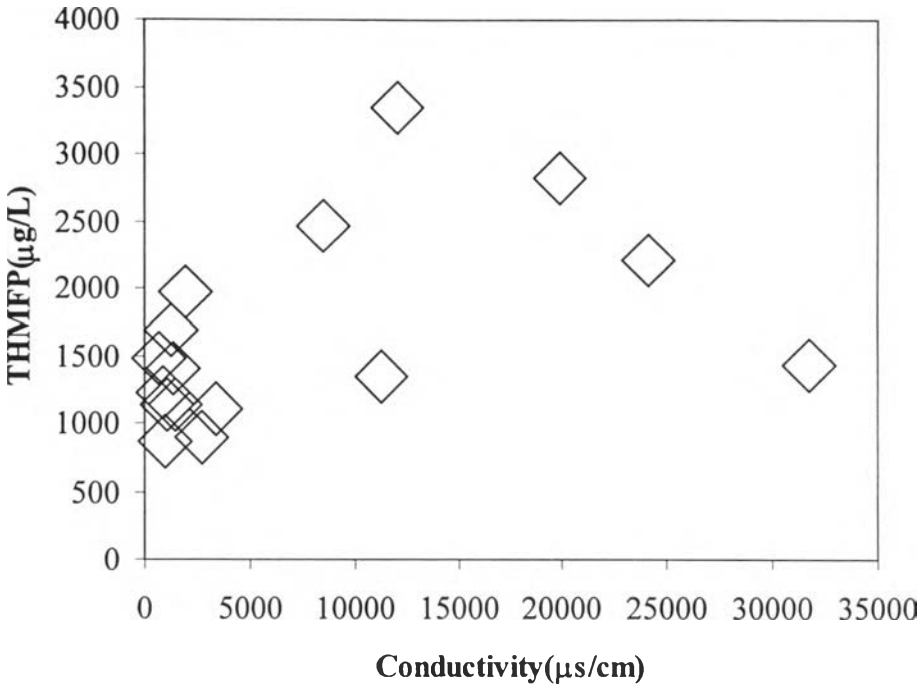

Figure B.1 Relationship between conductivity and THMFP in shrimp farm effluents (raw water)

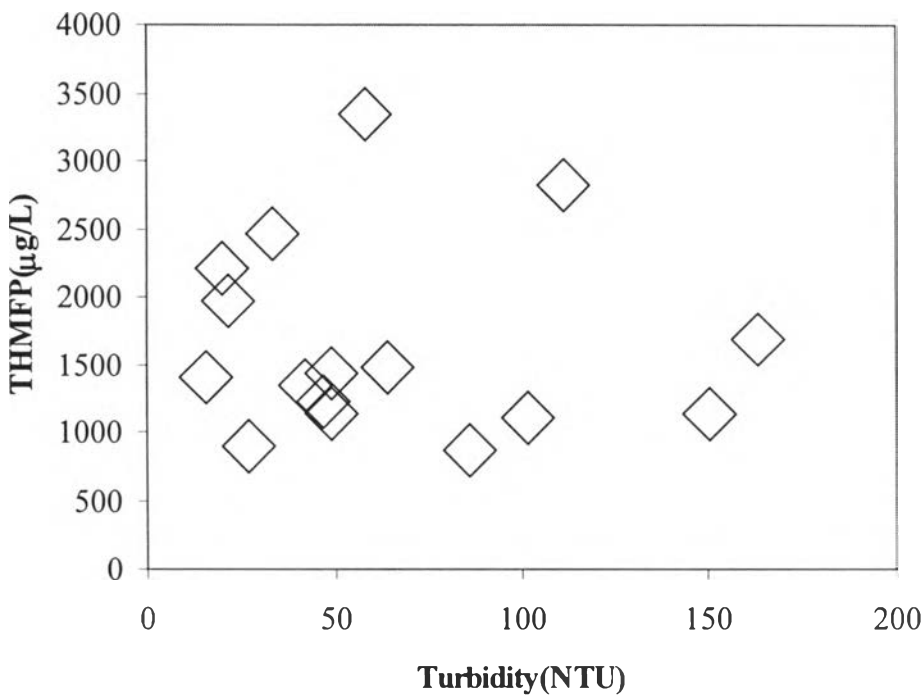

Figure B.2 Relationship between turbidity and THMFP in shrimp farm effluents (raw water)

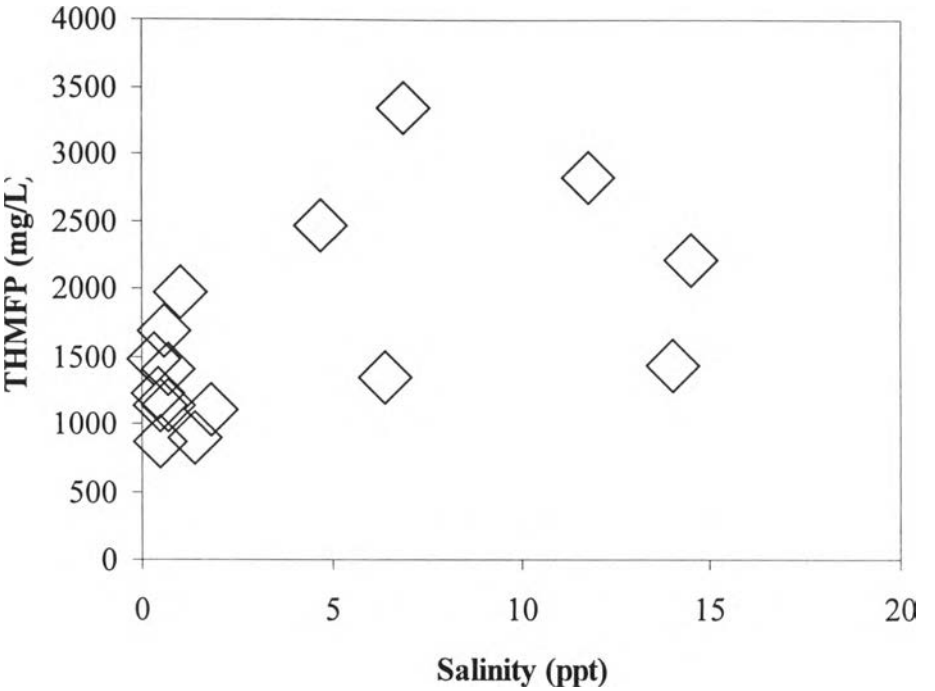

Figure B.3 Relationship between salinity and THMFP in shrimp farm effluents (raw water)

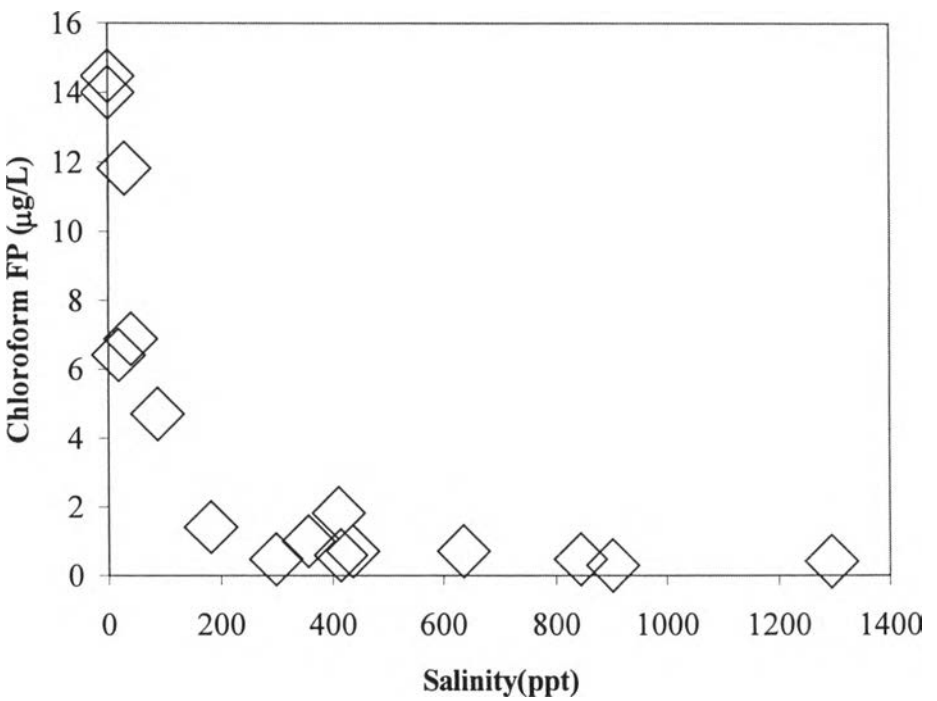

Figure B.4 Relationship between salinity and chloroform formation potential in shrimp

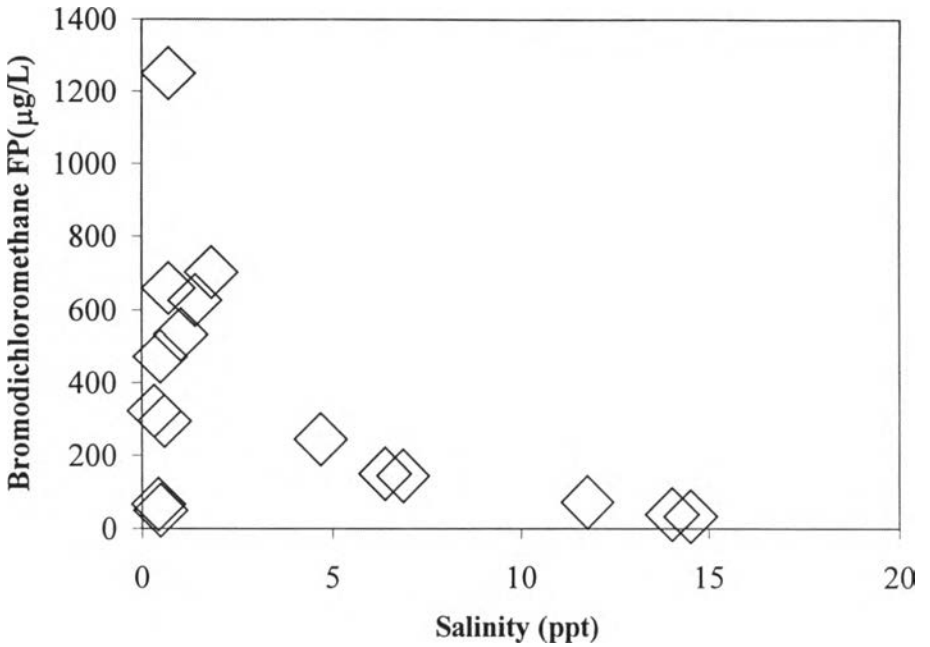

Figure B.5 Relationship between salinity and bromodichloromethane formation potential in shrimp farm effluents (raw water)

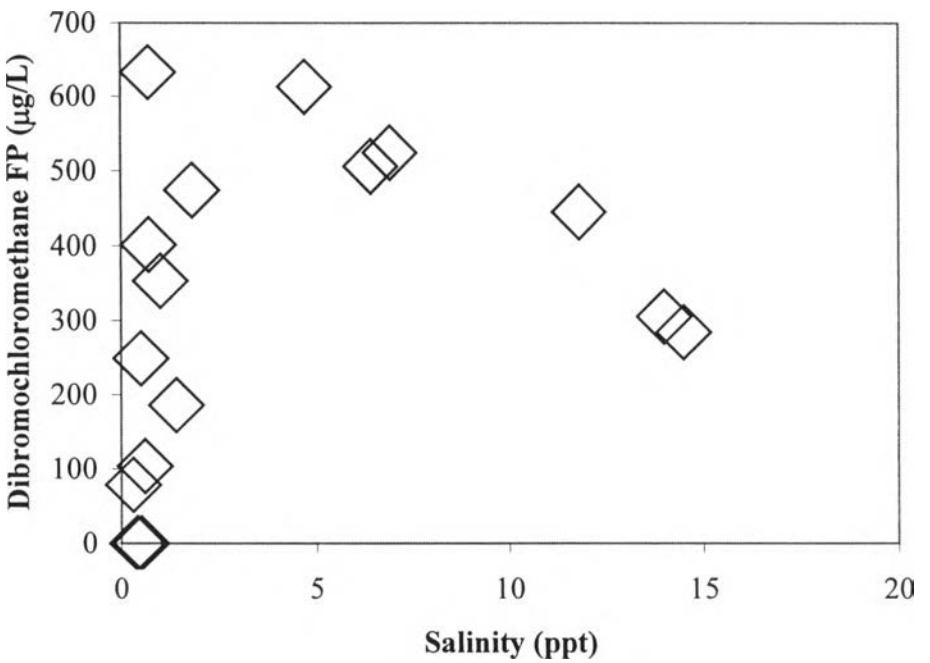

Figure B.6 Relationship between salinity and chlorodibromomethane formation potential

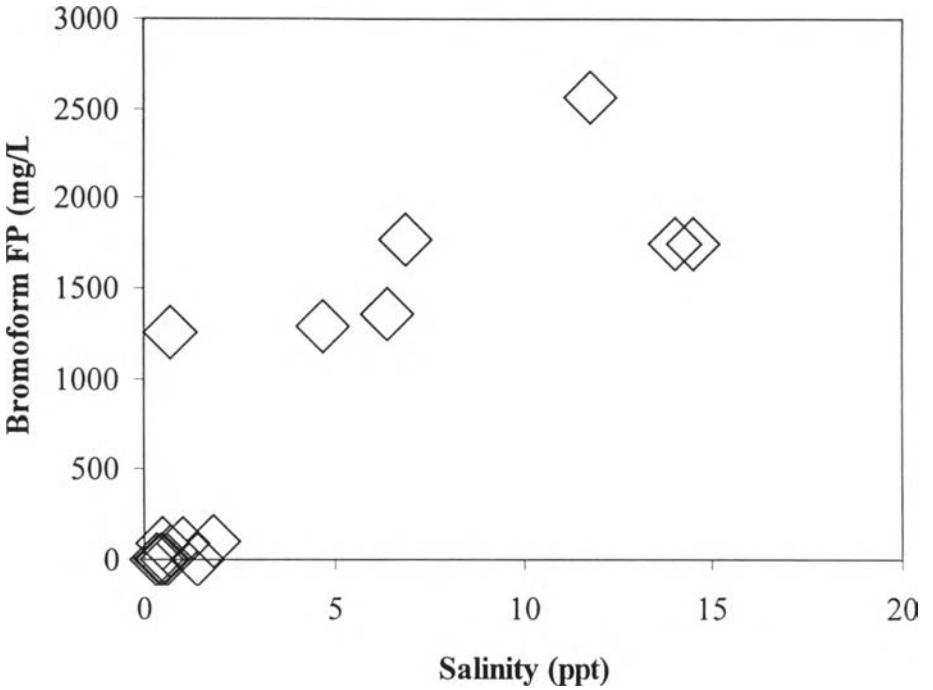

Figure B.7 Relationship between salinity and bromoform formation potential in shrimp farm effluents (raw water)

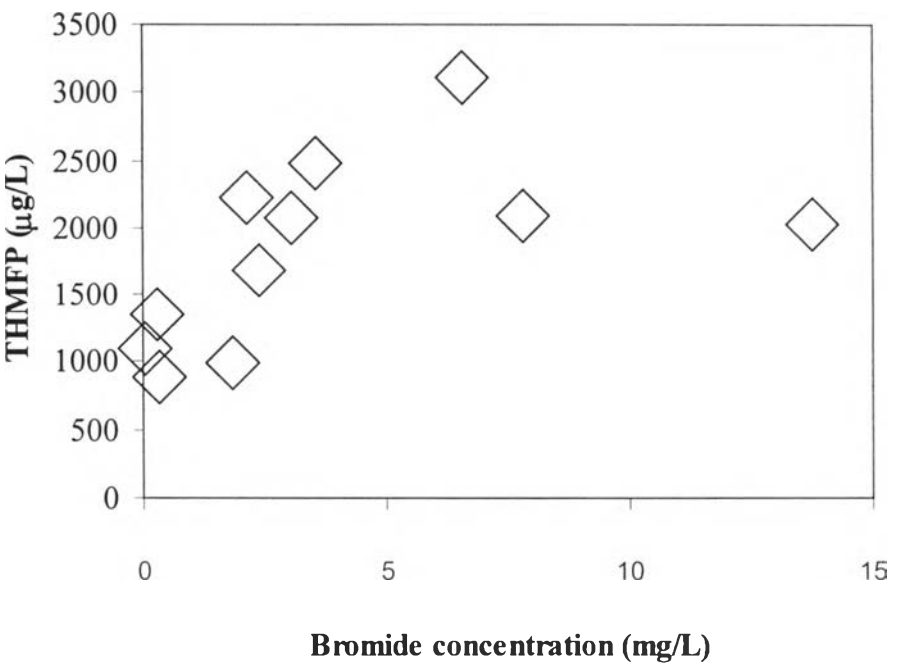

Figure B.8 Relationship between bromide concentration and THMFP in shrimp farm effluents (filtrated water)

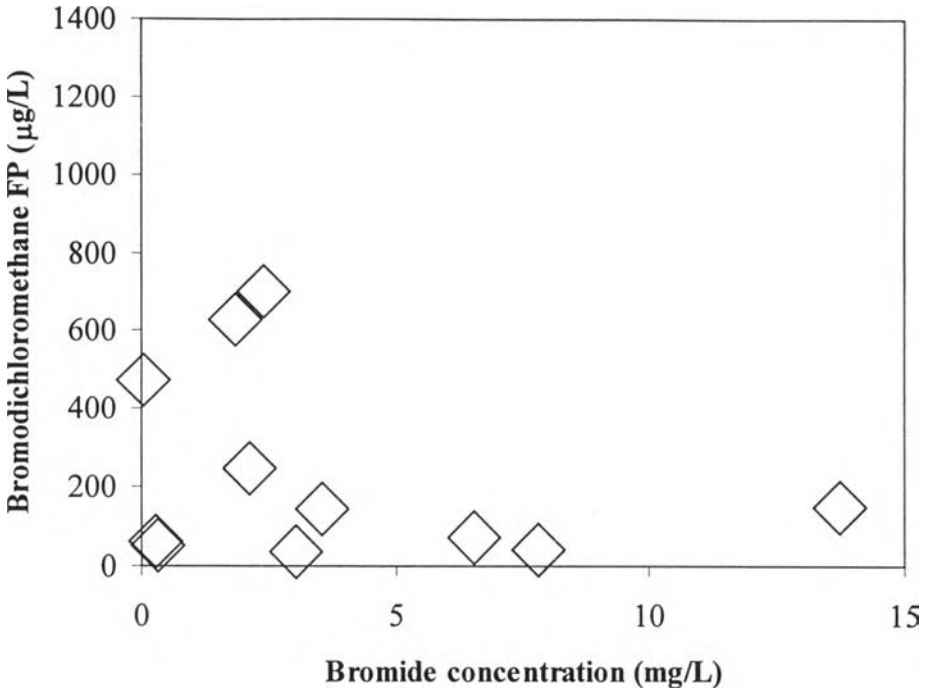

Figure B.9 Relationship between bromide concentration and bromodichloromethane formation potential in shrimp farm effluents (filtrated water)

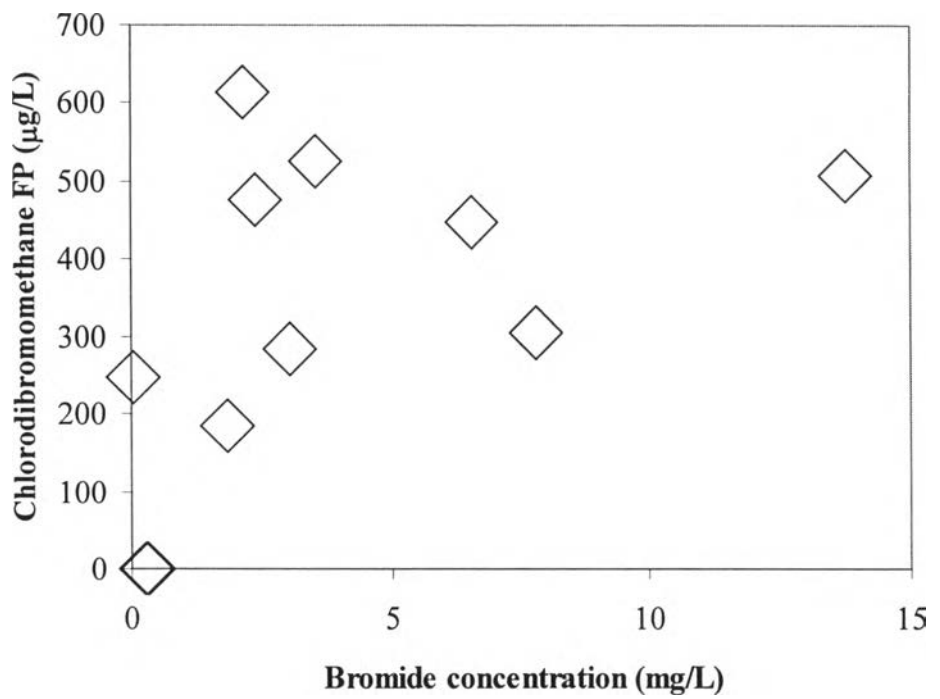

Figure B.10 Relationship between bromide concentration and chlorodibromomethane

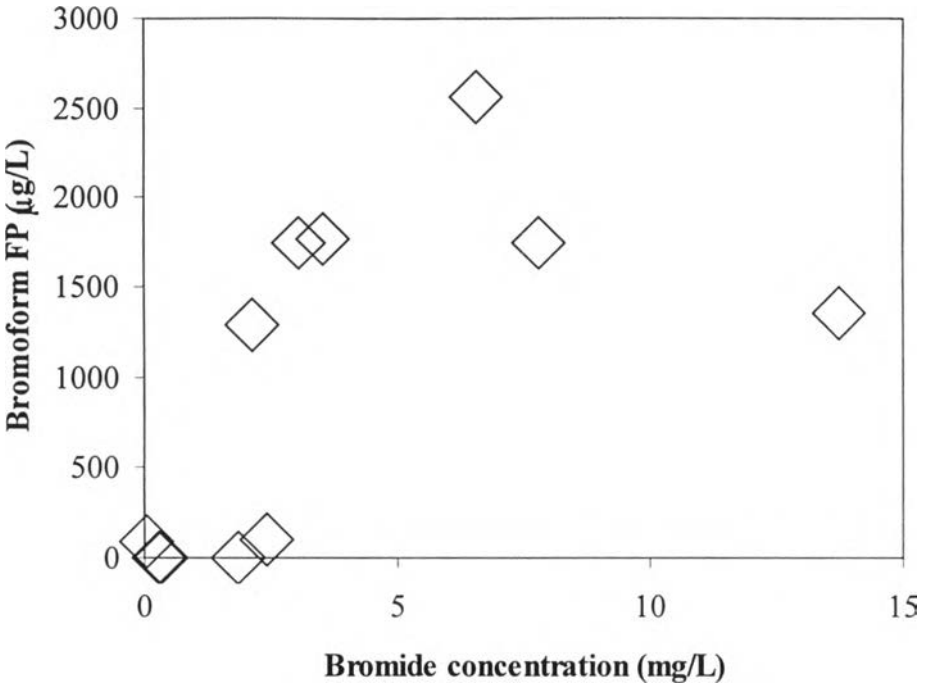

Figure B.11 Relationship between bromide concentration and bromoform formation potential in shrimp farm effluents (filtrated water)

Biography

Mr. Chaichana Chaiwatpongsakorn was born on November 26, 1978 in Bangkok, Thailand. He graduated from the Demonstration School of Satit Silpakorn University in Nakhonpathom Province. He received his Bachelor's Degree in Environmental Sciences and Technology from Mahidol University in 2001. He pursued a Master's Degree in the International Postgraduate Programs in Environmental Management, Inter-Department of Environmental Management, Chulalongkorn University, Bangkok, Thailand. He attained his Master Degree of Science in Environmental Management in May 2004.