METHOD 552.2

DETERMINATION OF HALOACETIC ACIDS AND DALAPON IN DRINKING WATER BY LIQUID-LIQUID EXTRACTION, DERIVATIZATION AND GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTION

Revision 1.0

J.W. Hodgeson (USEPA), J. Collins and R.E. Barth (Technology Applications Inc.) - Method 552.0, (1990)

J.W. Hodgeson (USEPA), D. Becker (Technology Applications Inc.) - Method 552.1, (1992)

D.J. Munch, J.W. Munch (USEPA) and A.M. Pawlecki (International Consultants, Inc.), Method 552.2, Rev. 1.0, (1995)

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DETERMINATION OF HALOACETIC ACIDS AND DALAPON IN DRINKING WATER BY LIQUID-LIQUID EXTRACTION, DERIVATIZATION AND GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTION

1.0 SCOPE AND APPLICATION

1.1 This is a gas chromatographic (GC) method[1-8] applicable to the determination of the listed halogenated acetic acids in drinking water, ground water, raw source water and water at any intermediate treatment stage. In addition, the chlorinated herbicide, Dalapon, may be determined using this method.

Analyte	Chemical Abstract Services Registry Number
Bromochloroacetic Acid (BCAA)	5589-96-3
Bromodichloroacetic Acid (BDCAA)	7113-314-7
Chlorodibromoacetic Acid (CDBAA)	5278-95-5
Dalapon	75-99-0
Dibromoacetic Acid (DBAA)	631-64-1
Dichloroacetic Acid (DCAA)	79-43-6
Monobromoacetic Acid (MBAA)	79-08-3
Monochloroacetic Acid (MCAA)	79-11-8
Tribromoacetic Acid (TBAA)	75-96-7
Trichloroacetic Acid (TCAA)	76-03-9

1.2 This method is applicable to the determination of the target analytes over the concentration ranges typically found in drinking water[1,2,4]. Experimentally determined method detection limits (MDLs) for the above listed analytes are provided in Table 2. Actual MDLs may vary according to the particular matrix analyzed and the specific instrumentation employed. The haloacetic acids are observed ubiquitously in chlorinated drinking water supplies at concentrations ranging from <1 to >50 µg/L.

1.3 This method is designed for analysts skilled in liquid-liquid extractions, derivatization procedures and the use of GC and interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 9.3.

1.4 When this method is used for the analyses of waters from unfamiliar sources, it is strongly recommended that analyte identifications be confirmed by GC using a dissimilar column or by GC/MS if concentrations are sufficient.

2.0 SUMMARY OF METHOD

2.1 A 40 mL volume of sample is adjusted to pH <0.5 and extracted with 4 mL of methyl-tert-butyl-ether (MTBE). The haloacetic acids that have been partitioned into the organic phase are then converted to their methyl esters by the addition of acidic methanol followed by slight heating. The acidic extract is neutralized by a backextraction with a saturated solution of sodium bicarbonate and the target analytes are identified and measured by capillary column gas chromatography using an electron capture detector (GC/ECD). Analytes are quantitated using procedural standard calibration.

3.0 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 to a sample aliquot in known amount(s) before extraction or other processing and is measured with the same procedures used to measure other sample components. The purpose of the SA is to monitor method performance with each sample.

3.3 Laboratory Duplicates (LD1 AND LD2) -- Two aliquots of the same sample designated as such in the laboratory. Each aliquot is extracted, derivatized and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

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

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

3.6 Field Reagent Blank (FRB) -- An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of

the FRB is to determine if method analytes or other interferences are present in the field environment.

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

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

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

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

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

3.12 Quality Control Sample (QCS) -- A solution of method analytes of known concentration which is used to fortify an aliquot of reagent water or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.13 Laboratory Performance Check Solution (LPC) -- A solution of selected method analytes used to evaluate the performance of the instrumental system with respect to a defined set of method criteria.

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

3.15 Material Safety Data Sheet (MSDS) -- Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire and reactivity data including storage, spill, and handling precautions.

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

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

3.18 Continuing Calibration Check (CCC) -- A calibration standard containing one or more method analytes, which is analyzed periodically to verify the accuracy of the existing calibration curves or response factors for those analytes.

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or elevated baselines in chromatograms. All reagents and apparatus must be routinely demonstrated to be free from interferences under the conditions of the analysis by analyzing laboratory reagent blanks as described in Section 9.5. Subtracting blank values from sample results is not permitted.

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

4.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Each new bottle of solvent should be analyzed before use. An interference free solvent is a solvent containing no peaks yielding data at greater than or equal to the MDL (Table 2) and at the retention times of the analytes of interest. Purification of solvents by distillation in all-glass systems may be required.

4.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. Routine between-sample rinsing of the

sample syringe and associated equipment with MTBE can minimize sample cross-contamination. After analysis of a sample containing high concentrations of analytes, one or more injections of MTBE should be made to ensure that accurate values are obtained for the next sample.

4.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the water sampled. Analyte identifications should be confirmed using the confirmation column specified in Table 1 or by GC/MS if the concentrations are sufficient.

4.4 Bromochloroacetic acid coelutes with an interferant on the DB-1701 confirmation column. The interferant has been tentatively identified as dimethyl sulfide. However, because of the difference in peak shapes, the peak for the ester of BCAA tends to "ride on" the interferant peak and quantitative confirmation can be performed by manual integration that includes only the peak area of the target ester.

4.5 Methylation using acidic methanol results in a partial decarboxylation of tribromoacetic acid[8]. Therefore a substantial peak for bromoform will be observed in the chromatograms. Its elution does not, however, interfere with any other analytes. Furthermore, this demonstrates the need for procedural standards to establish the calibration curve by which unknown samples are quantitated.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound must be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be minimized. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified[9-11] for the information of the analyst.

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

6.0 APPARATUS AND EQUIPMENT

6.1 Sample Containers -- Amber glass bottles, approximately 50 mL, fitted with Teflon-lined screw caps.

6.2 Extraction Vials -- 60 mL clear glass vials with teflon-lined screw caps.

6.3 Vials -- Autosampler, 2.0 mL vials with screw or crimp cap and a teflon-faced seal.

6.4 Standard Solution Storage Containers -- 10-20 mL amber glass vials with teflon-lined screw caps.

6.5 Graduated Conical Centrifuge Tubes with Teflon-Lined Screw Caps -- 15 mL with graduated 1 mL markings.

6.6 Block Heater (or Sand Bath) -- Capable of holding screw cap conical centrifuge tubes in Section 6.4.

6.7 Pasteur Pipets -- Glass, disposable.

6.8 Pipets -- 2.0 mL and 4.0 mL, Type A, TD, glass.

6.9 Volumetric Flasks -- 5 mL and 10 mL.

6.10 Micro Syringes -- 10 µL, 25 µL, 50 µL, 100 µL, 250 µL, 500 µL, and 1000 µL.

6.11 Balance -- analytical, capable of weighing to 0.0001 g.

6.12 Gas Chromatograph -- Analytical system complete with gas chromatograph equipped for electron capture detection, split/splitless capillary or direct injection, temperature programming, differential flow control, and with all required accessories including syringes, analytical columns, gases and strip-chart recorder. A data system is recommended for measuring peak areas. An autoinjector is recommended for improved precision of analyses. The gases flowing through the electron capture detector should be vented through the laboratory fume hood system.

6.13 Primary GC Column -- DB-5.625 [fused silica capillary with chemically bonded (5% phenyl)-methylpolysiloxane)] or equivalent bonded, fused silica column, 30m x 0.25mm ID, 0.25 µm film thickness.

6.14 Confirmation GC Column -- DB-1701 [fused silica capillary with chemically bonded (14% cyanopropylphenyl)-methylpolysiloxane)] or equivalent bonded, fused silica column, 30 m x 0.25 mm ID, 0.25 µm film thickness.

7.0 REAGENTS AND STANDARDS

7.1 Reagent Water -- Reagent water is defined as a water in which an interference is not observed greater than or equal to the MDL of each analyte of interest.

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

7.1.2 Reagent water is monitored through analysis of the laboratory reagent blank (Section 9.5).

7.2 Solvents

7.2.1 Methyl-tert-Butyl Ether, High Purity -- Demonstrated to be free of analytes and interferences, redistilled in glass if necessary.

7.2.2 Methanol, High Purity -- Demonstrated to be free of analytes and interferences.

7.2.3 Acetone, High Purity -- Demonstrated to be free of analytes and interferences.

7.3 Reagents

7.3.1 Sodium Sulfate, Na_2SO_4, ACS Granular, Anhydrous -- If interferences are observed, it may be necessary to heat the sodium sulfate in a shallow tray at 400°C for up to four hours to remove phthalates and other interfering organic substances. Alternatively, it can be extracted with methylene chloride in a Soxhlet apparatus for 48 hours. Store in a capped glass bottle rather than a plastic container.

7.3.2 Copper II Sulfate Pentahydrate, $CuSO_4{\cdot}5H_2O$, ACS Reagent Grade.

7.3.3 Sodium Bicarbonate, $NaHCO_3$, ACS Reagent Grade.

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

7.4 Solutions

7.4.1 10% H_2SO_4/methanol Solution -- Use caution when preparing sulfuric acid solutions. To prepare a 10% solution, add 5 mL sulfuric acid dropwise (due to heat evolution) to 20-30 mL methanol contained in a 50.0 mL volumetric flask that has been placed in a cooling bath. Then dilute to the 50.0 mL mark with methanol.

7.4.2 Saturated Sodium Bicarbonate Solution -- Add sodium bicarbonate to a volume of water, mixing periodically until the solution has reached saturation.

7.5 Standards

7.5.1 1,2,3-trichloropropane, 99+% -- For use as the internal standard. Prepare an internal standard stock standard solution of 1,2,3-trichloropropane in MTBE at a concentration of approximately 1 mg/mL. From this stock standard solution, prepare a primary dilution standard in MTBE at a concentration of 25 µg/mL.

7.5.2 2,3-dibromopropionic Acid, 99+% -- For use as a surrogate compound. Prepare a surrogate stock standard solution of 2,3-dibromopropionic acid in MTBE at a concentration of approximately 1 mg/mL. From this stock standard solution, prepare a primary dilution standard in MTBE at a concentration of 10 µg/mL.

7.5.3 Stock Standard Solution-- Prepare separate stock standard solutions for each analyte of interest at a concentration of 1-5 mg/mL in MTBE. Method analytes may be obtained as neat materials or ampulized solutions (>99% purity) from a number of commercial suppliers. These stock standard solutions should be stored at -10°C and protected from light. They are stable for at least one month but should be checked frequently for signs of evaporation.

7.5.3.1. For analytes which are solids in their pure form, prepare stock standard solutions by accurately weighing approximately 0.01-0.05 g of pure material in a 10.0 mL volumetric flask. Dilute to volume with MTBE. When a compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard.

7.5.3.2. Stock standard solutions for analytes which are liquid in their pure form at room temperature can be accurately prepared in the following manner.

7.5.3.3. Place about 9.8 mL of MTBE into a 10.0 mL volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes to allow solvent film to evaporate from the inner walls of the volumetric, and weigh to the nearest 0.1 mg.

7.5.3.4. Use a 10 µL syringe and immediately add 10.0 µL of standard material to the flask by keeping the syringe needle just above the surface of the MTBE. Be sure that the standard material falls dropwise directly into the MTBE without contacting the inner wall of the volumetric.

7.5.3.5. Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in milligrams per milliliter from the net gain in weight.

7.5.4 Primary Dilution Standard (PDS) -- Prepare the primary dilution standard solution by combining and diluting stock standard solutions with MTBE (the surrogate stock standard solution was prepared in Section 7.5.2). This primary dilution standard solution should be stored at -10°C and protected from light. It is stable for at least one month but should be checked before use for signs of evaporation. As a guideline to the analyst, the primary dilution standard solution used in the validation of this method is described below.

	Concentration, µg/mL
Monochloroacetic Acid	60
Monobromoacetic Acid	40
Dalapon	40
Dichloroacetic Acid	60
Trichloroacetic Acid	20
Bromochloroacetic Acid	40
Dibromoacetic Acid	20
Bromodichloroacetic Acid	40
Chlorodibromoacetic Acid	100
Tribromoacetic Acid	200
2,3-Dibromopropionic Acid (Surr.)	100

This primary dilution standard is used to prepare calibration standards, which comprise five concentration levels of each analyte with the lowest standard being at or near the MDL of each analyte. The concentrations of the other standards should define a range containing the expected sample concentrations or the working range of the detector.

Note: When purchasing commercially prepared standards, solutions prepared in methanol must not be used because it has been found that the haloacetic acids are subject to spontaneous methylation when stored in this solvent[12]. Furthermore, tribromoacetic acid has been found to be unstable in methanol because it undergoes decarboxylation when stored in this solvent.

7.5.4.1. Include the surrogate analyte, 2,3-dibromopropionic acid, within the primary dilution standard prepared in Section 7.5.4. By incorporating the surrogate into the primary dilution standard, it is diluted alongside the target analytes in the standard calibration curve. This is done so that the peaks for the surrogate and the ester of chlorodibromo-acetic acid, which elute fairly closely, are relatively close in size and adequate resolution is therefore insured. Furthermore, if a sample should have a very large concentration of chlorodibromo-acetic acid, it may be impossible to obtain an accurate measurement of surrogate

recovery. If this happens, reextraction with a higher surrogate concentration would be an option.

7.5.6 Laboratory Performance Check Standard (LPC) -- A low level calibration standard can serve as the LPC standard.

8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Sample Vial Preparation

8.1.1 Grab samples must be collected in accordance with conventional sampling practices[13] using amber glass containers with TFE-lined screw-caps and capacities of at least 50 mL.

8.1.2 Prior to shipment to the field, add crystalline or granular ammonium chloride (NH_4Cl) to the sample container in an amount to produce a concentration of 100 mg/L in the sample. For a typical 50 mL sample, 5 mg of ammonium chloride is added.

Note: Enough ammonium chloride must be added to the sample to convert the free chlorine residual in the sample matrix to combined chlorine. Typically, the ammonium chloride concentration here will accomplish that. If high doses of chlorine are used, additional ammonium chloride may be required.

8.2 Sample Collection

8.2.1 Fill sample bottles to just overflowing but take care not to flush out the ammonium chloride.

8.2.2 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about three to five minutes). Remove the aerator so that no air bubbles can be visibly detected and collect samples from the flowing system.

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

8.2.4 After collecting the sample in the bottle containing the ammonium chloride, seal the bottle and agitate by hand for one minute.

8.3 Sample Storage/Holding Times

8.3.1 Samples must be iced or refrigerated at 4°C and maintained at these conditions away from light until extraction. Synthetic ice (i.e., blue ice) is not recommended. Holding studies performed to date have suggested that, in samples preserved with NH_4Cl, the analytes are stable for up to

14 days. Since stability may be matrix dependent, the analyst should verify that the prescribed preservation technique is suitable for the samples under study.

8.3.2 Extracts (Section 11.2.7) must be stored at 4°C or less away from light in glass vials with Teflon-lined caps. Extracts must be analyzed within seven days from extraction if stored at 4°C or within 14 days if stored at -10°C or less.

9.0 QUALITY CONTROL

9.1 Each laboratory that uses this method is required to operate a formal quality control (QC) program. Minimum quality control requirements are monitoring the laboratory performance check standard, initial demonstration of laboratory capability, performance of the method detection limit study, analysis of laboratory reagent blanks and laboratory fortified sample matrices, determination of surrogate compound recoveries in each sample and blank, monitoring internal standard peak area or height in each sample, blank and CCC, and analysis of QC samples. Additional QC practices may be added.

9.2 Laboratory Performance Check Standard (LPC)

At the beginning of an analysis set, prior to any calibration standard or sample analysis and after an initial solvent analysis, a LPC must be analyzed. This check standard insures proper performance of the GC by evaluation of the instrument parameters of detector sensitivity, peak symmetry, and peak resolution. It furthermore serves as a check on the continuity of the instrument's performance. In regards to sensitivity, it allows the analyst to ascertain that this parameter has not changed drastically since the analysis of the MDL study. Inability to demonstrate acceptable instrument performance indicates the need for re-evaluation of the instrument system. Criteria are listed in Table 8.

9.2.1 The sensitivity requirement is based on the EDLs published in this method. If laboratory EDLs differ from those listed in Table 2, concentrations of the LPC standard may be adjusted to be compatible with the laboratory EDLs.

9.2.2 If column or chromatographic performance cannot be met, one or more of the following remedial actions should be taken. Break off approximately 1 m of the injector end of the column and re-install, install a new column, adjust column flows or modify the oven temperature program.

9.3 Initial Demonstration of Capability (IDC)

9.3.1 Calibrate for each analyte of interest as specified in Section 10.0. Select a representative fortification concentration for each of the target analytes. Concentrations near those in Table 4 are recommended. Prepare four to seven replicates laboratory fortified blanks by adding an appropriate aliquot of the primary dilution standard or quality control sample to reagent water. (This reagent water should contain ammonium chloride at the same concentration as that specified for samples as per Section 8.1.2.) Analyze the LFBs according to the method beginning in Section 11.0.

9.3.2 Calculate the mean percent recovery and the standard deviation of the recoveries. For each analyte, the mean recovery value, expressed as a percentage of the true value, must fall in the range of 80-120% and the relative standard deviation should be less than 20%. For those compounds that meet these criteria, performance is considered acceptable and sample analysis may begin. For those compounds that fail these criteria, this procedure must be repeated using four to seven fresh samples until satisfactory performance has been demonstrated. Maintain these data on file to demonstrate initial capabilities.

9.3.3 Furthermore, before processing any samples, the analyst must analyze at least one laboratory reagent blank to demonstrate that all glassware and reagent interferences are under control.

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

9.3.5 The analyst is permitted to modify GC columns, GC conditions, internal standard or surrogate compounds. Each time such method modifications are made, the analyst must repeat the procedures in Section 9.3.1 through Section 9.3.4 and Section 9.4.

9.4 Method Detection Limit Study (MDL)

9.4.1. Prior to the analysis of any field samples, the method detection limits must be determined. Initially, estimate the concentration of an analyte which would yield a peak equal to five times the baseline noise and drift. Prepare seven replicate LFBs at this estimated concentration with reagent water that contains ammonium chloride at the same concentration as that specified for samples as per Section 8.1.2. Analyze the LFBs according to the method beginning in Section 11.0.

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

9.4.3. Since the statistical estimate is based on the 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 is the EDL (Table 2).

9.5 Laboratory Reagent Blanks (LRB) -- Each time a set of samples is extracted or reagents are changed, a LRB must be analyzed. If the LRB produces an interferant peak within the retention time window (Section 12.3) of any analyte that would prevent the determination of that analyte or a peak of concentration greater than the MDL for that analyte, the analyst must determine the source of contamination and eliminate the interference before processing samples. Field samples of an extraction set associated with an LRB that has failed the specified criteria are considered suspect.

Note: Reagent water containing ammonium chloride at the same concentrations as in the samples (Section 8.1.2) is used to prepare the LRB.

9.6 Laboratory Fortified Blank (LFB) -- Since this method utilizes procedural calibration standards, which are fortified reagent water, there is no difference between the LFB and the continuing calibration check standard. Consequently, the analysis of an LFB is not required (Section 10.2).

9.7 Laboratory Fortified Sample Matrix (LFM)

9.7.1 Chlorinated water supplies will usually contain significant background concentrations of several method analytes, especially dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA). The concentrations of these acids may be equal to or greater than the fortified concentrations. Relatively poor accuracy and precision may be anticipated when a large background must be subtracted. For many samples, the concentrations may be so high that fortification may lead to a final extract with instrumental responses exceeding the linear range of the electron capture detector. If this occurs, the extract must be diluted. In spite of these problems, sample sources should be fortified and analyzed as described below. By fortifying sample matrices and calculating analyte recoveries, any matrix induced analyte bias is evaluated.

9.7.2. The laboratory must add known concentrations of analytes to one sample per extraction set or a minimum of 10% of the samples, whichever is greater. The concentrations should be equal to or greater than the background concentrations in the sample selected for fortification. If the fortification level is less than the background concentration, recoveries are

not reported. Over time, samples from all routine sample sources should be fortified.

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

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

where: C = the fortifying concentration

In order for the recoveries to be considered acceptable, they must fall between 70% and 130% for all the target analytes.

9.7.4 If a recovery falls outside of this acceptance range, a matrix induced bias can be assumed for the respective analyte and the data for that analyte must be reported to the data user as suspect due to matrix effects.

9.8 Assessing Surrogate Recovery

The surrogate analyte is fortified into the aqueous portion of all continuing calibration standards, samples and laboratory reagent blanks. The surrogate is a means of assessing method performance in every analysis from extraction to final chromatographic performance.

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

9.8.2 If the extract reanalysis meets the surrogate recovery criterion, report only data for the reanalyzed extract.

9.8.3 If the extract reanalysis fails the 70-130% recovery criterion, the analyst should check the calibration by analyzing the most recently acceptable continuing calibration check standard. If the CCC fails the criteria of Section 10.2.1, recalibration is in order per Section 10.1. If the CCC is acceptable, it may be necessary to extract another aliquot of sample. If the sample re-extract also fails the recovery criterion, report all data for that sample as suspect.

9.9 Assessing the Internal Standard

9.9.1. The analyst must to monitor the IS response (peak area or peak height) of all injections during each analysis day. A mean IS response should be determined from the five-point calibration curve. The IS response for any run should not deviate from this mean IS response by more than 30%. It is also acceptable if the IS response of a injection is within 15% of the daily continuing calibration standard IS response.

9.9.2 If a deviation greater than this occurs with an individual extract, optimize instrument performance and inject a second aliquot of that extract.

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

9.9.2.2 If a deviation of greater than 30% is obtained for the reinjected extract, the analyst should check the calibration by analyzing the most recently acceptable CCC. If the CCC fails the criteria of Section 10.2.1, recalibration is in order per Section 10.1. If the CCC is acceptable, analysis of the sample should be repeated beginning with Section 11.0, provided the sample is still available. Otherwise, report results obtained from the reinjected extract, but annotate as suspect.

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

9.11 The laboratory may adapt additional QC practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. For example, field or laboratory duplicates may be analyzed to assess the precision of the environmental measurements or FRBs may be used to assess contamination of samples under site conditions, transportation and storage.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Initial Calibration Curve

10.1.1 Calibration is performed by extracting procedural standards, i.e.; fortified reagent water, by the procedure set forth in Section 11.0. A five-point calibration curve is to be prepared by diluting the primary dilution standard into MTBE at the appropriate levels. The desired amount of each MTBE calibration standard is added to separate 40 mL aliquots of reagent water to produce a calibration curve ranging from the detection limit to approximately 50 times the detection limit. (These MTBE calibration standards should be prepared so that 20 µL or less of the solution is added the water aliquots.) Also, the reagent water used for the procedural standards contains ammonium chloride at the same concentration as that in the samples as per Section 8.1.2.

10.1.2 Establish GC operating parameters equivalent to the suggested specifications in Table 1. The GC system must be calibrated using the internal standard (IS) technique. Other columns or conditions may be used if equivalent or better performance can be demonstrated.

10.1.2 Five calibration standards are required. The lowest should contain the analytes at a concentration near to but greater than the MDL (Table 2) for each compound. The others should be evenly distributed throughout the concentration range expected in the samples.

10.1.3 Inject 2 µL of each calibration standard extract and tabulate peak height or area response and concentration for each analyte and the internal standard.

10.1.4 Generate a calibration curve by plotting the area ratios (A_a / A_{is}) against the concentration C_a of the five calibration standards.

where: A_a = the peak area of the analyte
A_{is} = the peak area of the internal standard
C_a = the concentration of the analyte

This curve can be defined as either first or second order. Also, the working calibration curve must be verified daily by measurement of one or more calibration standards (Section 10.2). If the response for any analyte falls outside the predicted response by more than 30%, the calibration check must be repeated using a freshly prepared calibration standard. Should the retest fail, a new calibration curve must be generated.

10.1.5 Alternately, an average relative response factor can be calculated and used for quantitation. Relative response factors are calculated for each analyte at the five concentration levels using the equation below:

$$RRF = \frac{(A_a)\ (C_{is})}{(A_{is})\ (C_a)}$$

If the RRF value over the working range is constant (<20% RSD), the RRF can be assumed to be invariant and the average RRF used for calculations. Also, the average RRF must be verified daily by measurement of one or more calibration standards (Section 10.2). If the RRF for the continuing calibration standard deviates from the average RRF by more than 30%, the calibration check must be repeated using a freshly prepared calibration standard. Should the retest fail, a new calibration curve must be generated.

10.1.6 A data system may be used to collect the chromatographic data, calculate relative response factors, or calculate linear or second order calibration curves.

10.2 Continuing Calibration Check (CCC)

10.2.1 At least one CCC must be extracted with each set of samples. A CCC must be analyzed at the beginning of each analysis set, after every tenth sample analysis and after the final sample analysis, to ensure that the instrument is still within calibration. These checks should be at two different concentration levels. Calculate analyte recoveries for all target analytes. In order for the calibration check to be considered valid and subsequently for the preceding ten samples to be considered acceptable with respect to calibration, recoveries must fall between 70% and 130% for all the target analytes.

Note: Continuing calibration check standards need not necessarily be different extracts but can be injections from the same extract as long as the holding time requirements (Section 8.3.2) are met.

10.2.2 If this criteria cannot be met, the continuing calibration check standard extract is re-injected in order to determine if the response deviations observed from the initial analysis are repeated. If this criteria still cannot be met, a second CCC should be extracted and analyzed or a CCC that has already been analyzed and has been found to be acceptable should be run. If this second CCC fails, then the instrument is considered out of calibration and needs to be recalibrated.

11.0 PROCEDURE

11.1 Sample Extraction

11.1.1 Remove the samples from storage (Section 8.3.1) and allow them to equilibrate to room temperature.

11.1.2 Place 40 mL of the water sample into a precleaned 60 mL glass vial with a Teflon-lined screw cap using a graduated cylinder.

11.1.3 Add 20 µL of surrogate standard (10.0 µg/mL 2,3-dibromopropionic acid in MTBE per Section 7.5.2).

Note: When fortifying an aqueous sample with either surrogate or target analytes contained in MTBE, be sure that the needle of the syringe is well below the level of the water. After injection, cap the sample and invert once. This insures that the standard solution is mixed well with the water.

11.1.4 Adjust the pH to less than 0.5 by adding at least 2 mL of concentrated sulfuric acid. Cap, shake and then check the pH with a pH meter or narrow range pH paper.

11.1.5 Quickly add approximately 2 g of copper II sulfate pentahydrate and shake until dissolved. This colors the aqueous phase blue and therefore allows for the analyst to better distinguish between the aqueous phase and the organic phase in this microextraction.

11.1.6 Quickly add 16 g of muffled sodium sulfate and shake for three to five minutes until almost all is dissolved. Sodium sulfate is added to increase the ionic strength of the aqueous phase and thus further drive the haloacetic acids into the organic phase. The addition of this salt and the copper II sulfate should be done quickly so that the heat generated from the addition of the acid (Section 11.1.4) will help dissolve the salts.

11.1.7 Add 4.0 mL MTBE and place on the mechanical shaker for 30 minutes. (If hand-shaken, two minutes is sufficient if performed vigorously).

11.1.8 Allow the phases to separate for approximately five minutes.

11.2 Methylation

11.2.1 Using a pasteur pipet, transfer approximately 3 mL of the upper MTBE layer to a 15 mL graduated conical centrifuge tube.

11.2.2 Add 1 mL 10% sulfuric acid in methanol to each centrifuge tube.

11.2.3 Cap the centrifuge tubes and place in the heating block (or sand bath) at 50°C and maintain for two hours. The vials must fit snugly into the heating block to ensure proper heat transfer. At this stage, methylation of the method analytes is attained.

11.2.4 Remove the centrifuge tubes from the heating block (or sand bath) and allow them to cool before removing the caps.

11.2.5 Add 4 mL saturated sodium bicarbonate solution to each centrifuge tube in 1 mL increments. Exercise caution when adding the solution because the evolution of CO_2 in this neutralization reaction is rather rapid.

11.2.6 Shake each centrifuge tube for two minutes. As the neutralization reaction moves to completion, it is important to continue to exercise caution by venting frequently to release the evolved CO_2.

11.2.7 Transfer exactly 1.0 mL of the upper MTBE layer to an autosampler vial. A duplicate vial should be filled using the excess extract.

11.2.8 Add 10 µL of internal standard to the vial to be analyzed. (25 µg/mL 1,2,3-trichloropropane in MTBE per Section 7.5.1).

11.2.9 Analyze the samples as soon as possible. The sample extract may be stored up to seven days if kept at 4°C or less or up to 14 days if kept at -10°C or less. Keep the extracts away from light in amber glass vials with Teflon-lined caps.

11.3 Gas Chromatography

11.3.1 Table 1 summarizes recommended GC operating conditions and retention times observed using this method. Figure 1 illustrates the performance of the recommended primary column with the method analytes. Figure 2 illustrates the performance of the recommended confirmation column with the method analytes. Concentrations of the analytes of these chromatograms are those listed in Table 4 for the fortified reagent water samples. Other GC columns or chromatographic conditions may be used if the requirements of Section 9.0 are met.

11.3.2 Calibrate the system (Section 10.1) or verify the existing calibration by analysis of a CCC daily as described in Section 10.2.

11.3.3 Inject 2 µL of the sample extract. Record the resulting peak sizes in area or height units.

11.3.4 If the response for the peak exceeds the working range of the system, dilute the extract, add an appropriate additional amount of internal standard and reanalyze. The analyst must not extrapolate beyond the calibration range established.

12.0 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 peak corresponds, within limits (Section 12.2), to the retention time of a standard compound, then the identification is considered positive. Calculate analyte

concentrations in the samples and reagent blanks from the calibration curves generated in Section 10.1.

12.2 If an average relative response factor has been calculated (Section 10.1.5), analyte concentrations in the samples and reagent blanks are calculated using the following equation:

$$C_a = \frac{(A_a)\ (C_{is})}{(A_{is})\ (RRF)}$$

12.3 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatogram.

13.0 METHOD PERFORMANCE

13.1 In a single laboratory, recovery and precision data were obtained at three concentrations in reagent water (Tables 3 and 4). The MDL and EDL data are given in Table 2. In addition, recovery and precision data were obtained at a medium concentration for dechlorinated tap water (Table 5), high ionic strength reagent water (Table 6) and high humectant ground water (Table 7).

14.0 POLLUTION PREVENTION

14.1 This method utilizes a micro-extraction procedure which requires the use of very small quantities of organic solvents. This feature reduces the hazards involved with the use of large volumes of potentially harmful organic solvents needed for conventional liquid-liquid extractions. This method also uses acidic methanol as the derivatizing reagent.

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

15.0 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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17. TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

FIGURE 1. ELUTION OF METHOD ANALYTES ON THE PRIMARY COLUMN (DB-5.625)

FIGURE 2. ELUTION OF METHOD ANALYTES ON THE CONFIRMATION COLUMN (DB-1701)

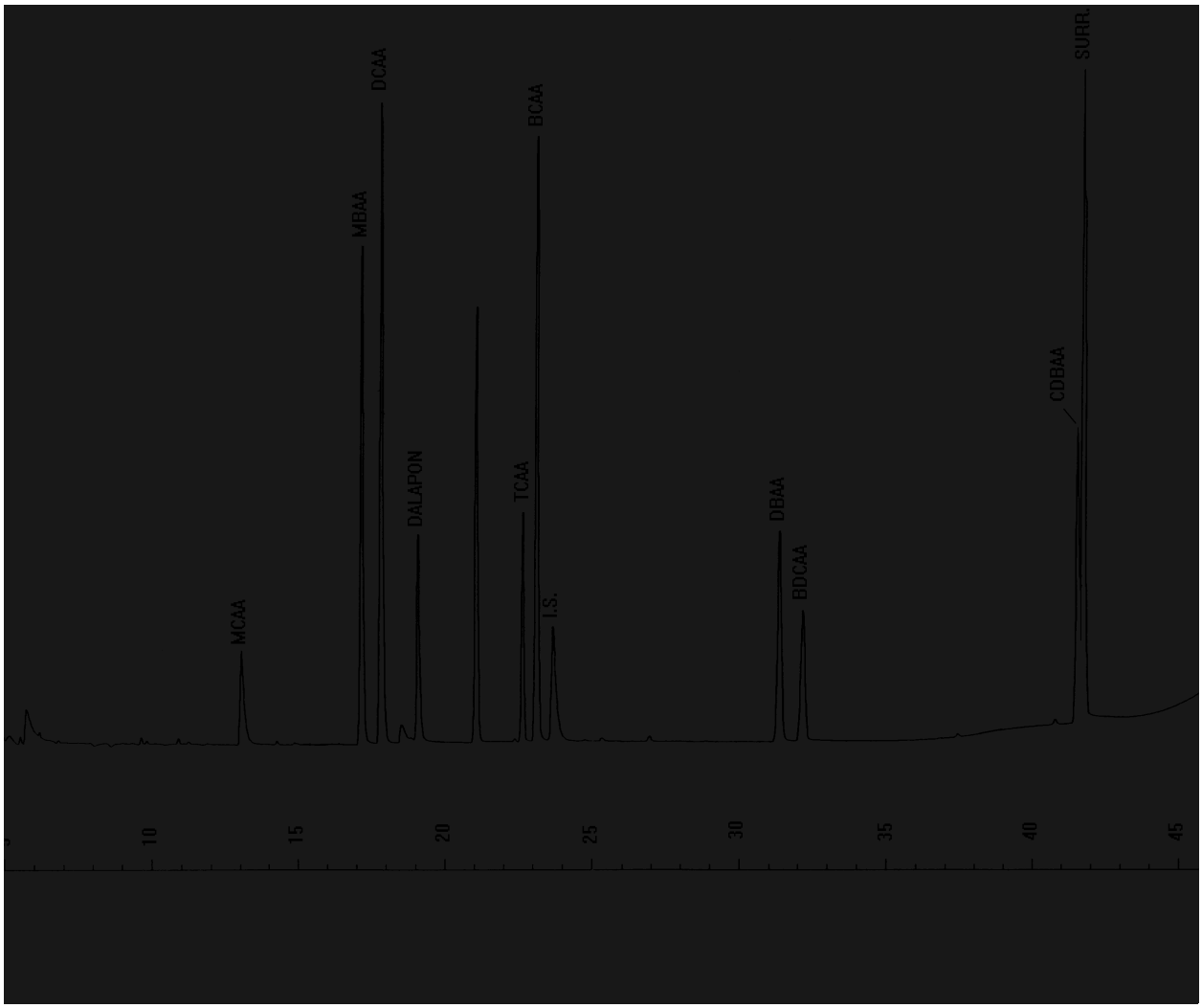

TABLE 1. RETENTION DATA AND CHROMATOGRAPHIC CONDITIONS

Analyte	Retention Time, minutes	
	Column A	Column B
Monochloroacetic Acid (MCAA)	13.03	13.70
Monobromoacetic Acid (MBAA)	17.15	17.33
Dichloroacetic Acid (DCAA)	17.80	17.88
Dalapon	19.08	17.73
Trichloroacetic Acid (TCAA)	22.67	20.73
Bromochloroacetic Acid (BCAA)	23.15	22.87
1,2,3-Trichloropropane (I.S.)	23.70	22.35
Dibromoacetic Acid (DBAA)	31.38	30.27
Bromodichloroacetic Acid (BDCAA)	32.18	28.55
Chlorodibromoacetic Acid (CDBAA)	41.57	38.78
2,3-Dibromopropionic Acid (SURR)	41.77	39.72
Tribromoacetic Acid (TBAA)	49.22	47.08

Column A: DB-5.625, 30 m x 0.25 mm i.d., 0.25 µm film thickness, Injector Temp. = 200°C, Detector Temp. = 260°C, Helium Linear Velocity = 24 cm/sec. at 35°C, Splitless injection with 30 second delay.

Program: Hold at 35°C for 10 minutes, ramp to 75°C at 5°C/min. and hold 15 minutes, ramp to 100°C at 5°C/min. and hold five minutes, ramp to 135°C at 5°C/min. and hold two minutes.

Column B: DB-1701, 30 m x 0.25 mm i.d., 0.25 µm film thickness, Injector Temp. = 200°C, Detector Temp. = 260°C, Linear Helium Velocity = 25 cm/sec. at 35°C, splitless injection with 30 second delay.

Program: Hold at 35°C for 10 minutes, ramp to 75°C at 5°C/min. and hold 15 minutes, ramp to 100°C at 5°C/min. and hold five minutes, ramp to 135°C at 5°C/min. and hold 0 minutes.

TABLE 2. ANALYTE ACCURACY AND PRECISION DATA AND METHOD DETECTION LIMITS[a]

LEVEL 1 IN REAGENT WATER

Analyte	Fortified Conc. µg/L	Mean. Meas. Conc. µg/L	Std. Dev. µg/L	Rel. Std. Dev. %	Method Detection Limit[b] µg/L	Estimated Detection Limit[c] µg/L
MCAA	0.600	0.516	0.087	17	0.273	0.60
MBAA	0.400	0.527	0.065	12	0.204	0.20
DCAA	0.600	0.494	0.077	16	0.242	0.24
Dalapon	0.400	0.455	0.038	8.4	0.119	0.40
TCAA	0.200	0.219	0.025	11	0.079	0.20
BCAA	0.400	0.498	0.080	16	0.251	0.25
DBAA	0.200	0.238	0.021	8.8	0.066	0.20
BDCAA	0.400	0.357	0.029	8.1	0.091	0.40
CDBAA	1.00	1.19	0.149	12	0.468	0.75
TBAA	2.00	1.91	0.261	14	0.820	1.5

[a]Produced by analysis of seven aliquots of fortified reagent water.

[b]The MDL is a statistical estimate of the detection limit. To determine the MDL for each analyte, the standard deviation of the mean concentration of the seven replicates is calculated. This standard deviation is then multiplied by the student's t-value at 99% confidence and n-1 degrees of freedom (3.143 for seven replicates). The result is the MDL.

[c]The EDL is defined as either the MDL or a level of a compound in a sample yielding a peak in the final extract with a signal to noise (S/N) ratio of approximately five, whichever is greater.

TABLE 3. ANALYTE ACCURACY AND PRECISION DATA[a]

LEVEL 2 IN REAGENT WATER

Analyte	Fortified Conc. µg/L	Mean. Meas. Conc. µg/L	Std. Dev. µg/L	Rel. Std. Dev. %	Mean Recovery %
Monochloroacetic Acid	1.50	1.42	0.103	7.3	94.7
Monobromoacetic Acid	1.00	1.02	0.051	5.0	102
Dichloroacetic Acid	1.50	1.27	0.122	9.6	84.7
Dalapon	1.00	0.935	0.087	9.3	93.5
Trichloroacetic Acid	0.500	0.465	0.048	10	93.0
Bromochloroacetic Acid	1.00	0.869	0.049	5.6	86.9
Dibromoacetic Acid	0.500	0.477	0.044	9.2	95.4
Bromodichloroacetic Acid	1.00	1.07	0.098	9.2	107
Chlorodibromoacetic Acid	2.50	2.62	0.150	5.7	105
Tribromoacetic Acid	5.00	5.19	0.587	11	104

[a]Produced by analysis of seven aliquots of fortified reagent water.

TABLE 4. ANALYTE ACCURACY AND PRECISION DATA[a]

LEVEL 4 IN REAGENT WATER

Analyte	Fortified Conc. µg/L	Mean. Meas. Conc. µg/L	Std. Dev. µg/L	Rel. Std. Dev. %	Mean Recovery %
Monochloroacetic Acid	6.00	5.24	0.664	13	87.3
Monobromoacetic Acid	4.00	4.36	0.475	11	109
Dichloroacetic Acid	6.00	6.89	0.782	11	115
Dalapon	4.00	3.87	0.147	3.8	96.8
Trichloroacetic Acid	2.00	1.74	0.144	8.3	87.0
Bromochloroacetic Acid	4.00	4.33	0.402	9.3	108
Dibromoacetic Acid	2.00	1.87	0.113	6.0	93.5
Bromodichloroacetic Acid	4.00	3.93	0.377	9.6	98.2
Chlorodibromoacetic Acid	10.0	11.4	0.866	7.6	114
Tribromoacetic Acid	20.0	24.0	1.82	7.6	120

[a]Produced by analysis of seven aliquots of fortified reagent water.

TABLE 5. ANALYTE ACCURACY AND PRECISION DATA[a,b]

LEVEL 3 IN DECHLORINATED TAP WATER[c]

Analyte	Background Conc. µg/L	Forti-fied Conc. µg/L	Mean Meas. Conc. µg/L	Std. Dev. µg/L	Rel. Std. Dev. %	Mean Rec. %
Monochloroacetic Acid	<0.6	3.00	2.53	0.090	3.6	84.3
Monobromoacetic Acid	0.420	2.00	2.20	0.034	1.5	89.0
Dichloroacetic Acid	0.625	3.00	3.77	0.096	2.5	105
Dalapon	<0.4	2.00	1.96	0.157	8.0	98.0
Trichloroacetic Acid	0.300	1.00	1.12	0.167	15	82.0
Bromochloroacetic Acid	1.23	2.00	2.91	0.062	2.1	84.0
Dibromoacetic Acid	1.27	1.00	2.35	0.110	4.7	108
Bromodichloroacetic Acid	0.588	2.00	2.52	0.388	15	96.6
Chlorodibromoacetic Acid	1.23	5.00	6.36	0.502	7.9	103
Tribromoacetic Acid	<2.0	10.0	11.8	1.65	14	118

[a]Produced by analysis of seven aliquots of fortified reagent water.
[b]Background level subtracted.
[c]Chlorinated surface water from a local utility to which ammonium chloride was added as the dechlorinating agent.

TABLE 6. ANALYTE ACCURACY AND PRECISION DATA[a,b]

LEVEL 3 IN HIGH IONIC STRENGTH WATER[c]

Analyte	Background Conc. µg/L	Forti-fied Conc. µg/L	Mean Meas. Conc. µg/L	Std. Dev. µg/L	Rel. Std. Dev. %	Mean Rec. %
Monochloroacetic Acid	0.761	3.00	3.32	0.429	13	85.3
Monobromoacetic Acid	1.47	2.00	3.19	0.099	3.1	86.0
Dichloroacetic Acid	1.50	3.00	4.44	0.264	5.9	98.0
Dalapon	0.675	2.00	2.39	0.259	11	85.8
Trichloroacetic Acid	1.01	1.00	1.75	0.110	6.3	74.0
Bromochloroacetic Acid	2.06	2.00	3.71	0.269	7.3	82.5
Dibromoacetic Acid	4.36	1.00	5.48	0.255	4.7	112
Bromodichloroacetic Acid	1.07	2.00	3.37	0.308	9.1	115
Chlorodibromoacetic Acid	2.48	5.00	7.94	1.00	13	109
Tribromoacetic Acid	4.63	10.0	17.2	1.55	9.0	126

[a]Produced by analysis of seven aliquots of fortified reagent water.
[b]Background level subtracted.
[c]Chlorinated ground water from a water source displaying a hardness of 460 mg/L as $CaCO_3$.

TABLE 7. ANALYTE ACCURACY AND PRECISION DATA[a]

LEVEL 3 IN HIGH HUMIC CONTENT GROUND WATER[b]

Analyte	Background Conc. µg/L	Forti-fied Conc. µg/L	Mean Meas. Conc. µg/L	Std. Dev. µg/L	Rel. Std. Dev. %	Mean Rec. %
Monochloroacetic Acid	<0.6	3.00	2.91	0.082	2.8	97.0
Monobromoacetic Acid	<0.4	2.00	1.99	0.105	5.3	99.5
Dichloroacetic Acid	<0.6	3.00	2.88	0.104	3.6	96.0
Dalapon	<0.4	2.00	2.00	0.227	11	100.0
Trichloroacetic Acid	<0.2	1.00	0.618	0.053	8.6	61.8
Bromochloroacetic Acid	<0.4	2.00	1.82	0.059	3.2	91.0
Dibromoacetic Acid	<0.2	1.00	0.715	0.020	2.8	71.5
Bromodichloroacetic Acid	<0.4	2.00	1.99	0.164	8.2	99.5
Chlorodibromoacetic Acid	<1.0	5.00	5.50	0.218	4.0	110.0
Tribromoacetic Acid	<2.0	10.0	9.67	1.13	12	96.7

[a]Produced by analysis of seven aliquots of fortified reagent water.
[b]Background level subtracted.

TABLE 8. LABORATORY PERFORMANCE CHECK SOLUTION

Parameter	Analyte	Conc. µg/mL in MTBE	Acceptance Criteria
Sensitivity	MCAA	0.006	Detection of analyte; S/N[a] >3
Chromatographic performance	BCAA	0.004	PGF[b] between 0.80 and 1.15
Column performance	CDBAA Surrogate (2,3-DBPA)	0.010 0.010	Resolution[c] >0.50

[a]S/N = a ratio of peak signal to baseline noise.

peak signal - measured as height of peak.
baseline noise - measured as maximum deviation in baseline (in units of height) over a width equal to the width of the base of the peak.

[b]PGF -- Peak Gaussian factor

$$PGF = \frac{1.83 \times W_{1/2}}{W_{1/10}}$$

where: $W_{1/2}$ = the peak width at half height in seconds
$W_{1/10}$ = the peak width in seconds at one-tenth height (in seconds)

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

$$R = \frac{t}{W_{ave}}$$

where: t = the difference in elution times between the two peaks
W_{ave} = the average peak width of the two peaks (measurements take at baseline)

This is a measure of the degree of separation of two peaks under specific chromatographic condtions.