METHOD 552.1

DETERMINATION OF HALOACETIC ACIDS AND DALAPON IN DRINKING WATER BY ION-EXCHANGE LIQUID-SOLID EXTRACTION AND GAS CHROMATOGRAPHY WITH AN ELECTRON CAPTURE DETECTOR

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Jimmie W. Hodgeson

David Becker (Technology Applications Inc.)

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

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1.0 SCOPE AND APPLICATION

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

Analyte	Chemical Abstract Services Registry Number
Monochloroacetic Acid	79-11-8
Dichloroacetic Acid	79-43-6
Trichloroacetic Acid	76-03-9
Monobromoacetic Acid	79-08-3
Bromochloroacetic Acid	5589-96-8
Dibromoacetic Acid	631-64-1
Dalapon	75-99-0

1.2 This is a liquid-solid extraction method and is designed as a simplified alternative to the liquid-liquid extraction approach of Method 552 for the haloacetic acids. This method also provides a much superior technique for the determination of the herbicide, dalapon, compared to the complex herbicide procedure described in Method 515.1. The procedure also represents a major step in the incorporation of pollution prevention in methods development, in that the use of large volumes of organic solvents is eliminated.

1.3 This method is applicable to the determination of the target analytes over the concentration ranges typically found in drinking water[2,3], subject to the method detection limits (MDL) listed in Table 2. The MDLs observed may vary according to the particular matrix analyzed and the specific instrumentation employed. The haloacetic acids are observed ubiquitously in chlorinated supplies at concentrations ranging from <1 to >50 µg/L.

1.4 Reduced analyte recoveries may be observed in high ionic strength matrices, particularly waters containing elevated sulfate concentrations. Improved recoveries may be obtained by sample dilution at the expense of higher MDLs. This effect is discussed more extensively in Section 4.2.

1.5 Tribromoacetic acid has not been included because of problems associated with stability and chromatography with this method. Mixed bromochloroacetic acids have recently been synthesized. Bromochloroacetic acid is present in

chlorinated supplies and method validation data are provided here. Commercial standards are now available for this compound. The mixed trihalogenated acids may also be present. These are not included because of current problems with purity and the chromatography for these compounds.

1.6 This method is designed for analysts skilled in extract concentration techniques, derivatization procedures and the use of GC and interpretation of gas chromatograms.

1.7 When this method is used for the analyses of waters from unfamiliar sources, analyte identifications must be confirmed by at least one additional qualitative technique, such as gas chromatography/mass spectrometry (GC/MS) or by GC using dissimilar columns.

2.0 SUMMARY OF METHOD

2.1 A 100-mL volume of sample is adjusted to pH 5.0 and extracted with a preconditioned miniature anion exchange column.

NOTE: The use of liquid-solid extraction disks is certainly permissible as long as all the quality control criteria specified in Section 9.0 of this method are met. The analytes are eluted with small aliquots of acidic methanol and esterified directly in this medium after the addition of a small volume of methyl-tert-butyl ether (MTBE) as co-solvent. The methyl esters are partitioned into the MTBE phase and identified and measured by capillary column gas chromatography using an electron capture detector (GC/ECD).

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 taken in the laboratory 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 (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.

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 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.

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 gas chromatograms. All reagents and apparatus must be routinely demonstrated to be free from significant interferences under the conditions of the analysis by analyzing laboratory reagent blanks as described in Section 9.2.

4.1.1 For each set of samples analyzed, the reagent blank concentration values exceeding 0.1 µg/L should be subtracted from the sample concentrations. A persistent reagent blank of approximately 1 µg/L was observed for bromochloroacetic acid (BCAA) on the primary DB-1701 column. The background was clean on the DB-210 confirmation column and the MDL for BCAA in Table 2 was determined using this column.

4.1.2 Glassware must be scrupulously cleaned[4]. 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, dilute acid, and reagent water. Drain and heat in an oven or muffle furnace at 400°C for one hour. Do not heat volumetric ware. Thermally stable materials such as PCBs may not be eliminated by this treatment. Thorough rinsing with reagent grade acetone may be substituted for the heating. After drying and cooling, store glassware in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

4.1.3 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required. The extraction solvent, MTBE, may need to be redistilled.

4.2 The major potential interferences in this ion-exchange procedure are other naturally occurring ions in water sources, principally sulfate. This is the only ion thus far demonstrated as an interference, when present at concentrations possibly occurring in drinking water sources. Sulfate as an effective counter ion displaces the haloacids from the column when present at concentrations above 200 mg/L. Table 4 illustrates this effect for fortified reagent water containing 500 mg/L and 400 mg/L of Na_2SO_4 and NaCl respectively (approximately 3.7 millimole (mM) in both cases). Markedly reduced

recoveries are observed for all analytes in the presence of high concentrations of sulfate. Reduced recoveries may be observed for the monohaloacetic acids in very high ionic strength waters, as illustrated for the sample with 400 mg/L NaCl. However, normal recoveries were observed from a water sample containing the same molar concentration of $CaCl_2$. The only preventive measure currently available for high ionic strength waters is sample dilution. Dilution by a factor of 5 will suffice in the vast majority of cases, although a factor of 10 may be required in a few extreme sites (e.g., western waters with sulfate >1000 mg/L). The MDLs will still be approximately 1 µg/L for a dilution factor of 5. However, for many chlorinated supplies the monohaloacetic acids may occur at concentrations near 1 µg/L. In any event, this is the recommended method to determine dalapon.

4.3 The acid forms of the analytes are strong organic acids which react readily with alkaline substances, and can be lost during sample preparation. Glassware must be acid rinsed with 1:9 hydrochloric acid: water prior to use to avoid analyte losses due to adsorption.

4.4 Organic acids and phenols, especially chlorinated compounds, are the most direct potential interferences with the determination. The procedure includes a methanol wash step after the acid analytes are adsorbed on the column. This step eliminates the potential for interferences from neutral or basic, polar organic compounds present in the sample.

4.5 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.

4.6 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. Tentative identifications should be confirmed using the confirmation column specified in Table 1 or by the use of gas chromatography with mass spectrometric detection.

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 data handling sheets should also be made available to all personnel involved in the chemical

analysis. Additional references to laboratory safety are available and have been identified[5-7] for the information of the analyst.

5.2 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. For such individuals a mask may be required. Protective clothing and gloves should be used and MTBE should be used only in a chemical fume hood or glove box.

6.0 EQUIPMENT AND SUPPLIES

6.1 Sample Containers -- Amber glass bottles, approximately 250 mL, fitted with Teflon-lined screw caps. At least 200 mL of sample should be collected.

6.2 Gas Chromatograph (GC) -- Analytical system complete with GC equipped for electron capture detection, split/splitless capillary 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. The gases flowing through the electron capture detector should be vented through the laboratory fume hood system.

6.3 Primary GC Column -- DB-1701 or equivalent bonded, fused silica column, 30 m x 0.32 mm ID, 0.25 µm film thickness. Another type of column may be used if equivalent or better separation of analytes can be demonstrated.

6.4 Confirmatory GC Column -- DB-210 or equivalent bonded, fused silica column, 30 m x 0.32 mm ID, 0.50 µm film thickness. Another type of column may be used if equivalent or better separation of analytes can be demonstrated.

6.5 Pasteur Pipets -- Glass disposable.

6.6 pH Meter -- Wide range with the capability of accurate pH measurements at pH 5 ±0.5.

6.7 Amber Colored Bottles (15 mL) -- With Teflon-lined screw caps.

6.8 Liquid-Solid Extraction Vacuum Manifold -- Available from a number of suppliers.

6.9 LSE Cartridges (1 mL) and Frits -- Also available from a number of suppliers. The use of LSE disks instead of cartridges is permissible as long as all the quality control criteria in Section 9.0 of this method are met.

6.10 Reservoirs (75 mL) plus Adapters -- Available from J. T. Baker, Cat. No. 7120-03 and Cat. No. 7122-00.

6.11 Graduated Conical Centrifuge Tubes -- With teflon-lined screw caps (15 mL).

6.12 Screw Cap Culture Tubes -- Suggested size 13 x 100 mm.

6.13 Block Heater -- Capable of holding screw cap culture tubes in Section 6.12.

6.14 Vortex Mixer

7.0 REAGENTS AND STANDARDS

7.1 Reagent Water -- Reagent water is defined as a water in which an interference is not observed at 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 Test reagent water each day it is used by analyzing according to Section 11.0.

7.2 Methanol -- Pesticide quality or equivalent.

7.3 Methyl-Tert-Butyl Ether -- Nanograde, redistilled in glass if necessary. Ethers must be demonstrated to be free of peroxides. One test kit (EM Quant Test Strips), is available from EM Science, Gibbstown, NJ. Procedures for removing peroxides from the ether are provided with the test strips. Ethers must be periodically tested (at least monthly) for peroxide formation during use. Any reliable test kit may be used.

7.4 Sodium Sulfate -- ACS, granular, anhydrous. Heat in a shallow tray at 400°C for a minimum of four hours to remove phthalates and other interfering organic substances. Alternatively, extract with methylene chloride in a Soxhlet apparatus for 48 hours.

7.5 Sodium Hydroxide (NaOH), 1N -- Dissolve 4 g ACS grade in reagent water in a 100 mL volumetric flask and dilute to the line.

7.6 1,2,3-trichloropropane, 99+% -- For use as the internal standard.

7.7 2-Bromopropionic Acid -- For use as a surrogate compound.

7.8 10% Na_2SO_4/H_2O (By Weight) Solution -- Dissolve 10g Na_2SO_4 in 90 g reagent water.

7.9 10% H_2SO_4/MeOH Solution -- Prepare a solution containing 10 mL H_2SO_4 in 90 mL methanol.

7.10 1M HCl/MeOH -- Prepare a solution containing 8.25 mL HCl (ACS grade) with 91.75 mL methanol.

7.11 AG-1-X8 Anion Exchange Resin -- Rinse resin with three consecutive 500 mL aliquots of deionized water and store in deionized water. Available from Biorad, Richmond, CA.

7.12 Acetone -- ACS reagent grade or equivalent.

7.13 Ammonium Chloride -- ACS reagent grade or equivalent.

7.14 Sodium Sulfite -- ACS reagent grade or equivalent.

7.15 Stock Standard Solutions

7.15.1 Analytes and surrogates (Table 1) -- Prepare at 1-5 mg/mL in MTBE.

7.15.2 Internal standard fortifying solution -- Prepare a solution of 1,2,3-trichloropropane at 1 mg/mL by adding 36 µL of the neat material (Section 7.6) to 50 mL of MTBE. From this stock standard solution, prepare a primary dilution standard at 10 mg/L by the addition of 1-100 mL MTBE.

7.15.3 Surrogate standard fortifying solution -- Prepare a surrogate stock standard solution of 2-bromopropionic acid at a concentration of 1 mg/mL by accurately weighing approximately 10 mg of 2-bromopropionic acid, transferring it to a 10 mL volumetric, and diluting to the mark with MTBE. Prepare a primary dilution standard at a concentration of 2.5 µg/mL by diluting 250 µL of the stock standard to 100 mL with methanol.

8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Grab samples must be collected in accordance with conventional sampling practices[9] using amber glass containers with TFE-lined screw-caps and capacities in excess of 100 mL.

8.1.1 Prior to shipment to the field, to combine residual chlorine, add crystalline ammonium chloride (NH_4Cl) to the sample container in an amount to produce a concentration of 100 mg/L in the sample. Alternatively, add 1.0 mL of a 10 mg/mL aqueous solution of NH_4Cl to the sample bottle for each 100 mL of sample bottle capacity immediately prior to sample collection. Granular ammonium chloride may also be added directly to the sample bottle.

8.1.2 After collecting the sample in the bottle containing the dechlorination reagent, seal the bottle and agitate for one minute.

8.1.3 Samples must be iced or refrigerated at 4°C and maintained at these conditions away from light until extraction. Holding studies performed to date have suggested that, in samples dechlorinated with NH_4Cl, the

analytes are stable for up to 28 days. Since stability may be matrix dependent, the analyst should verify that the prescribed preservation technique is suitable for the samples under study.

8.1.4 Extract concentrates (Section 11.3.6) should be stored at 4°C or less away from light in glass vials with Teflon-lined caps. Extracts should be analyzed within 48 hours following preparation.

9.0 QUALITY CONTROL

9.1 Minimum quality control (QC) requirements are initial demonstration of laboratory capability, determination of surrogate compound recoveries in each sample and blank, monitoring internal standard peak area or height in each sample and blank, analysis of laboratory reagent blanks, laboratory fortified blanks, laboratory fortified sample matrices, and QC samples. Additional QC practices are recommended.

9.2 Laboratory Reagent Blanks (LRB) -- Before processing any samples, the analyst must analyze at least one 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 within the retention time window (Section 11.4.4) of any analyte, the LRB produces an interference significantly in excess of that anticipated (Section 4.1.1), determine the source of contamination and eliminate the interference before processing samples.

9.3 Initial Demonstration of Capability

9.3.1 Select a representative fortified concentration for each of the target analytes. Concentrations near Level 2 (Table 4) are recommended. Prepare four to seven replicate laboratory fortified blanks (LFB) by adding an appropriate aliquot of the primary dilution standard or another certified quality control sample. Be sure to add the internal standard, 1,2,3-trichloropropane, and the surrogate compound, 2 bromopropionic acid, to these samples (See Section 11.0). Analyze the LFBs according to the method beginning in Section 11.0 and calculate mean recoveries and standard deviation for each analyte.

9.3.2 Calculate the mean percent recovery, the standard deviation of the recoveries, and the MDL[10]. For each analyte, the mean recovery value, expressed as a percentage of the true value, must fall in the range of 70-130% and the standard deviation should be less than 30%. For those compounds that meet these criteria, performance is considered acceptable and sample analysis may begin. For those compounds that fail these criteria, this procedure must be repeated using a minimum of four fresh samples until satisfactory performance has been demonstrated. Maintain this data on file to demonstrate initial capabilities.

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

9.3.4 The analyst is permitted to modify GC columns, GC conditions, detectors, extraction techniques, concentration techniques (i.e., evaporation techniques), internal standard or surrogate compounds. Each time such method modifications are made, the analyst must repeat the procedures in Section 9.3.1 and also analyze a laboratory fortified matrix sample.

9.4 Assessing Surrogate Recovery

9.4.1 When surrogate recovery from a sample or blank 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.

9.4.2 If the extract reanalysis fails the 70-130% recovery criterion, the problem must be identified and corrected before continuing. It may be necessary to extract another aliquot of sample.

9.4.3 If the extract reanalysis meets the surrogate recovery criterion, report only data for the reanalyzed extract. If sample extract continues to fail the recovery criterion, report all data for that sample as suspect.

9.4.4 Develop and maintain control charts on surrogate recovery as described in Section 9.6.2. Charting of surrogate recoveries is an especially valuable activity, since these are present in every sample and the analytical results will form a significant record of data quality.

9.5 Assessing the Internal Standard

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

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

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

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

9.5.3 If consecutive samples fail the IS response acceptance criteria, immediately analyze a medium calibration standard.

9.5.3.1 If the calibration standard provides a response factor (RF) within 20% of the predicted value, then follow procedures itemized in Section 9.5.2 for each sample failing the IS response criterion.

9.5.3.2 If the check standard provides a response factor which deviates more than 20% of the predicted value, then the analyst must recalibrate (Section 10.0).

9.6 Laboratory Fortified Blank (LFB)

9.6.1 The laboratory must analyze at least one LFB sample with every 20 samples or one per sample set (all samples extracted within a 24-hour period), whichever is greater. Fortified concentrations near Level 2 (Table 4) are recommended. Calculate percent recovery (R). If the recovery of any analyte falls outside the control limits (see Section 9.6.2), that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

9.6.2 Prepare control charts based on mean upper and lower control limits, $R \pm 3\ S_R$. The initial demonstration of capability (Section 9.3) establishes the initial limits. After each four to six new recovery measurements, recalculate R and S_R using all the data, and construct new control limits. When the total number of data points reach 20, update the control limits by calculating R and S_R using only the most recent 20 data points. At least quarterly, replicates of LFBs should be analyzed to determine the precision of the laboratory measurements. Add these results to the ongoing control charts to document data quality.

9.7 Laboratory Fortified Sample Matrix

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. Table 6 illustrates the relatively poor accuracy and precision which may be anticipated when a large background must be subtracted. The water supply used in the development of this method contained only moderate concentrations of DCAA and TCAA. For many supplies, 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. Poor accuracies and high precisions across all analytes likely indicate the presence of interfering ions, especially sulfate, and the requirement for sample dilution.

9.7.2 The laboratory must add known concentrations of analytes to a minimum of 10% of samples or one sample per sample set, whichever is greater. The concentrations should be equal to or greater than the background concentrations in the sample selected for fortification. Ideally, the concentration should be the same as that used for the laboratory fortified blank (Section 9.6). 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 background concentration, B, measured in the unfortified sample, i.e.:

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

where C is the fortifying concentration. Compare these values to control limits appropriate for reagent water data collected in the same fashion (Section 9.6).

9.7.4 If the analysis of the unfortified sample reveals the absence of measurable background concentrations, and the added concentrations are those specified in Section 9.6, then the appropriate control limits would be the acceptance limits in Section 9.6.

9.7.5 If the sample contains measurable background concentrations of analytes, calculate mean recovery of the fortified concentration, R, for each such analyte after correcting for the background concentration (Section 9.7.3). Compare these values to reagent water recovery data, R*, at comparable fortified concentrations from Tables 2, 4, and 5. Results are considered comparable if the measured recoveries fall within the range,

$$R \pm 3S_c,$$

where S_c is the estimated percent relative standard deviation in the measurement of the fortified concentration. By contrast to the measurement of recoveries in reagent water (Section 9.6.2) or matrix samples without background (Section 9.7.3), the relative standard deviation, S_c, must be expressed as the statistical sum of variation from two sources, the measurement of the total concentration as well as the

measurement of background concentration. In this case, variances, defined as S^2, are additive and S_c can be expressed as,

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

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

where S_a and S_b are the percent relative standard deviations of the total measured concentration and the background concentration respectively. The value of S_a may be estimated from the mean measurement of A above or from data at comparable concentrations from Tables 2, 4, and 5. Likewise, S_b can be measured from repetitive measurements of the background concentration or estimated from comparable concentration data from Tables 2, 4, and 5.

9.7.6 If the recovery of any such analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control (Section 9.6), the recovery problem encountered with the fortified sample is judged to be matrix related, not system related. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

9.8 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.

9.9 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 field reagent blanks may be used to assess contamination of samples under site conditions, transportation and storage.

10.0 CALIBRATION AND STANDARDIZATION

10.1 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.

10.2 Internal Standard Calibration Procedure -- This approach requires the analyst to select one or more internal standards which are compatible in analytical behavior with the method analytes. For the single laboratory precision and accuracy data reported in Tables 2-9, one internal standard, 1,2,3-trichloropropane, was used as a concentration of 0.4 µg/mL in the final 5.0-mL concentrate.

10.2.1 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.

10.2.2 Prepare primary dilution standard solutions by combining and diluting stock standard solutions with methanol. As a guideline to the analyst, the primary dilution standard solution used in the validation of this method is described here. Stock standard solutions were prepared in the 1-2 mg/mL range for all analytes and the surrogate. Aliquots of each stock standard solution (approximately 50-250 µL) were added to 100-mL methanol to yield a primary dilution standard containing the following approximate concentrations of analytes:

	Concentration, µg/mL
Monochloroacetic acid	3
Monobromoacetic acid	2
Dalapon	2
Dichloroacetic acid	3
2-Bromopropionic acid	1
Trichloroacetic acid	1
Bromochloroacetic acid	2
Dibromoacetic acid	1

The primary dilution standards are used to prepare calibration standards, which comprise at least three concentration levels (optimally five) 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.

10.2.2.1 Calibration standards -- Calibration is performed by extracting procedural standards, i.e.; fortified reagent water. A five-point calibration curve may be prepared by fortifying a 100- mL reagent water samples at pH 5 with 20, 50, 100, 250, and 500 µL of the primary dilution standard prepared above. Alternatively, three levels of calibration solutions may be prepared. Analyze each calibration standard in triplicate according to the procedure outlined in Section 11.0. In addition, a reagent water blank must be analyzed in triplicate.

10.2.3 Include the surrogate analyte, 2-bromopropionic acid, within the calibration standards prepared in Section 10.2.2.

10.2.4 Inject 2 µL of each standard and calculate the relative response for each analyte (RR_a) using the equation:

$$RR_a = A_a / A_{is}$$

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

10.2.5 Generate a calibration curve of RR_a versus analyte concentration of the standards expressed in equivalent µg/L in the original aqueous sample. The working calibration curve must be verified daily by measurement of one or more calibration standards. If the response for any analyte falls outside the predicted response by more than 15%, the calibration check must be repeated using a freshly prepared calibration standard. Should the retest fail, a new calibration curve must be generated.

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

11.0 PROCEDURE

11.1 Preparation and Conditioning of Extraction Columns

11.1.1 Preparation -- Place 1 mL liquid-solid extraction cartridges (Section 6.9) onto the vacuum manifold. Place frits into the tubes and push down to place them flat on the bottom. Add the AG-1-X8 resin solution dropwise to the tubes with a Pasteur pipet until there is a solid layer of resin 10 mm in height. Add reagent water and apply vacuum to settle out the suspended resin particles. Do not allow the resin to go dry. At this point extraction of samples can begin or the columns can be stored for later use by maintaining the resin under water and sealing the top with aluminum foil.

11.1.2 Conditioning -- Attach adapters and 75 mL reservoirs to the liquid-solid extraction cartridges. To condition the columns, add to the reservoirs and pass the following series of solvents in 10 mL aliquots through the resin under vacuum: methanol, reagent water, 1 M HCl/MeOH, reagent water, 1 M NaOH, and reagent water. The conditioning solvents should pass through the resin at the rate of ≈ 2 mL/min. without allowing the resin bed to dry and the sample should be added (Section 11.2.3) immediately after the last reagent water aliquot.

11.2 Sample Extraction and Elution

11.2.1 Remove the samples from storage (Section 8.1.3) and allow them to equilibrate to room temperature.

11.2.2 Adjust the pH of a 100 mL sample to 5 ±0.5 using 1:2 H_2SO_4 water and check the pH with a pH meter or narrow range pH paper.

11.2.3 Add 250 µL of the surrogate primary dilution standard (Section 7.15.3) to each sample.

11.2.4 Transfer the 100 mL sample to the reservoir and apply a vacuum to extract the sample at the rate of ≈ 2 mL/min.

11.2.5 Once the sample has completely passed through the column add 10 mL MeOH to dry the resin.

11.2.6 Remove the reservoirs and adapters, disassemble the vacuum manifold and position screw cap culture tubes (Section 6.12) under the columns to be eluted. Reassemble the vacuum manifold, add 4 mL 10% H_2SO_4/methanol to the column and elute at the rate of approximately 1.5 mL/min. Turn off the vacuum and remove the culture tubes containing the eluants.

11.3 Solvent Partition

11.3.1 Add 2.5 mL MTBE to each eluant and agitate in the vortex mixer at a low setting for about five seconds.

11.3.2 Place the capped culture tubes in the heating block (Section 6.13) at 50°C and maintain for one hour. At this stage, quantitative methylation of all method analytes is attained.

11.3.3 Remove the culture tubes from the heating block and add to each tube 10 mL of 10% by weight of sodium sulfate in reagent water (Section 7.8). Agitate each solution for 5-10 seconds in the vortex mixer at a high setting.

11.3.4 Allow the phases to separate for approximately five minutes. Transfer the upper MTBE layer to a 15 mL graduated conical centrifuge tube (Section 6.11) with a pasteur pipet. Repeat the extraction two more times with approximately 1 mL MTBE each time. Combine the MTBE sample extracts in the graduated centrifuge tube.

11.3.5 Add 200 µL of the internal standard fortifying solution (Section 7.15.2) to each extract and add MTBE to each to a final volume of 5 mL.

11.3.6 Transfer a portion of each extract to a vial and analyze using GC-ECD. A duplicate vial should be filled from excess extract. Analyze the samples as soon as possible. The sample extract may be stored up to 48 hours if kept at 4°C or less away from light in glass vials with Teflon-lined caps.

11.4 Gas Chromatography

11.4.1 Table 1 summarizes recommended GC operating conditions and retention times observed using this method. Figure 1 illustrates the performance of the recommended column with the method analytes. Other GC columns, chromatographic conditions, or detectors may be used if the requirements of Section 9.3 are met.

11.4.2 Calibrate the system daily as described in Section 10.0. The standards and extracts must be in MTBE.

11.4.3 Inject 2 µL of the sample extract. Record the resulting peak size in area units.

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

11.4.5 If the response for the peak exceeds the working range of the system, dilute the extract and reanalyze.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Calculate analyte concentrations in the sample and reagent blanks from the response for the analyte relative to the internal standard (RR_a) using the equation in Section 10.2.4.

12.2 For samples processed as part of a set where recoveries falls outside of the control limits established in Section 9.0, results for the affected analytes must be labeled as suspect.

13.0 METHOD PERFORMANCE

13.1 In a single laboratory (EMSL-Cincinnati), recovery and precision data were obtained at three concentrations in reagent water (Tables 2, 4, and 5). In addition, recovery and precision data were obtained at a medium concentration for high ionic strength reagent water (Table 3), dechlorinated tap water, high humectant ground water, and an ozonated surface water (Tables 6-9). The MDL[10] data are given in Table 2.

14.0 POLLUTION PREVENTION

14.1 This method utilizes the new LSE technology which requires the use of very small quantities of organic solvents. This feature eliminates 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 in place of the highly toxic diazomethane. These features make this method much safer for use by the analyst in the laboratory and much less harmful to the environment.

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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17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. RETENTION DATA AND CHROMATOGRAPHIC CONDITIONS

Analyte	Retention Time (min) Column A	Column B
Monochloroacetic Acid (MCAA)	5.16	9.44
Monobromoacetic Acid (MBAA)	7.77	11.97
Dalapon	8.15	11.97
Dichloroacetic Acid (DCAA)	8.37	11.61
2-Bromopropionic acid[b]	8.80	12.60
Trichloroacetic Acid (TCAA)	11.43	13.34
1,2,3-Trichloropropane[a]	12.62	12.91
Bromochloroacetic Acid (BCAA)	12.92	14.20
Dibromoacetic Acid (DBAA)	15.50	16.03

Column A: DB-1701, 30 m x 0.32 mm i.d., 0.25 µm film thickness, Injector Temp. = 200°C, Detector Temp. = 260°C, Helium Linear Velocity = 27 cm/sec, Splitless injection with 30 second delay.

Program: Hold at 50°C for 10 minutes, to 200°C at 10°C/min. and hold five minutes, to 230°C at 10°C/min. and hold five minutes.

Column B: DB-210, 30 m x 0.32 mm i.d., 0.50 µm film thickness, Injector Temp. = 200°C, Detector Temp. = 260°C, Linear Helium Flow = 25 cm/sec, splitless injection with 30 second delay.

Program: Hold at 50°C for 10 minutes, to 200°< at 10°C/min and hold five minutes, to 230°C at 10°C/min. and hold five minutes.

[a]Internal Standard.
[b]Surrogate Compound.

TABLE 2. ANALYTE RECOVERY 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. (%)	Mean Recovery (%)	Method Detection Limit (µg/L)
Monochloroacetic Acid	1.5	1.47	0.07	4.6	98	0.21
Monobromoacetic Acid	1.0	0.73	0.08	7.9	73	0.24
Dichloroacetic Acid	1.5	1.65	0.14	7.7	110	0.45
2-Bromopropionic Acid[b]	0.05	0.47	0.03	5.6	94	0.08
Trichloroacetic Acid	0.50	0.30	0.02	4.0	60	0.07
Bromochloroacetic acid	1.0	0.75	0.03	3.4	75	0.10
Dibromoacetic Acid	0.50	0.29	0.03	6.4	58	0.09
Dalapon	1.0	0.81	0.10	12	81	0.32

[a]Produced by analysis of seven aliquots of fortified reagent water (Reference 10).
[b]Surrogate Compound.

TABLE 3. RECOVERY AND PRECISION DATA IN HIGH IONIC STRENGTH WATERS

MEAN RECOVERY ±RSD[a]

Analyte	Fortified Conc. (µg/L)	Reagent Water (RW)	Reagent Water + 500 mg/L Na_2SO_4[b]	Reagent Water + 400 mg/L NaCl[b]
Monochloroacetic Acid	7.5	109 ± 1.5	–	46 ± 10
Monobromoacetic Acid	5.0	83 ± 18	5.0 ± 10	50 ± 13
Dichloroacetic Acid	7.5	107 ± 3.6	59 ± 2.4	114 ± 0.1
2-Bromopropionic Acid	2.5	108 ± 1.8	32 ± 0.3	137 ± 2.1
Trichloroacetic Acid	2.5	101 ± 0.4	8 ± 3.0	64 ± 11
Bromochloroacetic Acid	5.0	101 ± 2.6	85 ± 0.7	107 ± 3.5
Dibromoacetic Acid	2.5	93 ± 1.9	40 ± 22	89 ± 5.0
Dalapon	5.0	93 ± 1.9	57 ± 5.3	99 ± 1.7

[a]Based on the analysis of three replicate samples.
[b]Molar concentration of added salt is 3.7 mM in both cases.

TABLE 4. ANALYTE RECOVERY 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	7.5	7.73	0.18	2.3	103
Monobromoacetic Acid	5.0	3.95	0.65	16	79
Dichloroacetic Acid	7.5	8.06	0.16	2.0	108
2-Bromopropionic Acid[b]	2.5	2.57	0.06	2.4	103
Trichloroacetic Acid	2.5	2.32	0.14	5.8	93
Bromochloroacetic Acid	5.0	5.22	0.12	2.2	104
Dibromoacetic Acid	2.5	2.41	0.09	3.4	96
Dalapon	5.0	4.03	0.36	7.5	97

[a]Produced by the analysis of seven aliquots of fortified reagent water.
[b]Surrogate Compound.

TABLE 5. ANALYTE RECOVERY AND PRECISION DATA[a]

LEVEL 3 IN REAGENT WATER

Analyte	Fortified Conc. (µg/L)	Mean Meas. Conc. (µg/L)	Std. Dev. (µg/L)	Rel. Std. Dev. (%)	Mean Recovery (%)
Monochloroacetic Acid	15.0	14.5	0.15	1.0	99
Monobromoacetic Acid	10.0	7.82	0.68	8.4	78
Dichloroacetic Acid	15.0	15.1	6.09	0.6	101
2-Bromopropionic Acid	5.0	4.98	0.08	1.5	100
Trichloroacetic Acid	5.0	4.89	0.07	1.4	98
Bromochloroacetic Acid	10.0	10.3	0.25	2.4	103
Dibromoacetic Acid	5.0	4.85	0.04	0.7	97
Dalapon	10.0	9.02	0.16	1.8	90

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

TABLE 6. ANALYTE RECOVERY AND PRECISION DATA[a]

DECHLORINATED TAP WATER

Analyte	Fortified Conc. (µg/L)	Mean[b] Meas. Conc. (µg/L)	Std. Dev. (µg/L)	Rel. Std. Dev. (%)	Mean Recovery (%)
Monochloroacetic Acid	7.5	5.70	0.63	11	76
Monobromoacetic Acid	5.0	4.57	0.45	9.8	91
Dichloroacetic Acid	7.5	5.62	0.76	14	75
2-Bromopropionic Acid[c]	7.5	2.22	0.16	7.2	89
Trichloroacetic Acid	2.5	1.48	0.42	28	59
Bromochloroacetic Acid	5.0	5.70	0.92	16	114
Dibromoacetic Acid	2.5	2.42	0.13	5.4	97
Dalapon	5.0	4.69	0.21	4.5	94

[a]Produced by the analysis of seven aliquots of fortified dechlorinated tap water.
[b]Significant background concentrations (>5-15 µg/L) have been subtracted from these values for dichloroacetic acid, trichloroacetic acid, bromochloroacetic acid, and dibromoacetic acid.
[c]Surrogate Compound.

TABLE 7. ANALYTE RECOVERY AND PRECISION DATA[a]

HIGH HUMIC CONTENT GROUND WATER

Analyte	Fortified Conc. (µg/L)	Mean Meas. Conc. (µg/L)	Std. Dev. (µg/L)	Rel. Std. Dev. (%)	Mean Recovery (%)
Monochloroacetic Acid	7.5	3.55	0.32	8.9	47
Monobromoacetic Acid	5.0	2.21	0.21	11	44
Dichloroacetic Acid	7.5	7.60	0.08	1.1	101
2-Bromopropionic Acid[b]	2.5	1.83	0.09	4.9	73
Trichloroacetic Acid	2.5	2.37	0.12	5.1	95
Bromochloroacetic Acid	5.0	5.53	0.16	2.9	111
Dibromoacetic Acid	2.5	2.58	0.13	5.0	103
Dalapon	5.0	4.92	0.29	6.0	90

[a]Produced by the analysis of seven aliquots of fortified high humic content ground water.
[b]Surrogate compound.

TABLE 8. ANALYTE RECOVERY AND PRECISION DATA[a]

HIGH HUMIC CONTENT GROUND WATER DILUTED 1:5

Analyte	Fortified Conc. (µg/L)	Mean Meas. Conc. (µg/L)	Std. Dev. (µg/L)	Rel. Std. Dev. (%)	Mean Recovery (%)
Monochloroacetic Acid	1.5	1.50	0.17	11	100
Monobromoacetic Acid	1.0	0.97	0.06	6.2	97
Dichloroacetic Acid	1.5	1.89	0.16	8.5	126
2-Bromopropionic Acid[b]	0.5	0.49	0.01	2.0	98
Trichloroacetic Acid	0.5	0.28	0.03	11	56
Bromochloroacetic Acid	1.0	0.43	0.07	16	43
Dibromoacetic Acid	0.5	0.30	0.02	6.7	60
Dalapon	1.0	0.88	0.12	14	88

[a]Produced by the analysis of seven aliquots of fortified high humic content ground water diluted 1:5.
[b]Surrogate compound.

TABLE 9. ANALYTE RECOVERY AND PRECISION DATA[a]

OZONATED RIVER WATER

Analyte	Fortified Conc. (µg/L)	Mean Meas. Conc. (µg/L)	Std. Dev. (µg/L)	Rel. Std. Dev. (%)	Mean Recovery (%)
Monochloroacetic Acid	7.5	6.22	0.91	15	83
Monobromoacetic Acid	5.0	4.28	0.34	7.9	86
Dichloroacetic Acid	7.5	7.09	0.22	3.1	94
2-Bromopropionic Acid[b]	2.5	2.31	0.09	3.7	92
Trichloroacetic Acid	2.5	2.65	0.13	4.9	106
Bromochloroacetic Acid	5.0	5.20	0.18	3.5	104
Dibromoacetic Acid	2.5	2.36	0.09	3.8	94
Dalapon	5.0	5.08	0.17	3.4	102

[a]Produced by the analysis of seven aliquots of fortified ozonated river water.
[b]Surrogate compound.

FIGURE 1. Gas Chromatogram of Haloacetic Acids Including the Internal Standard and Surrogate Compound Using the DB-1701 Column and the Conditions Listed in Table 1