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Method of Analysis at the U.S. Geological Survey California Water Science Center, Sacramento Laboratory—Determination of Haloacetic Acid Formation Potential, Method Validation, and Quality-Control Practices

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By Barbara C. Zazzi, Kathryn L. Crepeau, Miranda S. Fram,
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Conversion Factors

Multiply	By	To obtain
drams	16	ounces

Abbrevations

min, minute
g, gram
m, meter
M, Molar
mg/L, milligrams per liter
mg/mL, milligrams per milliliter
mL, milliliter
N, normal
µg/L, micrograms per liter
µg/mL, micrograms per milliliter
µL, microliter
Std, standard
Br^-, bromide ion, bromide dissolved, bromide
$CBrCl_2CO_2H$, bromodichloroacetic acid
CBr_2ClCO_2H, dibromochloroacetic acid
CBr_3CO_2H, tribromoacetic acid
CCl_3CO_2H, trichloroacetic acid
$CHBrClCO_2H$, bromochloroacetic acid
$CHBr_2CO_2H$, dibromoacetic acid
CH_2BrCO_2H, monobromoacetic acid
$CHCl_2CO_2H$, dichloroacetic acid
$CH_2ClCHBrCH_3$, 2-bromo-1-chloropropane
CH_2ClCO_2H, monochloroacetic acid
$CH_3CHBrCO_2H$, 2-bromopropionic acid
Cl_2, chlorine
H_2SO_4, sulfuric acid
H_3BO_3, boric acid
HCl, hydrochloric acid
NaOCl, sodium hypochlorite
NaOH, sodium hydroxide
Na_2SO_3, sodium sulfite
Na_2SO_4, sodium sulfate
NH_3-N, ammonia-nitrogen

Acronyms

CCV, continuing calibration verification
DBP, disinfection byproduct
DOC, dissolved organic carbon
ECD, electron capture detector
GC, gas chromatograph
GC-ECD, gas chromatograph-electron capture detector
HAA, haloacetic acid
HAAFP, haloacetic acid formation potential
IS, internal standard
LIMS, Laboratory Information Management System
MCL, maximum contaminant level
MDL, method detection limit
MTBE, methyl-*tert*-butyl ether
NWIS, National Water Information System
QCS , quality-control sample
QCSS, quality-control standard solution
RSD, relative standard deviation
RT, retention time
SHAAFP, specific haloacetic acid formation potential
THM, trihalomethane
THMFP, trihalomethane formation potential
USEPA, U.S. Environmental Protection Agency

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Abstract

An analytical method for the determination of haloacetic acid formation potential of water samples has been developed by the U.S. Geological Survey California Water Science Center, Sacramento Laboratory. The haloacetic acid formation potential is measured by dosing water samples with chlorine under specified conditions of pH, temperature, incubation time, darkness, and residual-free chlorine. The haloacetic acids formed are bromochloroacetic acid, bromodichloroacetic acid, dibromochloroacetic acid, dibromoacetic acid, dichloroacetic acid, monobromoacetic acid, monochloroacetic acid, tribromoacetic acid, and trichloroacetic acid. They are extracted, methylated, and then analyzed using a gas chromatograph equipped with an electron capture detector. Method validation experiments were performed to determine the method accuracy, precision, and detection limit for each of the compounds. Method detection limits for these nine haloacetic acids ranged from 0.11 to 0.45 microgram per liter. Quality-control practices include the use of blanks, quality-control samples, calibration verification standards, surrogate recovery, internal standard, matrix spikes, and duplicates.

Introduction

Haloacetic acids (HAA) are halogenated organic compounds commonly found in treated drinking water. HAA, like trihalomethanes (THM), are undesirable disinfection byproducts (DBP) that form during the disinfection stage of the drinking-water treatment process. Natural organic carbon in the source water reacts with disinfectants [usually chlorine (Cl_2)] added during treatment to form HAA and other DBP. HAA are of concern because some of the compounds have been identified as potential carcinogens and toxic to digestive and urinary organs (Herren-Freund and others, 1987; Deangelo and others, 1991; Lin and others, 1993). This method is designed to quantify nine haloacetic acids: bromochloroacetic acid, bromodichloroacetic acid, dibromochloroacetic acid, dibromoacetic acid, dichloroacetic acid, monobromoacetic acid, monochloroacetic acid, tribromoacetic acid, and trichloroacetic acid (*table 1*). Federal regulations currently mandate a maximum contaminant level (MCL) of 60 µg/L (micrograms per liter) for the sum of five haloacetic acids: monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid (U.S. Environmental Protection Agency, 1998).

The amount of HAA formed from a given amount of dissolved organic carbon (DOC) depends on the chemical structure of the DOC, contact time between the Cl_2 and DOC, concentration of bromide (Br^-) in the water, amount of Cl_2 added, concentration of residual Cl_2, pH, and temperature of the water (Reckhow and others, 1990). The HAA formation potential (HAAFP) is defined as the amount of HAA formed under specific conditions of pH, contact time, residual Cl_2 concentration, and temperature, and is reported in units of micrograms per liter. The specific HAAFP (SHAAFP) is the HAAFP normalized to the DOC concentrations and is reported in units of millimoles of HAA per mole of carbon in the DOC. SHAAFP is a measure of the reactivity of the DOC to form HAA.

There are at least two standard methods for measuring HAA: U.S. Environmental Protection Agency (USEPA) Method 552.2 (U.S. Environmental Protection Agency, 1995) and Standard Method 6251 (American Public Health Association and others, 1995). Both methods are similar in that the HAA are extracted, methylated, and analyzed using a gas chromatograph (GC) equipped with an electron capture detector (GC-ECD). However, the Standard Method 6251 uses diazomethane as a derivatizing agent to form the methyl esters that can be analyzed by GC-ECD, while the USEPA method uses acidic methanol with slight heating to form these same methyl esters. The U.S. Geological Survey (USGS) California Water Science Center, Sacramento Laboratory uses a modified version of the USEPA method.

Purpose and Scope

This report presents detailed descriptions of the analytical procedures and quality-assurance/quality-control protocols used for determination of HAAFP by the USGS California Water Science Center, Sacramento laboratory. The method accuracy, precision, and detection limits were determined.

Table 1. Formulas and calibration ranges for the nine haloacetic acids and internal standard compounds analyzed by the U.S. Geological Survey method.

[Measurements shown in micrograms per liter]

Analyte	Formula	Calibration range
Bromochloroacetic acid	$CHBrClCO_2H$	0.2–100
Bromodichloroacetic acid	$CBrCl_2CO_2H$	0.2–100
Dibromochloroacetic acid	CBr_2ClCO_2H	0.5–250
Dibromoacetic acid	$CHBr_2CO_2H$	0.1–50
Dichloroacetic acid	$CHCl_2CO_2H$	0.3–150
Monobromoacetic acid	CH_2BrCO_2H	0.2–100
Monochloroacetic acid	CH_2ClCO_2H	0.3–150
Tribromoacetic acid	CBr_3CO_2H	1–500
Trichloroacetic acid	CCl_3CO_2H	0.1–50
2-bromo-1-chloropropane	$CH_2ClCHBrCH_3$	internal standard
2-bromopropionic acid (surrogate)	$CH_3CHBrCO_2H$	0.5–250

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Method of Analysis of Haloacetic Acid Formation Potential

Scope and Application

This method is designed to be used on water samples to determine the HAAFP under controlled, standard conditions of pH, temperature, darkness, contact time between Cl_2 and the water sample, and residual Cl_2. Because the HAAFP depends on the experimental conditions, data generated from this method only should be compared to data generated under the same experimental conditions. This method was modified from the USEPA Method 552.2 to determine HAA in drinking water, surface water, or ground water (*table 1*), and is suitable for filtered natural waters and experimentally produced water samples. The calibration range for each of the nine HAA is listed in *table 1*. Water samples that produce higher concentrations of HAA should be diluted prior to analysis.

Summary of Method

Water samples are collected and filtered to remove suspended particulate matter. The DOC and ammonia-nitrogen (NH_3-N) concentrations in each water sample are used to determine the appropriate amount of Cl_2 dose solution to add. The samples are dosed with sufficient Cl_2 to satisfy sample Cl_2 demand and leave a residual Cl_2 concentration of 2–4 milligrams per liter (mg/L). A buffer is added to maintain a sample pH of 8.3 during chlorination. After the samples are dosed, they are incubated in the dark for 7 days at 25°C (77°F).

At the end of the 7 days, the pH and residual-free Cl_2 are measured and the samples are quenched with sodium sulfite (Na_2SO_3) solution to neutralize any remaining free Cl_2. A 40 milliliter (mL) volume of sample is adjusted to pH < 0.5 and extracted with 2 mL of methyl *tert*-butyl ether (MTBE). The organic phase containing the HAA is separated, and the HAA are converted into their methyl esters by the addition of acidic methanol with slight heating. A second extraction using dilute sodium hydroxide concentrates the methyl ester compounds in the organic phase. The target analytes are identified and measured by GC-ECD. Analytes are quantified by using a procedural standard calibration curve. The primary differences between this method and the USEPA Method 552.2 are that different compounds are used for the surrogate and internal standard, smaller and silanized reaction vials are used, the final extract volume is half as much, and the second extraction is done with NaOH rather than sodium bicarbonate.

Equipment and Materials

The equipment and materials used for analysis of HAAFP are listed below. The organic carbon-free water is produced on-site with a recirculation Picotech water system (Hydro Service and Supplies, Inc.). Inlet water for the Picotech water system is deionized and produced on-site with a Culligan deionizing system (Culligan International Company). Scheduled routine maintenance and replacement of cartridges are done on both systems. The organic carbon-free water is tested frequently by analysis of DOC and trihalomethane formation potential (Bird and others, 2003; Crepeau and others, 2004).

Equipment and materials used for analysis of haloacetic acid formation potential. (Product and firm names are listed for documentation purposes only.)

Sample Containers

Baked amber glass bottles with Teflon-lined lids

Ammonia and chlorine measurements

Ammonia salicylate and cyanurate reagent powder pillows (Hach, Loveland, Colorado)

Hach N-diethyl-p-phenylenediamine free-chlorine reagent powder pillows, catalog number 14077-28 or dispenser catalog number 10445 (Hach, Loveland, Colorado)

2-dram Opticlear vials, screw thread, catalog number 60910-2 (Kimble Glass, Inc.)

Pipettes, 1- and 5-milliliter adjustable Oxford Benchmate (Nichiryo Co., LTD) with disposable plastic tips (Labsource, Fisherbrand, or equivalent)

Spectrophotometer, Genesys20 (ThermoSpectronic)

Dilution

Bottle-top dispenser, adjustable from 10 to 109 milliliter (Fisher/Wheaton, Pittsburg, Pennsylvania)

Glass beakers and graduated cylinders 25–100 milliliter (Fisher Scientific, Pittsburg, Pennsylvania)

Organic-free water, produced on-site with Pico-pure water system (Hydro Service and Supplies, Inc.)

Pipettes, 1- and 5-milliliter adjustable Oxford Benchmate (Nichiryo Co., LTD) with disposable plastic tips (Labsource, Fisherbrand, or equivalent)

Dosing and Quenching

Analytical balance, accuracy of 0.050 gram ±0.0001 gram

Boric acid (Mallinckrodt analytical reagent grade or equivalent)

Dilute hydrochloric acid and dilute sodium hydroxide for pH adjustment (0.1 N, Fisher Scientific, Pittsburg, Pennsylvania)

pH buffer 7 and 10 (U.S. Geological Survey Ocala Water-Quality Laboratory, Ocala, Florida)

pH meter, Orion model 420A with Triode gel electrode (Orion Research Inc., Beverly, Massachusetts)

Sodium hydroxide pellets (American Chemical Society reagent grade, Aldrich Chemical, Milwaukee, Wisconsin)
Sodium hypochlorite 4–6 percent (Fisher purified grade, Fisher Scientific, Pittsburg, Pennsylvania)

Sodium sulfite, anhydrous (American Chemical Society reagent grade, Fisher Scientific, Pittsburg, Pennsylvania)

40-milliliter vials, amber borosilicate, TraceClean (VWR Scientific, West Chester, Pennsylvania)

Extraction

Copper II sulfate pentahydrate (Certified American Chemical Society, Fisher Scientific, Pittsburg, Pennsylvania)

Graduated cylinders (50 milliliter)

methyl *tert*-butyl ether (J.T. Baker, Mallinckrodt Baker, Inc., Phillipsburg, New Jersey)

Sodium sulfate (Certified American Chemical Society, Fisher Scientific, Pittsburg, Pennsylvania)

Sulfuric acid (American Chemical Society reagent grade, Fisher Scientific, Pittsburg, Pennsylvania)

60-milliliter vials

Methylation

Autosampler vials, 4-milliliter amber, silanized (National Scientific Company)

Autosampler Target DP vials, amber with silanized inserts (National Scientific Company)

Glass pipettes (2 milliliter)

Ice bath

Sodium hydroxide diluted to 0.1 Normal (Fisher Scientific, Pittsburg, Pennsylvania)

Volumetric glassware

Water bath (50ºC)

10 percent (volume/volume) sulfuric acid in pesticide grade methanol (Fisher Scientific, Pittsburg, Pennsylvania)

Haloacetic acid analysis

Autosampler, Hewlett-Packard 6890 (Wilmington, Delaware)

Column, Rtx-5, 30 meters in length, 0.25-millimeter

internal diameter with 0.25-micron film thickness and Integra-Guard (guard column) Catalog number 10223-127 (Restek, Bellefonte, Pennsylvania)

Gas chromatograph, Hewlett-Packard 5890 (Wilmington, Delaware)

Nitrogen, ultra-high purity (Praxair, Sacramento, California)

Standards

2-bromopropionic acid 1 mg/mL in methyl *tert*-butyl ether (Supelco, Bellefonte, Pennsylvania) 2-bromo-1-chloropropane 2 mg/mL in methanol (Supelco, Bellefonte, Pennsylvania)

Nine haloacetic acid mix in methyl *tert*-butyl ether (Supelco, Bellefonte, Pennsylvania)

Neat solutions of individual haloacetic acids (Sigma-Aldrich, St. Louis, Missouri)

Volumetric glassware (5 milliliter, Fisher Scientific, Pittsburg, Pennsylvania)

Glassware is washed with Liquinox soap and rinsed with copious amounts of organic carbon-free water. The glassware openings are covered with aluminum foil and the glassware is baked in a muffle furnace at 450ºC for 4 hours. The baked glassware is stored with the foil still on in closed drawers or cabinets until needed.

The sodium sulfate (Na_2SO_4) is baked in a muffle furnace at 400ºC for up to 4 hours to remove phthalates and other potentially interfering organic substances. The baked Na_2SO_4 then is stored in a clean, capped glass bottle.

The 10 percent sulfuric acid (H_2SO_4)/methanol solution that is used for methylation must be prepared in a hood and with the appropriate personal protective equipment worn by the laboratory staff. This solution is prepared by adding 5 mL of concentrated H_2SO_4 drop-wise to 20–30 mL of methanol in a 50-mL volumetric flask. The flask should be placed in an ice bath during addition of the H_2SO_4 because the reaction is strongly exothermic. Once the solution has cooled, methanol is added to the volumetric flask to give a final volume of 50 mL.

Standards

Surrogate

A surrogate compound, 2-bromopropionic acid ($CH_3CHBrCO_2H$), is added to the samples to monitor the efficiency of extraction and methylation of HAA. This compound is chemically similar to the HAA but not produced in significant enough amounts by chlorination of DOC to prevent its use as the surrogate. 2-bromopropionic acid is used as the surrogate compound because the surrogate (2,3-dibromopropionic acid) listed in USEPA Method 552.2 coelutes with dibromochloroacetic acid on the GC column (Rtx-5, 5 percent diphenyl/95-percent dimethyl polysiloxane). A stock solution of 2-bromopropionic acid in MTBE at a certified concentration of 1 milligram per milliliter (mg/mL) is used to make the working surrogate solution in MTBE at a concentration of 10 micrograms per milliliter (µg/mL) by diluting 100-microliter stock solution with MTBE to a final volume of 10 mL using a volumetric flask and gas-tight syringe. Twenty microliters (µL) of the working surrogate solution are added to the sample just prior to extraction of the HAA to give 2-bromopropionic acid a concentration of 5 µg/L.

Internal Standard

An internal standard (IS) that elutes with the methylated HAA during GC analysis is added to the samples and the HAA calibration standards. The measured peak areas for the analytes are normalized to the peak area of the IS to compensate for any small differences in GC injection volume or matrix effects on sample volitization in the injector between samples. 2-bromo-1-chloropropane ($CH_2ClCHBrCH_3$) is used as the IS because the IS (1,2,3-trichloropropane) listed in USEPA Method 552.2 coelutes with bromochloroacetic acid on the Rtx-5 column. An IS stock solution of 2-bromo-1-chloropropane in methanol is purchased at a certified concentration of 2 mg/mL. From this stock standard solution, the working IS solution in MTBE, at a concentration of 10 µg/mL, is prepared by diluting 50-microliter stock solution with MTBE to a final volume of 10 mL using a volumetric flask and gas-tight syringe. Ten µL of the working IS solution are added to every vial just prior to GC analysis to give an IS concentration of 0.4 µg/mL in the extract.

Calibration Standard Solutions

A primary stock standard solution containing all nine HAA in MTBE is purchased and used to prepare the working standards used for calibration. The stock standard solution is stored at –10°C and protected from light. It is stable for at least 1 month but should be checked for signs of evaporation. When purchasing commercially prepared standards, solutions prepared in methanol must not be used because the HAA are subject to spontaneous methylation when stored in this solvent (Xie and others, 1993). Furthermore, tribromoacetic acid is unstable in methanol because it undergoes decarboxylation when stored in this solvent (USEPA Method 552.2). The Supelco mix for USEPA Method 552.2 contains a mix of nine acids in the concentrations listed in *table 2*.

The working standard solutions, C, B, and A, are prepared by combining the stock standard solution and surrogate stock solution to give the concentrations listed in *table 2*. Working standard solution C is prepared first by combining 250 µL of the stock standard solution and 250 µL of the surro-

gate stock solution to give a final volume of 500 µL in a vial. The working standard solution B is prepared by diluting working standard solution C by a factor of ten with MTBE. One hundred µL of working standard solution C are measured with a gas-tight syringe and diluted to a final volume of 1 mL in a volumetric flask. The working standard solution A is prepared by diluting working standard solution B by a factor of ten with MTBE. One hundred µL of working standard solution B are measured with a gas-tight syringe and diluted to a final volume of 1 mL in a volumetric flask.

These working standard solutions are used to prepare procedural calibration standards, which comprise nine concentration levels of each analyte, with the lowest standard being at or near the method detection limit (MDL) of each analyte.

Quality-Control Standard Solution

The quality-control standard solution (QCSS) is an independent standard solution used to prepare quality-control samples to verify the calibration standards (see "Quality-Control Samples" section of this report). The QCSS is prepared by weighing 0.05 gram (g) of each neat compound into individual 5-mL volumetric flasks and diluting to volume with MTBE. The resulting concentration of these stock standards is 10,000 mg/L. Forty µL of each stock standard solution is then mixed and the combined solution diluted to a final volume of 2 mL with MTBE. This solution, QCSS A, contains 200 mg/L of each of the nine HAA compounds. QCSS B is prepared by diluting QCSS A by a factor of ten (200-µL QCSS A to a final volume of 2 mL with MTBE) to give a final concentration of 20 mg/L for each of the nine HAA compounds.

Sample Collection and Storage

Water samples for HAAFP analysis should be collected using baked glass, Teflon, or stainless steel sampling containers. For example, shallow surface-water grab samples can be collected directly into baked amber glass bottles, and deeper surface-water-integrated samples can be collected with Teflon or stainless steel Van Dorn-type samplers for transfer into baked amber glass bottles. Exposure to organic solvents must be avoided. If the sampler is cleaned with methanol, copious amounts of water must be used to rinse the sampler to ensure that the methanol is removed completely prior to collecting the sample.

Water samples must be filtered prior to analysis of the HAAFP. Samples are filtered in the field or laboratory within 24 hours of collection. Procedures for collecting and filtering samples, such as those given in Chapters A4 and A5 of the National Field Manual for the Collection of Water-Quality Data (Radtke and others, 2002), can be used if modified to avoid contact between the sample and solvents or plastics. No preservatives are added to the samples. Each sample is assigned a unique number as it is logged into the Laboratory Information Management System (LIMS) (LabWorks, Analytical Automation Specialists, Inc.) and is stored at 4°C (39°F) until analyzed.

Laboratory Procedures

Formation of Haloacetic Acids

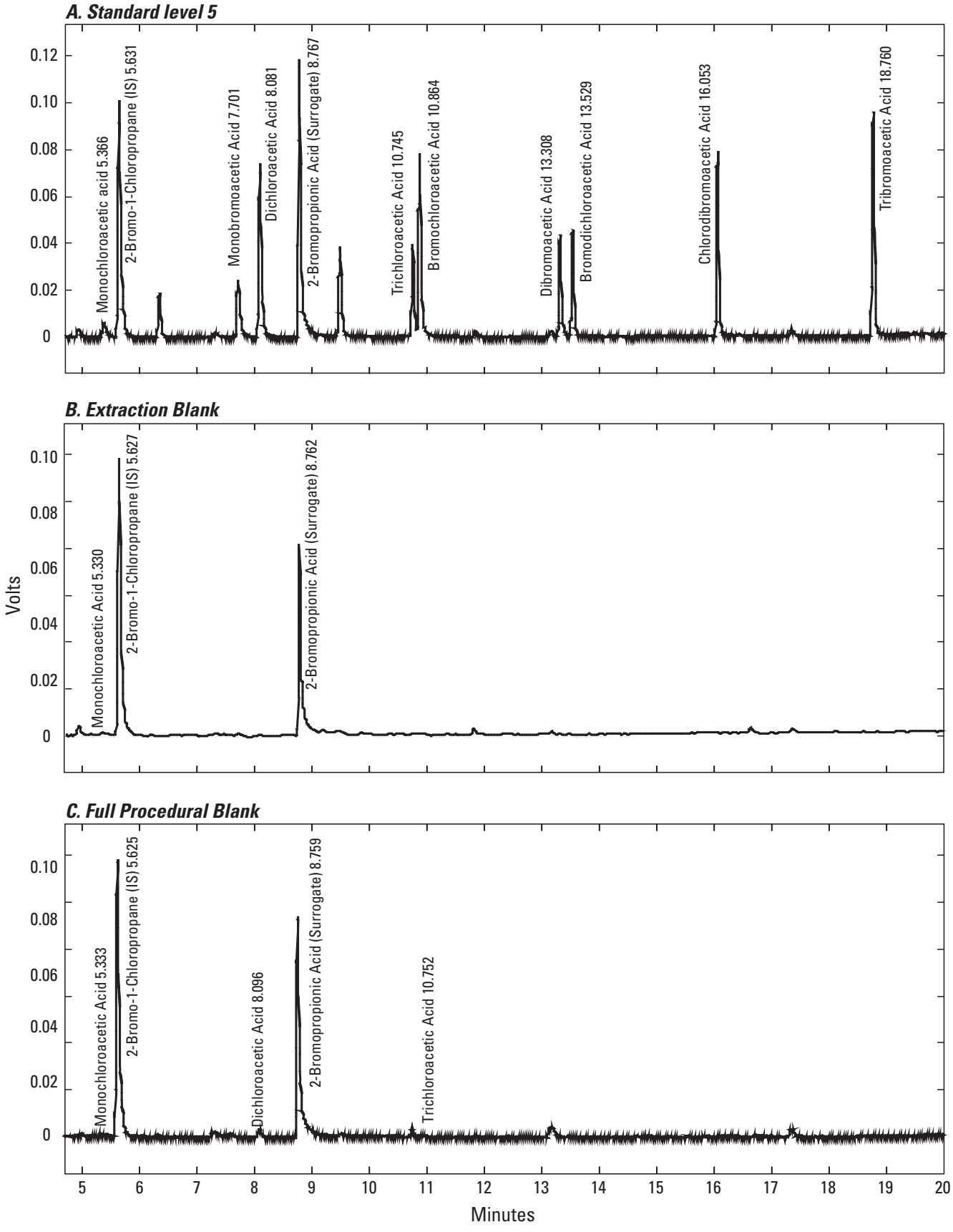
The procedure to form HAA by chlorination of water samples is the same as the procedure to form THM in the

Table 2. Haloacetic acid and surrogate concentrations in the stock standard solution and the three working standard solutions C, B, and A that are prepared in methyl *tert*-butyl ether.

[Certificate of analysis accompanying stock standard solution lists actual concentration of haloacetic acid compounds to four significant figures. Because the actual concentrations vary slightly between lots, nominal concentrations in micrograms per milliliter are listed here instead. —, stock standard solution does not contain the surrogate compound]

Haloacetic acid	Stock standard solution (µg/mL)	Working standard solution C (µg/mL)	Working standard solution B (µg/mL)	Working standard solution A (µg/mL)
Bromochloroacetic acid	400	200	20	2
Bromodichloroacetic acid	400	200	20	2
Dibromochloroacetic acid	1,000	500	50	5
Dibromoacetic acid	200	100	10	1
Dichloroacetic acid	600	300	30	3
Monobromoacetic acid	400	200	20	2
Monochloroacetic acid	600	300	30	3
Tribromoacetic acid	2,000	1,000	100	10
Trichloroacetic acid	200	100	10	1
2-bromopropionic acid (surrogate)	—	500	50	5

Figure 1. Chromatograms for (A) level-5 calibration standard, (B) extraction blank, and (C) full procedural blank. Peaks are labelled with analyte name and retention time in minutes. IS, internal standard.



method for determination of THMFP (Crepeau and others, 2004). The procedure is summarized briefly here. The DOC and NH_3-N concentrations of the sample are measured and used to calculate the appropriate amount of Cl_2 used to dose the samples. Samples with a DOC concentration of 3 mg/L or greater usually are diluted with organic-carbon-free water prior to chlorination. If both HAAFP and THMFP are being determined for the sample, the same dilution factor is used for both analyses. A dose solution containing 3,000 to 4,000 mg/L residual-free Cl_2 derived from sodium hypochlorite (NaOCl) and buffered to a pH of 8.3 with 1 molar (M) H_3BO_3 and 0.11 M NaOH is prepared. The pH of the sample is adjusted to a range between 8.3 and 8.7 by addition of dilute NaOH or hydrochloric acid (HCl). The sample is poured into three 40-mL amber glass vials with Teflon-faced septa, and sufficient dosing solution is added to satisfy the Cl_2 demand of the DOC and NH_3-N and to leave a residual-free Cl_2 concentration of 2–4 mg/L after the incubation period. The vials are sealed headspace-free and incubated at 25°C (77°F) in the dark for 7 days. After incubation, one vial is opened to measure the pH and free Cl_2. The pH must be 8.3 ± 0.1 and the residual-free Cl_2 must be between 2 and 4 mg/L. If these parameters are not met, then the sample is redosed and incubated for another 7 days. The remaining two vials are quenched by adding sufficient Na_2SO_3 solution to neutralize the residual-free Cl_2. The samples are refrigerated and can be held up to 14 days before extraction.

Sample Extraction

The samples are removed from refrigeration and allowed to equilibrate to room temperature. Two aliquots of every sample are analyzed, one undiluted and one diluted 1:5 with organic-free water. For the undiluted sample aliquot, one quenched vial is opened and 40 mL of sample water is measured with a graduated cylinder (which has been calibrated "to deliver" at 20°C with a 1-percent tolerance) and poured into a precleaned 60-mL vial with a Teflon-lined screw cap. For the diluted sample aliquot, the second quenched vial is opened, and 8 mL of sample are pipetted into a 60-mL vial along with 32 mL of organic-free water. The final concentration result for each compound in a sample is derived only from analysis of the diluted aliquot if the concentration measured in the undiluted aliquot is higher than the concentration in the highest standard. Twenty µL of the 10.0 µg/mL 2-bromopropionic acid surrogate solution is added to every 60-mL vial. When adding surrogate or standard solutions to aqueous samples, the tip of the syringe must be well below the water level to avoid loss by volatilization. After injection of the surrogate solution, the sample vial is capped immediately and inverted to ensure mixing of solutions. The pH is adjusted to less than 0.5 by adding 2 mL of concentrated H_2SO_4. Two grams (g) of copper II sulfate pentahydrate and 16 g of Na_2SO_4 are added immediately to the sample using the heat produced from the H_2SO_4 addition to help dissolve the salts. The samples are shaken until the salts are dissolved (approximately 2–3 minutes). Then, 2.0 mL of MTBE are added to the samples and they are shaken vigorously for 2 minutes. The MTBE and aqueous layers are allowed to separate for approximately 5 minutes.

Methylation and Preparation for Gas Chromatograph Analysis

A disposable glass pipette is used to remove as much of the MTBE layer (upper) as possible (minimum of 1 mL) and to place it into a 4-mL silanized autosampler vial that will be used as the reaction vessel for the methylation step. Then, 0.5 mL of 10 percent (volume/volume) H_2SO_4 in methanol is added to each autosampler vial. The cap is tightened securely and the vials are placed in a water bath at 50°C (122°F) for 2 hours to allow for methylation of the analytes.

The vials are removed from the water bath and placed in an ice bath for 5 minutes. Two mL of 0.1 normal (N) NaOH is added to each vial and the vials are shaken for approximately 2 minutes. The MTBE and aqueous layers then are allowed to separate.

A second set of autosampler vials containing silanized glass inserts is used to hold the final samples for GC analyses. Ten µL of the IS solution (10 µg/mL 2-bromo-l-chloropropane) is placed in the silanized insert just prior to addition of the sample extract. Exactly 250-µL of the MTBE layer (upper) is transferred into the insert using a 250-µL fixed volume micropipettor. The vials are capped and shaken or mixed with a vortex mixer.

The samples should be analyzed on the GC as soon as possible after preparation because the final extract solutions deteriorate after a few days. Losses of dibromoacetic acid, dibromochloroacetic acid, and tribromoacetic acid in particular were observed. If the sample must be analyzed on the GC for a second time, it is recommended that a new aliquot of the water sample be processed rather than reanalyzing the old final extract samples.

This method for extraction and methylation uses only one-half the volume of MTBE that is required for USEPA Method 552.2 (U.S. Environmental Protection Agency, 1995). Therefore, the volume of excess final extract that must be disposed of as solvent waste is much less.

Gas Chromatography Procedures

Instrument Conditions

The instrument consists of a 6890 Hewlett Packard autosampler connected to a 5890 Hewlett Packard GC equipped with an Rtx-5 capillary column and an ECD. The autosampler is set to deliver 1-µL samples to the injection port of the GC. The GC operating configuration is summarized in *table 3*. *Figure 1A* illustrates the performance on the Rtx-5 column with the method analytes at standard level 5 (see *table 5* for concentrations), an extraction blank, and a full procedural

Table 3. Gas chromatograph with electron capture detector components and specifications.

Components	Specifications
Column	Rtx-5 30-meter × 0.25 millimeter internal diameter with 0.25 micrometer film thickness
Carrier gas	Nitrogen at 1 milliliter per minute flow at 40ºC
Oven	40ºC for 15 minutes, 40–110ºC at 7ºC/minute, 110–250ºC at 20ºC/minute
Injector	Split 10:1, 200ºC
Detector	Electron capture at 300ºC

blank. The peaks for all nine HAA, the IS and the surrogate compound are well resolved. Baseline separation is achieved for all peaks, except for trichloroacetic acid [retention time (RT) = 10.745 min] and bromochloroacetic acid (RT = 10.864 min), which nearly are baseline resolved. The identities of the peaks with retention times of 6.333 min and 9.479 min are not known. However, because these extra peaks are not present in chromatograms for full procedural blanks (*fig. 1C*), they likely are due to contaminants in the standards rather than contaminants introduced during sample preparation. The Rtx-5 column was chosen instead of the DB-5.625 column used in USEPA Method 552.2 because the response for the monochloroacetic acid was better, as was the general performance of the column.

Calibration

Calibration standards are prepared using the same extraction and methylation procedures as for water samples. Nine calibration standards are made by adding appropriate volumes of the working standard solutions A, B, and C to 40-mL aliquots of fortified organic-free water (*table 4*). The organic-free water is fortified with Cl_2 dosing solution and sodium sulfite quenching solution in approximately the same concentrations used for generating the HAA in water samples. These solutes may affect extraction efficiency of the HAA and, thus, should be present in the same concentrations in standards and samples. Three working standard solutions (A, B, and C) are used so that the volume of MTBE added to the calibration standard solutions is less than 20 µL for all nine calibration standards. The concentration of the nine HAA compounds and the surrogate compound in the nine calibration standards are listed in *table 5*.

The calibration curves are generated using the IS technique. Peak areas for the nine HAA compounds and the surrogate compound are normalized to the peak area of the IS in the same injection. Because the IS is presented in the same concentration in all of the final extracts analyzed on the GC, this normalization compensates for any small variations in GC injection volume or differences in matrix effects in the final extract solutions between samples.

The calibration curves for all nine HAA and the surrogate compound are quadratic. The coefficient of determination, R^2, is used to assess the fit between each quadratic equation and the data for each analyte from the nine standard solutions. The R^2 value must be 0.9980 or better or a new calibration curve must be generated.

Sample Analysis

Samples are analyzed immediately after extraction and methylation. The order of analysis begins with an MTBE instrument blank to verify that the instrument is free of contamination. Next, the standard curve is produced by analyzing the nine standards from lowest to highest concentrations, followed by another MTBE instrument blank. Then, the extraction blanks and samples are analyzed, followed by two continuing calibration verification standards and another MTBE instrument blank between sets of samples (see "Quality-Control Practices" section of this report). The final data for a sample may be combined from two or more different analyses where the data for each HAA analyte are taken from the dilution that fits within the standard curve.

Data Processing and Archiving

The HAAFP data are processed using EZChrom chromatography software and archived in the USGS California Water Science Center's LIMS. Data for selected samples also are entered into the USGS National Water Information System (NWIS) database.

EZChrom Software

In each of the samples, the software identifies the peaks of the nine HAA species, the IS, and the surrogate by their retention times and then converts measured peak areas to concentrations by normalizing the peak areas to the peak area of the IS and then converting normalized peak areas to

Table 4. Volumes of working standard solutions added to 40-milliliter samples of fortified organic-free water to make nine standard levels.

[µL, microliters]

Standard level	Working standard solution	Volume (µL)
1	A	4
2	A	8
3	A	20
4	B	4
5	B	8
6	B	20
7	C	4
8	C	8
9	C	20

concentrations using the standard calibration curves. The retention time for each compound must be within a 0.25-minute window of the expected value from the calibration curve. Full separation of the compounds is achieved with the Rtx-5 column at the analyzed concentrations (*fig. 1*). The analyst examines the chromatograms to verify that the peak identifications are correct. Compound interferences on the column are minimal due to the selectiveness of the extraction method. The EZChrom software automatically flags samples if the surrogate concentrations, reproducibility of the duplicate samples, or concentrations of the calibration verification standards are out of acceptable range (see "Quality Control Practices" section of this report). The analyst also examines these data. The individual chromatograms, calibration curve information, and quality-control data are archived and the archived site is linked to the LIMS.

Laboratory Information Management System

The data are first imported from EZChrom into a spreadsheet (Microsoft Excel) for verification and calculations. After all quality-control criteria for a set of samples are met satisfactorily, the data are transferred to the LIMS. The data are accessible to users of the LIMS after the analyst verifies the final concentrations.

Method Validation

The analytical method was validated by using spiked samples to determine accuracy and precision for the method, and spiked fortified organic-free water to establish MDLs. Acceptable percent recoveries of the various quality-control samples, such as the matrix spike samples, the quality-control samples, the continuing calibration verification standards, and the surrogate standards, are in the range of 70 to 130 percent for this method. However, tighter limits for each type of quality-control sample can be observed and are addressed in this report.

Accuracy and Precision

The accuracy of the analytical method was assessed by spike recovery experiments using surface-water samples from Orange County, California. The water samples were diluted 1:5 with organic-free water prior to dosing (to lower the background concentration of HAA to appropriate levels). The samples were spiked with 8 µL of working standard solution B prior to extraction (*table 6*). The spiked concentrations were equal to the concentrations in the level-5 calibration standard (*table 5*). Background concentrations of HAA in these samples had been measured previously. Forty-one samples were used in the spike recovery experiments. Method accuracy is expressed as the mean percent recovery of the spike concentration. The number of samples used to calculate the mean percent recovery varied between 23 and 41 for the nine HAA (*table 6*) because the measured concentrations (spike plus background) for some analytes in some samples exceeded the concentration in the level-9 calibration standard and, therefore, could not be quantified.

The percent recovery for each analyte is calculated from the following equation:

$$\text{percent recovery} = \frac{\left| C_{meas} - C_{backgr} \right|}{C_{fortified}} * 100 \qquad (1)$$

where

C_{meas} is the measured concentration,
C_{backgr} is the background concentration of the sample, and
$C_{fortified}$ is the concentration of analyte added to the sample

Table 5. Concentrations of haloacetic acids and surrogate compound in nine standard levels.

[Std, standard. µg/L, micrograms per liter]

Analyte	Std level 1 (µg/L)	Std level 2 (µg/L)	Std level 3 (µg/L)	Std level 4 (µg/L)	Std level 5 (µg/L)	Std level 6 (µg/L)	Std level 7 (µg/L)	Std level 8 (µg/L)	Std level 9 (µg/L)
Bromochloroacetic acid	0.2	0.4	1.0	2.0	4.0	10	20	40	100
Bromodichloroacetic acid	0.2	0.4	1.0	2.0	4.0	10	20	40	100
Dibromochloroacetic acid	0.5	1.0	2.5	5.0	10	25	50	100	250
Dibromoacetic acid	0.1	0.2	0.5	1.0	2.0	5.0	10	20	50
Dichloroacetic acid	0.3	0.6	1.5	3.0	6.0	15	30	60	150
Monobromoacetic acid	0.2	0.4	1.0	2.0	4.0	10	20	40	100
Monochloroacetic acid	0.3	0.6	1.5	3.0	6.0	15	30	60	150
Tribromoacetic acid	1.0	2.0	5.0	10	20	50	100	200	500
Trichloroacetic acid	0.1	0.2	0.5	1.0	2.0	5.0	10	20	50
2-bromopropionic acid (surrogate)	0.5	1.0	2.5	5.0	10	25	50	100	250

Table 6. Accuracy and precision for haloacetic acid method determined from analyses of spiked surface-water samples from Orange County, California.

[µg/L, micrograms per liter]

Analyte name	Number of samples	Spiked concentration (µg/L)	Mean percent recovery	Standard deviation (percent)
Bromochloroacetic acid	39	4.0	109	19
Bromodichloroacetic acid	37	4.0	107	26
Dibromochloroacetic acid	38	10.	104	22
Dibromoacetic acid	41	2.0	117	24
Dichloroacetic acid	39	6.0	109	23
Monobromoacetic acid	41	4.0	99	19
Monochloroacetic acid	36	6.0	106	22
Tribromoacetic acid	40	20.	107	30
Trichloroacetic acid	23	2.0	110	29

Precision is expressed as the percent relative standard deviation (RSD), which is calculated from the mean and the standard deviation of the replicate analyses:

$$RSD = \frac{s_x}{\bar{x}} * 100 \quad (2)$$

where

$$s_x = \sqrt{\frac{\sum (x - \bar{x})^2}{n - 1}} \quad (3)$$

and

$$\bar{x} = \frac{\sum x}{n} \quad (4)$$

and where

x is the value for an analysis,
n is the number of replicate analyses,
$\bar{x}$ is the mean of the replicate analyses,
s_x is the standard deviation of the replicate analyses, and
RSD is the relative percent standard deviation for the replicate analyses.

The mean percent recovery ranged from 99 to 117 percent and the percent RSD ranged from 17 to 28 percent. Ongoing accuracy and precision determinations are made by analyzing a set of spiked sample duplicates for 10 percent of the water samples analyzed.

Method Detection Limits

The MDL, as defined by the USEPA, is the minimum concentration that can be measured and reported as greater than zero at the 99-percent confidence level (U.S. Environmental Protection Agency, 1997).

The MDL was calculated using the formula:

$$MDL = s_x * t_{(n-1,\, \alpha = 0.01)} \quad (5)$$

where

MDL is the method detection limit
s_x is the standard deviation of the replicate analyses, and
n is the number of repliate analyses, and
$t_{(n-1,\, a = 0.01)}$ is the Student's t-test value for the 1-a (99-percent) confidence level for *n* replicate analyses (t = 2.988 for n = 8)

The MDLs were determined from eight replicate analyses of 40-mL samples of organic-free water spiked with 8 µL of working standard solution A. The spiked concentrations of the analytes (*table 7*) equaled the concentrations in the level-2 calibration standard (*table 5*). These eight replicate samples were extracted, methylated, and analyzed using the same procedures used for all samples. All eight were prepared on the same day. This spiked concentration was used because it contained all the analytes at concentrations less than five times the expected MDLs, but greater than the baseline noise and drift. The MDLs were calculated from the standard deviations about the mean concentrations for the nine HAA from the eight replicate samples using equation 5. The MDLs for the nine HAA range from 0.11 to 0.45 µg/L (*table 7*).

Quality-Control Practices

Analytical Sequence

The same analytical sequence is used each time the GC is run. The analytical sequence is given in *table 8*.

Table 7. Method detection limits for nine haloacetic acids and the surrogate compound determined from analysis of eight replicate samples of spiked organic-free water.

[µg/L, micrograms per liter]

Analyte	Spiked concentration (µg/L)	Standard deviation (µg/L)	Method detection limit (µg/L)
Bromochloroacetic acid	0.40	0.054	0.16
Bromodichloroacetic acid	0.40	0.036	0.11
Dibromochloroacetic acid	1.0	0.12	0.36
Dibromoacetic acid	0.20	0.048	0.14
Dichloroacetic acid	0.60	0.14	0.42
Monobromoacetic acid	0.40	0.083	0.25
Monochloroacetic acid	0.60	0.15	0.45
Tribromoacetic acid	2.0	0.13	0.39
Trichloroacetic acid	0.20	0.047	0.14
2-bromopropionic acid (surrogate)	1.0	0.083	0.25

Calibration Standard Level-2 Check

After the analysis sequence has started, the performance of calibration standard level-2 is checked to insure proper detector sensitivity, peak symmetry, and peak resolution. Peak area counts for the nine HAA in the level-2 calibration standard are recorded for every run to monitor the continuity of instrument performance. Drastic changes in peak area counts between runs or gradual drift in peak area counts during several runs indicate that corrective actions are required. The chromatographic separation between peaks in the two pairs of closely eluting peaks is examined. The peaks for dibromoacetic acid [retention time (RT) = 13.308 min] and bromodichloroacetic acid (RT = 13.529 min) should be fully resolved to the baseline, and the peaks for trichloroacetic acid (RT = 10.745 min) and bromochloroacetic acid (RT = 10.864 min) should be nearly resolved to the baseline. Inability to demonstrate acceptable instrument performance indicates the need for reevaluation of the instrument system. If column or chromatographic performance cannot be met, one or more of the following remedial actions should be taken: cut off approximately 0.3 to 0.5 meter (m) of the injector end of the column and reinstall, change injector liner, or install a new column. Peak shape and resolution also can be affected by adjusting column flows or modifying the oven temperature program.

Blanks

Three types of blanks are analyzed for the HAAFP method: instrument blanks, extraction blanks, and full procedural blanks. Instrument blanks composed of MTBE are analyzed at the beginning of the run; after the calibration-curve standards, QC standards, and continuing calibration verification standards; and between sets of samples within the run. The measured HAA concentration in the instrument blank must be less than half the concentration in the lowest calibration standard. This concentration corresponds to maximum permissible concentrations in the instrument blanks of 0.05µg/L for trichloroacetic acid and dibromoacetic acid; 0.1µg/Lfor monobromoacetic acid, bromochloroacetic acid, and bromodichloroacetic acid; 0.15µg/L for monochloroacetic acid and dichloroacetic acid; 0.25µg/L for dibromochloroacetic acid; and 0.5µg/L for tribromoacetic acid. If the instrument blanks have higher concentrations of HAA than permitted, corrective actions must be taken. The injector end of the column should be cut and reinstalled, the injection liner changed, or a new column installed.

Extraction blanks consist of organic-free water extracted and methylated along with the samples. This blank is used to test for contamination or interference in the extraction and methylation steps. Any compounds detected must have concentrations below the MDL.

Full procedural blanks consist of organic-free water that is dosed, incubated, and quenched like a sample. It is dosed to achieve a residual-free Cl_2 concentration of 2–4 mg/L. The full procedural blanks then are extracted and methylated along with the samples. This blank is used to test for overall cleanliness of sample handling during the dosing and quenching process and to demonstrate the presence/absence of any interference in the extraction and methylation process. Traces of monochloroacetic acid, dichloroacetic acid, and trichloroacetic acid, usually below the established MDL, commonly are found in the full procedural blanks (*fig. 1*). If concentrations higher than the MDL are observed, the source of contamination should be determined and eliminated. Samples associated with a contaminated full procedural blank are to be considered suspect and should be re-extracted, if possible.

Quality-Control Samples

The quality-control samples (QCS) are used to verify the primary calibration standards and are prepared from the QCSS A and B. The QCS50 is prepared by adding 10 µL of QCSSA to 40 mL of organic-free water to give a final concentration

Table 8. Sequence of blanks, calibration standards, quality-control standards, and unknown samples analyzed during one run of the gas chromatograph.

[MTBE, methyl *tert*-butyl ether; Std, standard; QCS, quality-control sample; µg/L, micrograms per liter; HAA, haloacetic acid; CCV, continuing calibration verification]

Vial number	Sample ID	Sample description
1	MTBE	Instrument blank
2	Std 1	Calibration standards
3	Std 2	Calibration standards
4	Std 3	Calibration standards
5	Std 4	Calibration standards
6	Std 5	Calibration standards
7	Std 6	Calibration standards
8	Std 7	Calibration standards
9	Std 8	Calibration standards
10	Std 9	Calibration standards
11	MTBE	Instrument blank
12	Extraction blank	Organic-free water carried through all extraction steps
13	Full procedural blank	Organic-free water carried through full procedure
14	QCS5	Quality-control standard containing 5 µg/L of each HAA
15	QCS50	Quality-control standard containing 50 µg/L of each HAA
16	MTBE	Instrument blank
17	Sample 1 diluted	Sample used for matrix spike, sample is diluted 1:5 with organic-free water
18	Matrix spike	1:4 diluted sample 1 spiked with std 5 concentrations of HAA
19	Matrix spike duplicate	1:4 diluted sample 1 spiked with std 5 concentrations of HAA
20	Sample 2	Sample
21	Sample 3	Sample
22	Sample 4	Sample
23	Sample 5	Sample
24	Sample 6	Sample
25	Sample 7	Sample
26	Sample 8	Sample
27	Sample 9	Sample
28	Sample 10	Sample
29	MTBE	Instrument blank
30	CCV – std 4	Continuing calibration verification-std level 4
31	CCV – std 5	Continuing calibration verification-std level 5
32	MTBE	Instrument
33	Sample 1	Same samples as in vials 17–29, but diluted 1:5 with organic-free water prior to extraction
34	Sample 2 diluted	Diluted sample
35	Sample 3 diluted	Diluted sample

Table 8. Sequence of blanks, calibration standards, quality-control standards, and unknown samples analyzed during one run of the gas chromatograph.—Continued

[MTBE, methyl *tert*-butyl ether; Std, standard; QCS, quality-control sample; µg/L, micrograms per liter; HAA, haloacetic acid; CCV, continuing calibration verification]

Vial number	Sample ID	Sample description
36	Sample 4 diluted	Diluted sample
37	Sample 5 diluted	Diluted sample
38	Sample 6 diluted	Diluted sample
39	Sample 7 diluted	Diluted sample
40	Sample 8 diluted	Diluted sample
41	Sample 9 diluted	Diluted sample
42	Sample 10 diluted	Diluted sample
43	MTBE	Instrument blank
44	CCV – std 4	Continuing calibration verification–std level 4
45	CCV – std 5	Continuing calibration verification–std level 5
46	MTBE	Instrument blank

of 50 µg/L for each of the nine HAA. The QCS5 is prepared by adding 10 µL of QCSSB to 40 mL of organic-free water to give a final concentration of 5 µg/L for each of the nine HAA. These samples are included with each sample set for extraction and methylation. QCS5 is used to check the low end of the calibration curve and QCS50 is used to check the high end of the calibration curve. The percent recovery and standard deviation were determined for 16 QCS5 and for 15 QCS50 samples (*table 9*). Acceptable recoveries are 70 to 130 percent of the true value for all nine HAA, although actual recoveries are generally better. The QCS analyzed during this study had recoveries ranging from 75 to 122 percent of the true value for all nine HAA. If the measured analyte concentrations are not of acceptable accuracy, then the following must be checked: (1) the standard solutions for degradation, (2) contamination, (3) instrument performance, and (4) the entire analytical procedure to locate and correct the source of the problem. Once the problem has been solved, the samples need to be re-extracted and analyzed, if possible.

Continuing Calibration Verification Standard

The continuing calibration verification (CCV) standards are used to verify that the calibration is accurate through the entire run. They are prepared by the same method as the procedural calibration standards and at the same concentration as standard levels 4 and 5. Acceptable mean-percent recovery values for this method are 70 to 130 percent for each of the nine HAA. The mean-percent recovery and standard deviation for the CCV standards (standard level 5) analyzed with the Orange County surface-water samples are presented in *table 10*. The mean-percent recovery values range from 86 to 113 percent for this sample set.

Surrogate Recovery

The surrogate analyte is added to the aqueous portion of all samples and blanks. The surrogate is a means of assessing method performance for every sample from extraction to final chromatographic performance. For the Orange County surface-water samples used to develop this method, the average surrogate recovery was 106 percent with a standard deviation of 17 percent. The surrogate recovery for this method should be between 70 and 130 percent. If the surrogate recovery is outside this range, check (1) standard solutions for degradation, (2) contamination, and (3) instrument performance. If those steps do not reveal the cause of the problem, the sample should be reextracted and reanalyzed, if possible. If the surrogate recovery of the reanalyzed sample meets the criterion, only data for the reextracted sample should be reported. If the reanalysis fails the 70–130 percent recovery criterion, the sample should be flagged as showing possible matrix interference and all data for that sample should be reported as estimated data.

Internal Standard Area Count

The EZChrom software uses the IS to quantify the samples. The IS response (peak area counts or peak height) is checked and under current (2002) conditions is approximately 230,000 area counts. For the Orange County surface water samples, the IS response varied from 189,000 to 291,000 area counts with a mean of 230,000 area counts and a standard deviation of 21,800. The analyst must monitor the IS response of all injections during each analysis day. The IS response for any sample should not deviate from this mean IS response by more than 30 percent. If the IS response is not within 30 percent for

Table 9. The percent recovery for nine haloacetic acids in replicate samples of quality-control standards.

[n, number of replicate samples; µg/L, micrograms per liter]

Analyte name	Quality-control sample 5 (n=16)			Quality-control sample 50 (n=15)		
	Concentration (µg/L)	Mean percent recovery	Standard deviation (percent)	Concentration (µg/L)	Mean percent recovery	Standard deviation (percent)
Bromochloroacetic acid	5.0	84	8.2	50.	80	7.6
Bromodichloroacetic acid	5.0	75	17	50.	84	13
Dibromochloroacetic acid	5.0	114	27	50.	122	19
Dibromoacetic acid	5.0	109	16	50.	116	27
Dichloroacetic acid	5.0	108	12	50.	97	8.6
Monobromoacetic acid	5.0	105	21	50.	102	8
Monochloroacetic acid	5.0	104	15	50.	103	23
Tribromoacetic acid	5.0	118	44	50.	118	27
Trichloroacetic acid	5.0	111	16	50.	110	18

an individual extract, check the chromatogram for coelution problems and, if necessary, optimize instrument performance and analyze a new extract. If this analyzed aliquot produces an acceptable IS response, report results for that aliquot.

Matrix Spikes

Matrix spikes are prepared by adding a known concentration of all nine analytes to one sample per extraction set or a minimum of 10 percent of the samples, whichever is greater. The concentrations should be equal to or greater than the background concentrations in the sample selected for spiking. Matrix spikes for the Orange County, California, surface-water samples were diluted 1:5 with organic-free water prior to dosing and then spiking with 8 µL of working standard solution B. Matrix spikes should be analyzed for samples from all routine sample sources.

The mean-percent recoveries for each analyte are calculated, and in order for the recoveries to be considered acceptable, they must fall between 70 and 130 percent for all the target analytes. If the recovery falls outside of this acceptance range and no other problems with the analysis could be determined, then a matrix-induced bias can be assumed for the respective analyte. The data for the analyte must be reported to the data user as suspect due to matrix effects.

Duplicates

The duplicates are used to assess the precision of the dosing and extraction process. The matrix spike duplicates are used to assess the validity of matrix interferences. The duplicates are prepared starting with the dosing process. Matrix spike duplicates are prepared prior to the extraction process by taking one sample vial and splitting it into three samples. These three samples are made by using 8 mL of sample and diluting to a final volume of 40 mL with 32 mL of organic-carbon-free water. Two of these diluted samples then are spiked with HAA and the third is used to assess background levels.

The percent relative difference between duplicate results should be less than or equal to 30 percent. The percent relative difference is determined by the following formula:

$$\text{percent relative difference} = \frac{2 * \left| C_A - C_B \right|}{C_A + C_B} * 100 \qquad (6)$$

where

C_A is the measured concentration in one of duplicates and

C_B is the measured concentration in the other duplicate

The percent relative differences for the duplicates and matrix spike duplicates for the Orange County surface-water samples ranged from 0.02 to 28.3 percent and 0 to 28.2 percent, respectively.

Instrument Maintenance

Instrument maintenance is performed on the autosampler, injection port, detector, and column prior to analyzing a new extraction batch or after analyzing 50 extracts, whichever comes sooner. In order to insure proper instrument performance, the injector and detector are baked at 350ºC according to instrument and column manufacturer's recommendation. The injector side of the analytical column is cut by approximately 0.3 to 0.5 m and reinstalled; the syringe on the autosampler is inspected for wear and sample residue. Also, the septum on the injector is replaced after approximately 100 injections or after analyzing two extraction batches.

Table 10. The mean percent recovery for the nine haloacetic acids in 28 analyses of continuing calibration verification standard level 5.

[µg/L, micrograms per liter; n, number of standards analyzed]

Analyte name	Concentration (µg/L)	Mean percent recovery (n = 28)	Standard deviation (percent)
Bromochloroacetic acid	4.0	105	8
Bromodichloroacetic acid	4.0	86	10
Dibromochloroacetic acid	10.	86	9
Dibromoacetic acid	2.0	97	12
Dichloroacetic acid	6.0	113	4
Monobromoacetic acid	4.0	108	8
Monochloroacetic acid	6.0	113	14
Tribromoacetic acid	20.	92	16
Trichloroacetic acid	2.0	95	11

Summary

This report provides a description of the analytical method and quality-control protocols for the determination of haloacetic acid (HAA) formation potential used by the U.S. Geological Survey California Water Science Center, Sacramento laboratory. HAA formation potential is defined as the amount of HAA produced by chlorination of a water sample under specified, standard conditions. Nine HAA compounds are measured: bromochloroacetic acid, bromodichloroacetic acid, dibromochloroacetic acid, dibromoacetic acid, dichloroacetic acid, monobromoacetic acid, monochloroacetic acid, tribromoacetic acid, and trichloroacetic acid.

The analytical method includes producing the HAA, extracting and methylating the HAA, and then analyzing the methylated compounds by gas chromatography. The HAA are formed from dissolved organic carbon in water samples by dosing filtered water samples with chlorine in the form of sodium hypochlorite under specified conditions of pH (8.3), temperature (25°C), chlorine contact time (7 days), residual-free chlorine at the end (2–4 mg/L), and darkness. A surrogate compound, 2-bromopropionic acid, is added to the samples after the residual-free chlorine is quenched. Samples then are acidified, sulphate salts are added, and the HAA compounds are extracted from the aqueous solution with methyl *tert*-butyl ether (MTBE). The compounds then are methylated by adding acidified methanol to the MTBE extracts and heating the mixture. The MTBE-methanol mixture then is extracted with dilute sodium hydroxide to yield the final MTBE extract containing the methylated HAA and surrogate. An internal standard (IS), 2-bromo-1-chloropropane, is added to the final extracts, and the extracts are analyzed by gas chromatography. Chromatographic separation between the nine methylated HAA, the methylated surrogate, and the IS compounds is achieved with an Rtx-5 column and the analytes are detected with an electron-capture detector. HAA concentrations in the samples are quantified using a standard curve constructed from aqueous solutions extracted and methylated by the same procedure. The calibration ranges for the nine HAA are 0.2–100 µg/L for bromochloroacetic acid, bromodichloroacetic acid, and monobromoacetic acid; 0.5–250 µg/L for dibromochloroacetic acid; 0.1–50 µg/L for dibromoacetic acid and trichloroacetic acid; 0.3–150 µg/L for dichloroacetic acid and monochloroacetic acid; and 1–500 µg/L for trichloroacetic acid. The accuracy, precision, and method detection limit (MDL) for the method were determined. The MDL for the nine HAA ranged from 0.11 to 0.45 µg/L. Accuracy and precision were assessed using matrix spike experiments with natural water samples. Mean percent recovery of spike concentrations of the nine HAA ranged from 99 to 117 percent, with percent standard deviation of the means of 17 to 28 percent. Quality-control, data storage, instrument maintenance, and corrective action protocols were described. Quality-control protocols entail regular analysis of a variety of quality-control samples: instrument, extraction, and full-procedural blanks; continuing calibration verification standards; duplicate samples; matrix spikes; and independent quality-control standards. The use of a surrogate and an IS also are quality-control measures. The HAAFP data and associated quality-control information are stored in the California Water Science Center's Laboratory Information Management System (LIMS), and also may be entered into the USGS National Water Information System database. Original chromatograms are archived and linked to the LIMS. Instrument maintenance and corrective actions are undertaken promptly.

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