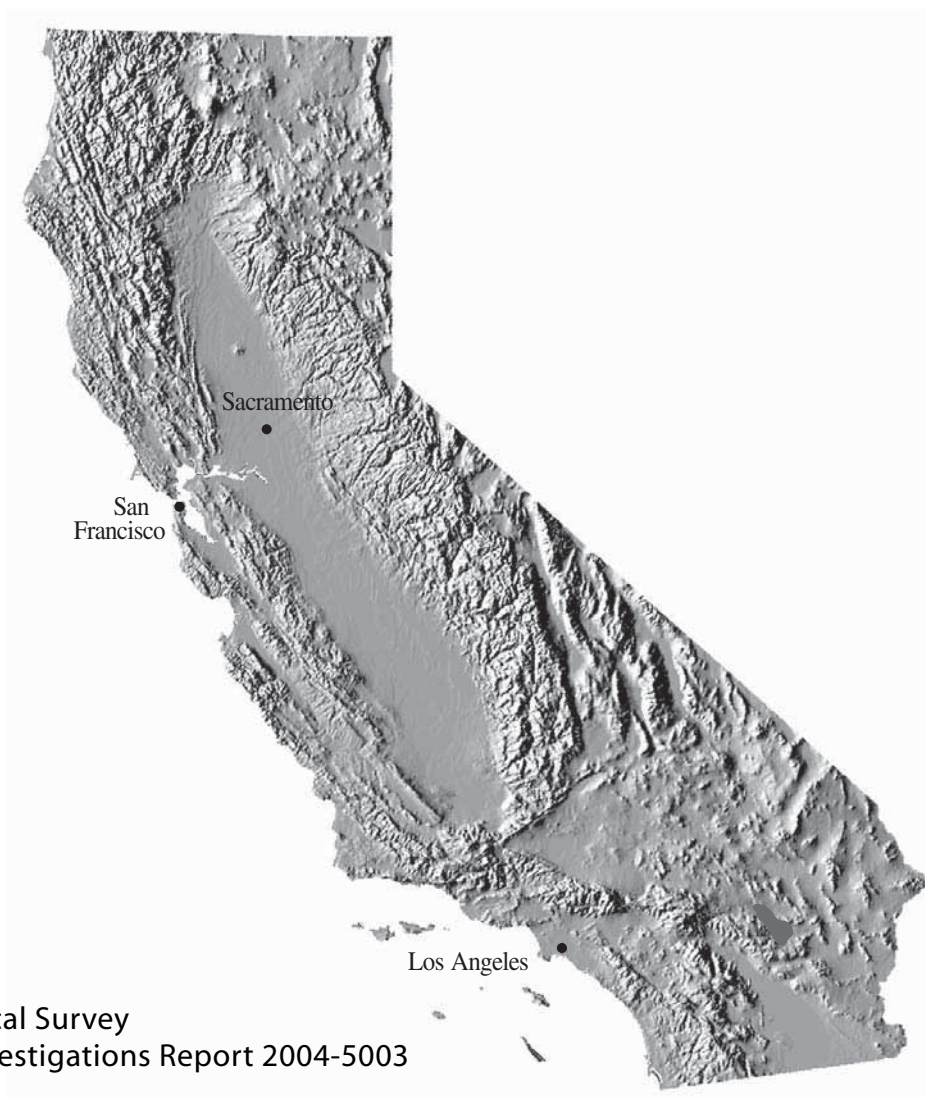


# Method of Analysis by the U.S. Geological Survey California District Sacramento Laboratory—Determination of Trihalomethane Formation Potential, Method Validation, and Quality-Control Practices



U.S. Geological Survey  
Scientific Investigations Report 2004-5003

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By Kathryn L. Crepeau, Miranda S. Fram, and Noël Bush

Scientific Investigations Report 2004-5003

**U.S. Department of the Interior  
U.S. Geological Survey**

**U.S. Department of the Interior**  
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## Conversion Factors, Abbreviations, and Acronyms

	Multiply	By	To obtain
	pound per square inch (lb/in <sup>2</sup> )	6.895	kilopascal (kPa)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32$$

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

## Abbreviations and Acronyms

### ABBREVIATIONS

d, days

Hz, hertz

m, meter

mg, milligram

mg/L, milligrams per liter

mL, milliliter

mL/min, milliliter per minute

mmol, millimole

mmol/mol, millimoles per mole

M, molar

nm, nanometers

µg/L, micrograms per liter

µg/mL, micrograms per milliliter

µL, microliter

µM, micromolar

µmol/L, micromoles per liter

µmol, micromole

V, volts

Br, elemental bromine

Br<sup>-</sup>, bromide ion; bromide dissolved, bromide

Cl, elemental chlorine

CH<sub>2</sub>Cl<sub>2</sub>, methylene chloride

CH<sub>2</sub>ClCHBrCH<sub>3</sub>, 2-bromo-1-chloropropane

CH<sub>3</sub>OH, methanol

CHBr<sub>3</sub>, bromoform

CHCl<sub>2</sub>Br, bromodichloromethane

CHCl<sub>3</sub>, chloroform

CHClBr<sub>2</sub>, dibromochloromethane

Cl<sup>-</sup>, chloride; chloride ion

Cl<sub>2</sub>, chlorine

dil, dilution

DOC, dissolved organic carbon

DPD, N-diethyl-p-phenylenediamine  
H<sup>+</sup>, hydrogen ion  
H<sub>2</sub>O, water  
H<sub>3</sub>BO<sub>3</sub>, boric acid  
HCl, hydrochloric acid  
HOBr, hypobromous acid  
HOCl, hypochlorous acid  
N<sub>2</sub>, nitrogen gas  
NaBr, sodium bromide  
NaOCl, sodium hypochlorite  
NaOH, sodium hydroxide  
Na<sub>2</sub>SO<sub>3</sub>, sodium sulfite  
NH<sub>3</sub>-N, ammonia-nitrogen  
OCl<sup>-</sup>, hypochlorite  
pKa, dissociation constant of acids  
POC, particulate organic carbon  
SDS-THM, simulated distribution system trihalomethanes  
STHMFP, specific trihalomethane formation potential  
STTHMFP, specific total trihalomethane formation potential  
THM, trihalomethane  
THMFP, trihalomethane formation potential  
TTHM, total trihalomethane  
TTHMFP, total trihalomethane formation potential

ACS, American Chemical Society  
DBP, disinfection by-product  
ECD, electron capture detector  
USEPA, U.S. Environmental Protection Agency  
GC, gas chromatograph  
ID, internal diameter  
LIMS, Laboratory Information Management System  
MCL, maximum contaminant level  
MDL, method detection limit  
NWIS, National Water Information System  
RSD, relative standard deviation  
TOC, total organic carbon  
UFC, Uniform Formation Condition  
USGS, U.S. Geological Survey  
VOC, volatile organic compound





# Method of Analysis by the U.S. Geological Survey California District Sacramento Laboratory— Determination of Trihalomethane Formation Potential, Method Validation, and Quality-Control Practices

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## Abstract

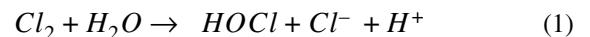
An analytical method for the determination of the trihalomethane formation potential of water samples has been developed. The trihalomethane formation potential is measured by dosing samples with chlorine under specified conditions of pH, temperature, incubation time, darkness, and residual-free chlorine, and then analyzing the resulting trihalomethanes by purge and trap/gas chromatography equipped with an electron capture detector. Detailed explanations of the method and quality-control practices are provided. Method validation experiments showed that the trihalomethane formation potential varies as a function of time between sample collection and analysis, residual-free chlorine concentration, method of sample dilution, and the concentration of bromide in the sample.

## Introduction

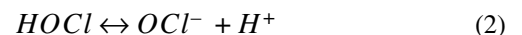
Trihalomethanes (THMs) are volatile, halogenated organic compounds that commonly are present in treated drinking water. THMs are one type of undesirable disinfection by-products (DBPs) that form during the disinfection stage of the drinking water-treatment process. Natural organic carbon present in the source water reacts with disinfectants [usually chlorine ( $\text{Cl}_2$ )] added during treatment to form THMs and other DBPs. Dissolved organic carbon (DOC) comprises the majority of the natural organic carbon in most drinking water source waters; particulate organic carbon (POC) usually is less important. THMs are of concern because they are carcinogenic

and have been reported to cause miscarriages (Waller, and others, 1998; Bove and others, 2002). THMs include chloroform ( $\text{CHCl}_3$ ), bromodichloromethane ( $\text{CHCl}_2\text{Br}$ ), dibromochloromethane ( $\text{CHClBr}_2$ ), and bromoform ( $\text{CHBr}_3$ ); the sum of these four compounds is the total trihalomethanes (TTHM). The TTHM concentrations in drinking water are regulated and the current maximum contaminant level (MCL) is 80 micrograms per liter ( $\mu\text{g/L}$ ) (U.S. Environmental Protection Agency, 1998).

THMs contain Cl and Br because the added  $\text{Cl}_2$  reacts with dissolved  $\text{Br}^-$  (bromide) as well as with the DOC.  $\text{Cl}_2$  is a strong oxidant and is added to water as  $\text{Cl}_2$  gas or sodium hypochlorite ( $\text{NaOCl}$ , bleach).  $\text{Cl}_2$  gas hydrolyzes rapidly to form hypochlorous acid ( $\text{HOCl}$ ), chloride ion ( $\text{Cl}^-$ ), and hydrogen ion ( $\text{H}^+$ ) (reaction 1):



$\text{HOCl}$  (reaction 2) dissociates to hypochlorite ( $\text{OCl}^-$ ) and  $\text{H}^+$  with a dissociation constant of acids ( $\text{pK}_a$ ) of 7.6. Both species are reactive.



$\text{HOCl}$  reacts with  $\text{Br}^-$  to form hypobromous acid ( $\text{HOBr}$ ) (reaction 3), and effectively scavenges all of the  $\text{Br}^-$  out of the water.



$\text{HOBr}$  reacts faster with DOC than  $\text{HOCl}$  to form THMs (Morris, 1978; Symons and others, 1993).

## 2 Method of Analysis—Determination of Trihalomethane Formation Potential, Method Validation, and Quality-Control Practices

The amount of THMs formed from a given amount of DOC depends on the chemical structure of the DOC, the contact time between DOC and  $\text{Cl}_2$ , the relative concentrations of DOC and  $\text{Cl}_2$  (residual  $\text{Cl}_2$ ), the initial  $\text{Br}^-$  concentration of the water, and the pH and temperature of the water (Reckhow and others, 1990). Trihalomethane formation potential (THMFP) is defined as the amount of THMs formed under specified conditions of pH, contact time, residual  $\text{Cl}_2$  concentration, and temperature and is reported in units of micrograms per liter or micromoles per liter of total THMs. The specific trihalomethane (STHMFP) is the THMFP normalized to the DOC concentration and is reported in units of millimoles of THM per mole of carbon in the DOC. STHMFP is a measure of the reactivity of the DOC to form THMs. Note that THMFP and STHMFP are equivalent to total trihalomethane formation potential (TTHMFP) and specific TTHMFP (STTHMFP), terms also used in the literature.

There are at least four standard methods for measuring THMFP: U.S. Environmental Protection Agency (EPA) method 510.1 and 502.2 (U.S. Environmental Protection Agency, 1983; 1995); THMFP Standard Method 5710B, 6232, and 6230D (American Public Health Association and others, 1995); Simulated Distribution System Trihalomethanes (SDS-THM) Standard Method 5710C (American Public Health Association and others, 1995); and Uniform Formation Condition (UFC) (Summers and others, 1996). Each method specifies different conditions of pH, contact time, temperature, and residual  $\text{Cl}_2$  and, thus, each method would yield different results for the THMFP of a water sample. The U.S. Geological Survey (USGS) Sacramento Laboratory uses a modified version of the EPA methods. The procedure and quality-assurance/quality-control procedures are modified from EPA methods 510.1 and 502.2 (U.S. Environmental Protection Agency, 1983; 1995), the USGS National Water Quality Laboratory volatile organic compound method (Connor and others, 1998), and the standard operating procedures for analysis of THMFP by the California Department of Water Resources Bryte Laboratory (Sid Fong, California Department of Water Resources, written commun., 1997).

### Purpose and Scope

This report presents detailed descriptions of the analytical procedures and quality-assurance/quality-control protocols used for determination of THM formation potential by the USGS California District, Sacramento Laboratory.

This report also presents evaluations of three procedural variables—sample aging, residual  $\text{Cl}_2$  tolerance, and method of dilution—on the THMFP. Ideally, all water samples would be analyzed immediately on arrival at the laboratory, but in reality, delays occur and samples are placed in refrigerated storage for a period of time prior to analysis. No preservatives, such as acid, are added to the samples during storage. The effect of “aging” of the water sample on the THMFP was determined by analyzing the same water sample weekly during a 6-week period. The  $\text{Cl}_2$  demand of a water sample is a function of DOC concentration and composition, ammonia-nitrogen ( $\text{NH}_3\text{-N}$ ) concentration, and the inorganic matrix of the sample and, thus, is difficult to predict precisely. Therefore, it is necessary to allow the residual-free  $\text{Cl}_2$  concentration to vary within a small range. The effect of residual  $\text{Cl}_2$  concentration on THMFP was determined by analyzing samples at a range of residual  $\text{Cl}_2$  concentrations. Many chlorinated water samples produced THM concentrations that are much higher than the concentration range measurable by the detector on the gas chromatograph (GC). Samples that have DOC concentrations greater than about 3 milligrams per liter (mg/L) must be diluted. The effect of different dilution procedures was examined by comparing THMFP of samples diluted before and after chlorination, and by comparing THMFP of samples diluted by different amounts.

Finally, this report presents an evaluation of the effect of  $\text{Br}^-$  concentration on THMFP. Water samples analyzed for THMFP in the USGS Sacramento Laboratory range from fresh to brackish in terms of salinity and, thus, have a wide range of  $\text{Br}^-$  concentrations. THMFP data are used to provide information about the DOC in the water sample, but this information may be confounded if  $\text{Br}^-$  alters the THM formation reaction. The effect of  $\text{Br}^-$  concentration on THMFP was evaluated by measuring THMFP of water samples with and without a  $\text{Br}^-$  spike.

### Acknowledgments

The authors gratefully acknowledge Ben Harper, Kelley Paxton, Tania Owen, and Barbara Zazzi for laboratory assistance with these experiments.

# Method of Analysis of Trihalomethane Formation Potential

## Scope and Application

An analytical method was developed for determining the THMFP of water samples; this method is designed for measuring THMFP under controlled, standard conditions of pH, temperature, darkness, contact time between  $\text{Cl}_2$  and the water sample, and residual  $\text{Cl}_2$  concentration. Because THMFP depends on experimental conditions, particularly pH and contact time, data obtained using this method must only be compared to data obtained from methods using the same conditions. This method is suitable for filtered ground-water and surface-water samples and for filtered-water samples produced in laboratory experiments. A modified procedure for unfiltered samples also is given. The calibration range for the method is 0.17 to 160  $\mu\text{g/L}$  of  $\text{CHCl}_3$  and 0.037 to 40  $\mu\text{g/L}$  of  $\text{CHCl}_2\text{Br}$ ,  $\text{CHClBr}_2$ ,  $\text{CHBr}_3$ , which corresponds to a DOC range in the water sample of approximately 0 to 3 mg/L. Water samples having higher DOC concentrations are diluted for analysis.

## Summary of Method

Water samples are collected and filtered to remove suspended particulate matter. The DOC and  $\text{NH}_3\text{-N}$  concentrations in the water samples are used to determine the appropriate amount of  $\text{Cl}_2$  solution to add. The water samples are diluted as necessary to keep the DOC in the range of 0 to 3 mg/L. The pH is adjusted and buffered to 8.3. After the samples are dosed, they are incubated for 7 days.

At the end of the 7 days, the pH and residual-free  $\text{Cl}_2$  are measured and the samples are quenched with sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) solution to neutralize any remaining free  $\text{Cl}_2$ . The THMs are purged from the sample matrix by bubbling nitrogen through an aliquot of the sample. The THMs are collected on an adsorbent trap and thermally desorbed into the inlet of a GC. The four THM species ( $\text{CHCl}_3$ ,  $\text{CHCl}_2\text{Br}$ ,  $\text{CHClBr}_2$ , and  $\text{CHBr}_3$ ) are separated by capillary gas chromatography and detected by an electron capture detector.

## Equipment and Materials

The equipment and materials used for analysis of THMFP are listed in [table 1](#).

The organic carbon-free water is produced onsite using a recirculating Picotech water system (Hydro Service and Supplies, Inc.). Inlet water for the Picotech system is deionized and is produced onsite with a Culligan deionizing system from Culligan International Company. The Picotech system is housed in a laboratory that contains no organic solvents, and the THMFP analysis procedure is performed in a laboratory

that contains no organic solvents in order to eliminate vapor-phase contamination of the water. Scheduled routine maintenance and replacement of cartridges are done on the Picotech and Culligan deionizing systems. The organic carbon-free water is tested frequently by analysis of DOC and THMFP (see “Blank Samples” section in this report).

Vials and other glassware items used for THMFP analysis are cleaned rigorously. Glassware is washed with Liquinox soap and rinsed with copious amounts of organic-free water. Openings are covered using aluminum foil and the glassware is baked at 450°C in a muffle furnace for 4 hours. Baked glassware is stored in closed drawers or cabinets until use. Glass-fiber filters are baked under the same conditions, wrapped in aluminum foil, and stored in closed drawers or cabinets. Samples are stored in baked amber glass bottles sealed with Teflon-lined caps. Bottles supplied by the USGS Ocala Water-Quality Laboratory are made of virgin glass and are baked at 500°C for 1.5 hours and, thus, are used without further cleaning.

## Sample Collection and Filtration

Water samples for THMFP analysis should be collected using baked glass, Teflon, or stainless-steel sampling containers. Exposure to organic solvents must be prevented. For example, shallow surface-water grab samples can be collected directly into baked amber glass bottles, and deeper surface-water grab samples can be collected using a Teflon or stainless-steel Van Dorn-type sampler for transfer into baked amber glass bottles. If the sampler is cleaned with methanol ( $\text{CH}_3\text{OH}$ ), copious amounts of water must be used to rinse the sampler to ensure that the  $\text{CH}_3\text{OH}$  is removed completely prior to collecting the sample. Samples must be filtered prior to analysis of the THMFP of the DOC. The THMFP of the total organic carbon (TOC) in the sample (the sum of the DOC and the particulate organic carbon) can be determined by analyzing the THMFP of unfiltered samples; however, care must be taken to assure that the sample is well mixed. Procedures for collecting and filtering samples, such as those given in chapters A4 and A5 of the USGS 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 it is stored at 4°C until analyzed.

## Dosing and Quenching Procedure

The samples are dosed with  $\text{Cl}_2$ , incubated at 25°C for as many as 7 days, quenched using sodium sulfite ( $\text{Na}_2\text{SO}_3$ ), and analyzed immediately by purge and trap/gas chromatography with an electron-capture detector.

## 4 Method of Analysis—Determination of Trihalomethane Formation Potential, Method Validation, and Quality-Control Practices

**Table 1.** Equipment and materials used for analysis of trihalomethane formation potential

[Sources for some items are listed to maintain quality standards. DPB, disinfection by-product]

---

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 DPD free-chlorine reagent powder pillows, # 14077-28 or Dispenser # 10445
2-dram Opticlear vials, screw thread, # 60910-2 (Kimble Glass, Inc.)
Spectrophotometer, Genesys20 (ThermoSpectronic)
Pipettes, 1- and 5-milliliter adjustable Oxford Benchmate (Nichiryo Co., LTD) with disposable plastic tips (Labsource, Fisherbrand, or equivalent)
Dilution
Glass beakers and graduated cylinders
Bottle-top dispenser, adjustable from 10 to 109 milliliter (Fisher/Wheaton)
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 $\pm$ 0.0001 gram
Boric acid (Mallinckrodt analytical reagent grade or equivalent)
Dilute NaOH or HCl for pH adjustment
Sodium hydroxide pellets (American Chemical Society reagent grade, Aldrich Chemical, Milwaukee, Wisconsin)
Sodium hypochlorite 4 to 6 percent (Fisher purified grade, Fisher Scientific, Pittsburgh, Pennsylvania)
40-milliliter vials, amber borosilicate, TraceClean (VWR Scientific, West Chester, Pennsylvania)
Sodium sulfite, anhydrous (American Chemical Society reagent grade, Fisher Scientific, Pittsburgh, Pennsylvania)
pH meter, Orion model 420A with Triode gel electrode (Orion Research Inc., Beverly, Massachusetts)
pH buffer 7 and 10 (U.S. Geological Survey Ocala Water-Quality Laboratory, Ocala, Florida)
Trihalomethane analysis
Gas chromatograph, Hewlett-Packard 5890 (Wilmington, Delaware)
Archon purge and trap auto sampler (Varian, Walnut Creek, California)
Sample concentrator (Tekmar 3100)
Column, 30-meter megabore DB-VRX (J & W Scientific, Folsom, California)
Nitrogen, ultra-high purity (Sierra Air Gas, Sacramento, California)
Helium, ultra-high purity (Sierra Air Gas, Sacramento, California)
Solvents
Methanol, purge and trap grade
Organic-free water, produced onsite with Pico-pure water system (Hydro Service and Supplies, Inc.)
Standards
Chloroform and trihalomethane mix in methanol (Supelco, Bellefonte, Pennsylvania)
Neat 2-bromo-1-chloro-propane (Supelco, Bellefonte, Pennsylvania)
Volumetric flasks

---

## Dose Calculation

The reactivity-based method used for determining the  $\text{Cl}_2$  dose is an empirical equation using the DOC and  $\text{NH}_3\text{-N}$  concentrations in the sample (California Department of Water Resources, 1994; Krasner and Scimenti, 1994). This dose will provide enough free  $\text{Cl}_2$  to satisfy the  $\text{Cl}_2$  demand of  $\text{NH}_3\text{-N}$  in the sample, react with the DOC to form THM, and leave residual-free  $\text{Cl}_2$  content of 2 to 4 mg/L at the end of the experiment. The formula for calculating the free  $\text{Cl}_2$  dose in mg/L is as follows:

$$\text{Free Cl}_2 \text{ dose} = [3 \times \text{DOC} + 10 \times \text{NH}_3\text{-N}] \times F_{\text{dose}} \times F_{\text{dil}} \quad (4)$$

where

- DOC is the dissolved organic carbon concentration, in mg/L,
- $\text{NH}_3\text{-N}$  is the ammonia nitrogen concentration, in mg/L,
- $F_{\text{dose}}$  is the dose factor, and
- $F_{\text{dil}}$  is the dilution factor.

The DOC of the sample is measured using a Shimadzu TOC 5000A analyzer. The DOC method and quality-assurance practices are described by Bird and others, 2003.

The  $\text{NH}_3\text{-N}$  content of the sample is measured using the Hach salicylate colorimetric method (Hach, 1997). The method is applicable to samples with  $\text{NH}_3\text{-N}$  contents of 0 to 0.5 mg/L. The concentration of  $\text{NH}_3\text{-N}$  in a sample is determined by the intensity of green color formed after the addition of two reagents. A 5-mL sample is measured into an optically clear vial and ammonia salicylate is added. The vials are shaken and placed in the dark. Light interferes with the chemical reaction. After 3 minutes, ammonia cyanurate is added. The vials are shaken and returned to the dark. After 15 minutes, the vials are placed in the spectrophotometer set at 655 nanometers (nm) to record the absorbance. If the measured absorbance is greater than the absorbance of the highest standard that is used to establish the linear standard calibration, then the sample is diluted and reanalyzed. The absorbance readings are recorded directly into the LIMS using an RS-232 connection between the spectrophotometer and a networked computer. The spectrophotometer is calibrated using standards so the absorbance readings can be converted to  $\text{NH}_3\text{-N}$  concentration.

The dose factor depends on the sample matrix and is an empirically determined value ranging from 1 to 3. Parameters considered by the analyst in determining the dose factor are the sample site, the DOC, the time of year, the  $\text{NH}_3\text{-N}$

concentration, and past results obtained using the same or similar water samples. The dilution factor depends on the amount of DOC in the sample. The DOC should be less than 3 mg/L to produce THMs within the calibration range of the instrument. The dilution factor generally ranges from 0.01 to 1. Samples containing  $\text{Br}^-$  may be split in aliquots prepared using different dilution factors to ensure that the concentration of each of the four THM species is within the ranges of the standard curve for at least one of the dilutions. The dose and dilution factors are recorded in the LIMS.

## Dosing

The samples are dosed using a solution containing 1 molar (M) boric acid ( $\text{H}_3\text{BO}_3$ )/0.11 M sodium hydroxide (NaOH) buffer and approximately 3,500 mg/L free  $\text{Cl}_2$  from sodium hypochlorite ( $\text{NaOCl}$ ). The pH and free  $\text{Cl}_2$  are tested daily and the solution is remade if either parameter is out of tolerance. The pH of the dose solution must be  $8.3 \pm 0.1$  and the free  $\text{Cl}_2$  must be between 3,000 and 4,000 mg/L. A new solution is made weekly. Samples are diluted with organic-free water to bring the DOC below 3 mg/L before dosing. 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). Three 40-mL amber vials are filled with sample and dosed by adding the appropriate volume of dose solution calculated from equation 4. The dose solution is added using a 100- or 250-microliter ( $\mu\text{L}$ ) gas-tight syringe. The sample vials are filled carefully and capped so that little or no sample is lost. They are capped immediately with zero headspace after dosing to prevent loss of the volatile THM compounds.

The free  $\text{Cl}_2$  of the dose solution or a sample is measured by the Hach N, N-diethyl-p-phenylenediamine (DPD) colorimetric method (Hach, 1997). The dose solution must be diluted for this measurement. A packet of DPD free- $\text{Cl}_2$  reagent is added to 5 mL of sample, shaken for 1 minute and the intensity of pink color is measured on the spectrophotometer set to measure absorbance at 530 nm. The spectrophotometer has been calibrated using standards so absorbance readings can be converted to free  $\text{Cl}_2$  concentration.

## Incubating

The dosed samples are stored in an incubator maintained at  $25^\circ\text{C}$  for 7 days. Samples may be stored for different periods of time if determination of THMFP at different  $\text{Cl}_2$ -DOC contact times is needed for a particular project.

## 6 Method of Analysis—Determination of Trihalomethane Formation Potential, Method Validation, and Quality-Control Practices

### Quenching and Acceptance Criteria

After completion of the incubation period, two vials of each sample are quenched with 50  $\mu\text{L}$  of 0.4 M  $\text{Na}_2\text{SO}_3$  solution to neutralize any remaining free  $\text{Cl}_2$ . The sample pH and free  $\text{Cl}_2$  are measured in the third vial that has not been quenched. The pH must be  $8.3 \pm 0.1$ , and the residual-free  $\text{Cl}_2$  must be between 2 and 4 mg/L. The residual-free  $\text{Cl}_2$  specified by the EPA method and by the standard method are 0.5 to 1.5 mg/L and 3 to 5 mg/L, respectively. For this method, we chose a residual-free  $\text{Cl}_2$  range, which is between these two other methods. If either of these parameters is out of range, the sample is reanalyzed.  $\text{Cl}_2$  concentration and pH data are recorded directly into the LIMS by RS-232 connections between the pH meter and spectrophotometer to the networked computer.

### Standards

#### Primary Standard Solution

A THM calibration mix containing 2,000 micrograms per milliliter ( $\mu\text{g}/\text{mL}$ ) of each of the four compounds in methanol and a 5,000- $\mu\text{g}/\text{mL}$   $\text{CHCl}_3$  standard in methanol are purchased from Supelco. A methanol solution containing 80- $\mu\text{g}/\text{mL}$   $\text{CHCl}_3$  and 20- $\mu\text{g}/\text{mL}$   $\text{CHCl}_2\text{Br}$ ,  $\text{CHClBr}_2$ , and  $\text{CHBr}_3$  is prepared by measuring 250  $\mu\text{L}$  of the THM calibration mix and 300  $\mu\text{L}$  of the  $\text{CHCl}_3$  standard and bringing to volume with methanol in a 25-mL volumetric flask. This solution is stored in a freezer and new solution is prepared every 2 months. The primary Standard Solution is diluted 25 times to give a solution containing 3.2- $\mu\text{g}/\text{mL}$   $\text{CHCl}_3$  and 0.8- $\mu\text{g}/\text{mL}$   $\text{CHCl}_2\text{Br}$ ,  $\text{CHClBr}_2$ , and  $\text{CHBr}_3$ . This diluted primary standard solution is used to make the three lowest calibration standard solutions.

#### Calibration Standard Solutions

A series of 14 aqueous solutions containing 0.2 to 160  $\mu\text{g}/\text{L}$  of  $\text{CHCl}_3$  and 0.04 to 40  $\mu\text{g}/\text{L}$  of the three brominated species are prepared from the primary standards for use as calibration standards. The solutions are prepared immediately prior to analysis by measuring 0.5 to 100  $\mu\text{L}$  of the primary standard solution using gas-tight syringes and bringing to volume with organic-free water in 50-mL volumetric flasks. The three lowest solutions are prepared by measuring 2.5 to 10  $\mu\text{L}$  of the diluted primary standard solution.

#### Surrogate Solution

A neat standard of 2-bromo-1-chloropropane ( $\text{CH}_2\text{ClCHBrCH}_3$ ) is purchased from Supelco. A methanol solution containing 0.3  $\mu\text{g}/\text{mL}$  of  $\text{CH}_2\text{ClCHBrCH}_3$  is prepared

by measuring 10  $\mu\text{L}$  of the neat standard with a gas-tight syringe and bringing it to volume with methanol in a 50-mL volumetric flask. Each sample receives 1  $\mu\text{L}$  of this surrogate solution injected automatically by the Varian Archon auto sampler, and the surrogate is an indicator of leaks in the instrument or of matrix effects from the water sample.

### Instrument Performance

#### Instrument Conditions

The purge and trap instrument is composed of a Varian Archon auto-sampler, connected to the Tekmar model 3100 concentrator and a Hewlett-Packard 5890 GC equipped with an electron capture detector (ECD). The instrument settings for the purge and trap using capillary column GC/ECD are summarized in [table 2](#).

**Table 2.** Instrument settings for the purge and trap capillary column gas chromatography/electron capture detector operation conditions

[N<sub>2</sub>, nitrogen gas; lb/in<sup>2</sup>, pound per square inch; °C, degrees Celsius; m, meter; mm, millimeter; ID, internal diameter; mL/min, milliliter per minute; °C/min, degrees Celsius per minute]

Purge and Trap Configurations	
Purge cycle	11 minutes with N <sub>2</sub> at 30 lb/in <sup>2</sup>
Dry purge	2 minutes with N <sub>2</sub> at 30 lb/in <sup>2</sup>
Carrier gas	Nitrogen
Desorb preheat	235°C
Desorb temperature	250°C for 1 minute
Bake cycle	260°C for 12 minute
Transfer line to gas chromatograph inlet	110°C
Valve temperature	110°C
Purge pressure	35 lb/in <sup>2</sup>
Trap	VOCARB 3000
Gas Chromatograph Configurations	
Column	DB-VRX 30-m $\times$ 0.45-mm ID
Carrier gas	Nitrogen at 10-mL/min flow at 35°C
Split flow	420 mL/min
Oven	35°C for 1 minute 35 to 80°C at 20°C/min 80 to 100°C at 5°C/min 100 to 125°C for 1 minute 125°C for 1 minute
Injector	Split 42:1, septum purge capped, 220°C
Detector	Electron capture at 200°C with nitrogen make-up and purge gas

The Varian Archon autosampler is set to run 5-mL samples and to automatically add a 1- $\mu$ L injection of the surrogate as the sample is transferred to the purge tube. After the sample is transferred, the autosampler begins a cleaning process in which heated water rinses the purge tube between samples. Once this process is complete, the autosampler pauses until the concentrator and the GC have finished with the sample before analyzing the next vial.

The Tekmar concentrator is set up with a 5-mL purge tube and VOCARB 3000 trap. When first installed, the trap is conditioned by heating to 270°C for 60 minutes. At the beginning of each new analysis, the bake cycle of the trap is run to remove possible contaminants. The efficiency of the trap is verified by tracking the change in area counts of the four compounds in one of the calibration verification standards. When the change in area count is greater than 20 percent, a new trap is installed.

The Hewlett-Packard 5890 GC is set up with a DB-VRX 30-m  $\times$  0.45-mm internal diameter (ID) column for the THM analysis. The transfer line from the Tekmar has been plumbed into the carrier gas inlet in the injector and the septum purge line has been capped. Each time the instrument is run, the gas flows and temperatures must be set and a new calibration curve is run. The column flow and the split flow are set to 10 and 420 mL/min, respectively. The ECD is turned on and heated to 200°C. The ECD signal must stabilize to a value below 15.0 (150 Hertz (Hz)) before starting the analyses.

The chromatogram is examined for changes in peak shape, contamination, and the baseline. A typical chromatogram for a mid-range standard is shown in [figure 1A](#). The peaks should be narrow and symmetrical and a flat baseline should be between peaks. If the peaks become wider than 0.3 minutes at the base or show strong tailing, the ECD make-up gas, column, and split flows should be rechecked; if the flows are correct, it may be necessary to replace the capillary column. The baseline between 1 and 2 minutes retention time is elevated slightly due to water vapor ([fig. 1B](#)). Note the difference in scale between [figures 1A](#) and [1B](#). If the water vapor peak is greater than 0.04 volts (V), then it may be necessary to replace the trap. The most common contaminant is methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>), which does not interfere with the compounds of interest because it has a retention time of 1.4 minutes ([fig. 1B](#)). The most common source of gross contamination of CH<sub>2</sub>Cl<sub>2</sub> is storage of methanol, primary standard solution, or surrogate standard used for THM analysis in a solvent cabinet or freezer that contains CH<sub>2</sub>Cl<sub>2</sub>. Small CH<sub>2</sub>Cl<sub>2</sub> peaks, such as the one in [figure 1B](#), occur when the adjacent laboratory is using large volumes of CH<sub>2</sub>Cl<sub>2</sub> for extractions.

## Calibration

An external standard calibration curve is prepared using a series of 14 aqueous calibration standards ranging in concentration from 0.2 to 160  $\mu$ g/L for CHCl<sub>3</sub> and from 0.04 to

40  $\mu$ g/L for CHCl<sub>2</sub>Br, CHClBr<sub>2</sub>, and CHBr<sub>3</sub>. A new calibration curve is analyzed when gas flows on the GC are adjusted, or if the results from check standards are out of acceptable range (see “Quality Control” section of this report). The calibration curves for the four THM species are nonlinear and fit with quadratic equations. The coefficient of determination, R<sup>2</sup>, is used to assess the fit between each quadratic equation and the data for each species from the 14 standard solutions. If the R<sup>2</sup> value is less than 0.9980, a new set of calibration standards is prepared and analyzed.

## Sample Analysis

Samples are analyzed as soon after quenching as possible, but are sometimes stored at 4°C for as many as 5 days prior to analysis. The order of analysis begins with two instrument blanks to verify no contamination in the instrument. Next, the standard curve is run from the lowest to the highest concentration, followed by an instrument blank. Then a set of as many as 10 samples is run followed by two calibration verification standards and instrument blanks between sets of samples (see “Quality Control” section of this report). Two full, procedural, duplicate samples are analyzed for every 10 samples (see “Quality Control” section of this report). In addition, multiple vials of individual samples are run if aliquots of the sample were prepared using different dilution factors. The final data for a sample may be combined from two or more different analyses where data for each THM species are taken from the dilution that fits within the standard curve ([table 3](#)). The data for an individual compound are chosen from the undiluted or least diluted sample.

## Data Processing and Storage Procedures

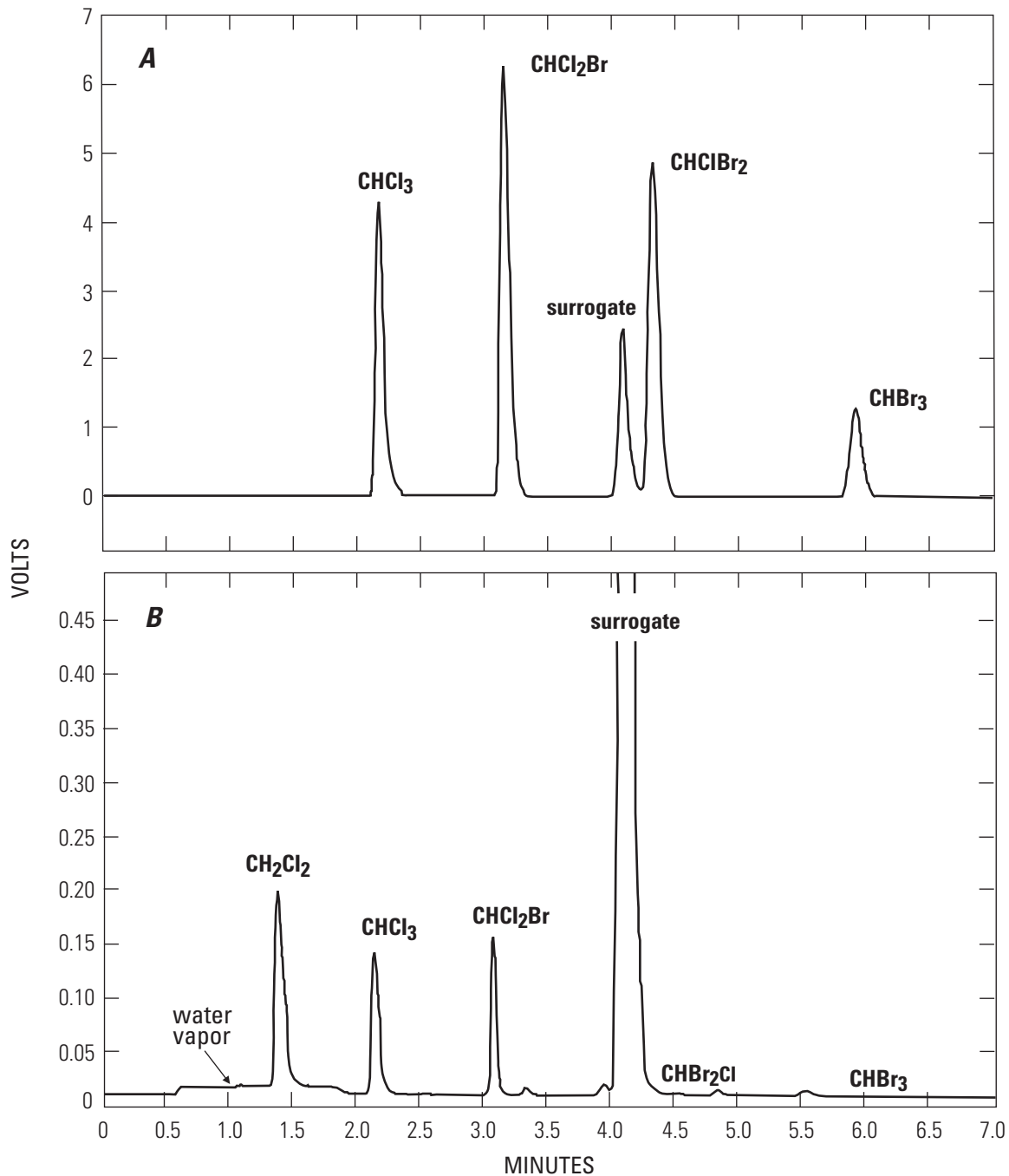
The data are processed using EZChrom software and LIMS.

### EZChrom Software

This software identifies the peaks of the four THM species and the surrogate by their retention times and then converts measured peak areas to concentrations using the standard curves. The analyst examines the chromatograms to verify that the peak identifications are correct. The measured concentrations are exported directly into the LIMS. The EZChrom software automatically flags samples if the surrogate concentrations, reproducibility of duplicate samples, or concentrations in the calibration verification standards are out of acceptable range (see “Quality Control” section of this report). The analyst also examines these data. The individual chromatograms, calibration curve information, and quality-control data are archived and the archive site is linked to the LIMS.



## 8 Method of Analysis—Determination of Trihalomethane Formation Potential, Method Validation, and Quality-Control Practices



**Figure 1.** Chromatograms of (A) a typical mid-range standard, and (B) an instrument blank run after a high standard containing the four trihalomethane species and methylene chloride (files 120502011 and 010203004). Note the difference in y-axis scales in panels A and B.

**Table 3.** Example to show combination of different gas chromatograph files for aliquots with different dose and instrument dilutions to make final choices from data[CHCl<sub>3</sub>, chloroform; CHCl<sub>2</sub>Br, bromodichloromethane; CHClBr<sub>2</sub>, dibromochloromethane; CHBr<sub>3</sub>, bromoform; µg/L, microgram per liter]

Sample	Dosing dilution	Injection dilution	Measured on GC				Corrected for dilutions			
			CHCl <sub>3</sub> (µg/L)	CHCl <sub>2</sub> Br (µg/L)	CHClBr <sub>2</sub> (µg/L)	CHBr <sub>3</sub> (µg/L)	CHCl <sub>3</sub> (µg/L)	CHCl <sub>2</sub> Br (µg/L)	CHClBr <sub>2</sub> (µg/L)	CHBr <sub>3</sub> (µg/L)
GR00199	1	1	<sup>1</sup> 100	<sup>2</sup> 250	<sup>2</sup> 200	<sup>1</sup> 20	100	250	200	20
GR00199 diluted	.1	1	<sup>1</sup> 9	27.5	22	<sup>1</sup> 1.8	90	275	220	18
GR00199 combined							100	275	220	20
GR00200	1	1	<sup>2</sup> 300	<sup>2</sup> 200	<sup>1</sup> 30	<sup>1</sup> 15	300	200	30	15
GR00200 diluted	1	.2	57	50	<sup>1</sup> 6.6	<sup>1</sup> 3.8	285	250	33	19
GR00200 combined							285	250	30	15

<sup>1</sup>If both concentrations are within the range of the calibration standards, then the concentration from the least diluted sample is chosen.<sup>2</sup>Concentration exceeds value in highest calibration standard; therefore, the concentration from the diluted sample is chosen.

## Laboratory Information Management System

Sample concentrations for each vial are calculated from the measured concentrations and the dose- and instrument-dilution factors. For samples analyzed at several different dose- and (or) instrument-dilution factors, the analyst must choose the appropriate vial from which to take the final concentration for each THM species, based on the value that fits within the standard curve. If more than one value fits within the standard curve, then the value produced from the least amount of dilution is chosen. The data are accessible to users of the LIMS after the analyst verifies the final concentrations. Procedures are being developed to export THMFP data from the LIMS to the U.S. Geological Survey National Water Information System (NWIS).

THMFP determined by this method refers to the result of incubation in the dark at 25°C and pH of 8.3 for 7 days with sufficient chlorine dose to leave a residual of 2 to 4 mg/L. THMFP is calculated as the sum of the mass concentrations of individual THMs, in µg/L. Non-detects are treated as zero in the sum. Both the sum and the individual THMs are reported. Alternative calculations of THMFP in µM are provided if required by a particular project.

STHMFP determined by this method is the ratio of THMFP, in millmoles per liter, to DOC, in moles per liter. It is equivalent to parts per thousand of organic carbon atoms that form THM.

Samples that contain little bromide generally produce THM concentrations ordered as CHCl<sub>3</sub> >> CHCl<sub>2</sub>Br >> CHClBr<sub>2</sub> > CHBr<sub>3</sub>, and non-detects are rare for the first two species. Samples with more bromide generally produce THM concentrations ordered as CHCl<sub>3</sub> ~ CHCl<sub>2</sub>Br ~ CHClBr<sub>2</sub> > CHBr<sub>3</sub>, and non-detects are rare for all four species. In any

case, the precision of reported THMFP is dominated by the precision of the largest-concentration species, which is about 1 percent, rather than by the value assigned to non-detects.

THMFP data include variability due to the precise chlorine residual and the effects of bromide concentration and possible dilution. The effective precision of the full procedure is estimated to be about 4 percent.

## Method Validation

A number of experiments were performed on three different natural water samples to validate the THMFP method. The first sample, AR, was collected from the American River at California State University, Sacramento, and had a DOC concentration of 1.6 mg/L. The second sample, SE, was a soil water extract and had a DOC concentration of 43 mg/L. The sample was produced by mixing Twitchell Island peat soil with organic-free water in a ratio of 15 grams (dry weight) of soil to 230 mL of water, followed by centrifugation and filtration to extract the water. The third sample, TW1, was collected from an agricultural drain on Twitchell Island and had a DOC concentration of 17 mg/L. The three water samples differ not only in their DOC concentration but also in the chemical composition of the DOC. Aliquots of AR were spiked with sodium bromide (NaBr) to create samples with different bromide (Br<sup>-</sup>) concentrations (ARBr1, ARBr2, and ARBr3). The initial Br<sup>-</sup> concentration of the samples were not measured, but can be estimated from the Br content of the THMs produced in the experiments. Assuming 50 percent of the Br<sup>-</sup> was incorporated in the THMs, the initial Br<sup>-</sup> concentration in the AR sample was estimated to be 0.006 mg/L.

## 10 Method of Analysis—Determination of Trihalomethane Formation Potential, Method Validation, and Quality-Control Practices

The composition and use of samples for the THMFP method validation experiments are summarized in [table 4](#). The following five experiments were performed on the water samples:

1. Method precision: Ten replicate analyses of THMFP were performed to determine method precision.
2. Sample aging: The samples were analyzed weekly for 6 weeks to determine the effect of delay between sample collection and analysis of THMFP.
3. Residual Cl<sub>2</sub>: The samples were dosed to yield residual-free Cl<sub>2</sub> concentrations ranging from 0.03 to 16 mg/L to determine the effect of residual-free Cl<sub>2</sub> concentration on THMFP.
4. Dilution: The samples were diluted prior to dosing and (or) after quenching to determine the effect of dilution method and amount on THMFP.
5. Br<sup>-</sup> concentration: The samples were spiked with different concentrations of NaBr to determine the effect of Br<sup>-</sup> concentration on THMFP and THM speciation.

Method detection limits (MDLs) for the individual THMs were not formally determined, because low concentrations are not the primary interest of data users. The lowest calibration standard for each of the four analytes provides a signal from the ECD at least 5 times background, so we estimate MDLs as less than these lowest standards.

**Table 4.** Samples used and tests performed for validation of the trihalomethane formation potential analytical method

[DOC, dissolved organic carbon; Br<sup>-</sup>, bromide ion. Experiments: 1, method precision; 2, sample aging; 3, residual chlorine; 4, dilution; 5, bromide concentration. mg/L, milligram per liter]

Sample	DOC (mg/L)	Br <sup>-</sup> (mg/L)	Experiments
AR	1.6	0.006	1, 2, 3, 4, 5
ARBr1	1.6	.11	5
ARBr2	1.6	.18	5
ARBr3	1.6	.27	3, 4, 5
SE	43	.12	1, 2
TW1	17	.23	4

### Method Precision

Method precision was estimated by analyzing 10 replicate aliquots of the AR and SE samples. Each aliquot was dosed individually. Precision is expressed as the percent relative standard deviation (RSD), which is calculated from the mean and the standard deviation of the replicate analyses:

$$RSD = \frac{s_x}{x} \times 100 \quad (5)$$

where

$$s_x = \sqrt{\frac{\sum (x - \bar{x})^2}{n - 1}} \quad (6)$$

and

$$\bar{x} = \frac{\sum x}{n} \quad (7)$$

and where

*RSD* is the percent relative standard deviation for the replicate analyses;

*s<sub>x</sub>* is the standard deviation of the replicate analyses;

$\bar{x}$  is the mean of the replicate analyses;

*x* is the value for an analysis; and

*n* is the number of replicate analyses.

Most of the RSD values are less than 1 percent ([table 5](#)); therefore, analytical precision is estimated to be 1 percent. Based on application of the American Society for Testing and Material rounding standard (American Society for Testing and Material, 1993), the last significant digit in the concentration data for the THM species is hundredths for values less than 10 µg/L, tenths for values between 10 and 200 µg/L, ones for values between 200 and 1,500 µg/L, and tens for values greater than 1,500 µg/L.

**Table 5.** Precision values calculated from 10 replicates each of American River and soil-extracted water

[CHCl<sub>3</sub>, chloroform; CHCl<sub>2</sub>Br, bromodichloromethane; CHClBr<sub>2</sub>, dibromochloromethane; CHBr<sub>3</sub>, bromoform. µg/L, microgram per liter; nd, not detected; RSD, relative standard deviation]

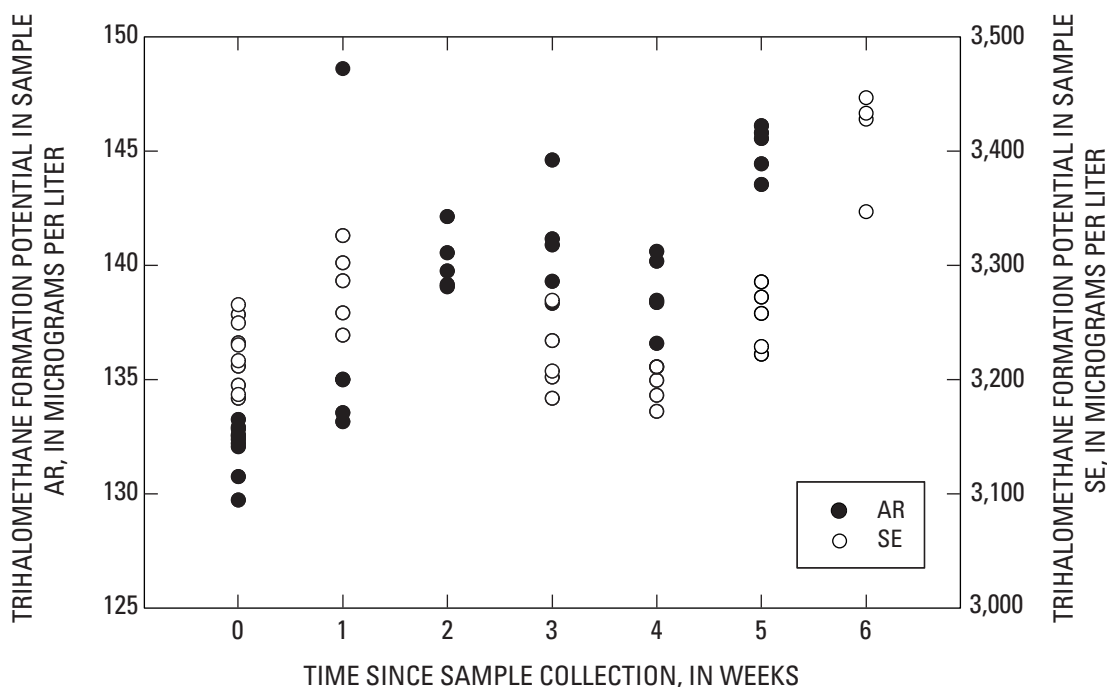
Statistical parameter	CHCl <sub>3</sub> (µg/L)	CHCl <sub>2</sub> Br (µg/L)	CHClBr <sub>2</sub> (µg/L)	CHBr <sub>3</sub> (µg/L)
<b>Sample AR</b>				
Mean	125.5	6.35	0.25	nd
Standard deviation	1.0	.03	.003	
RSD	.83	.52	1.27	
<b>Sample SE</b>				
Mean	3,100	123.6	3.51	nd
Standard deviation	28	.7	.14	
RSD	.92	.59	3.93	

### Effect of Sample Aging on Trihalomethane Formation Potential

Water samples AR and SE were analyzed weekly for 6 weeks following sample collection to assess the effect of sample aging on the total THMFP. The samples were stored in baked amber glass bottles at 4°C between analyses. No preservative was added to the samples. Ten replicate aliquots of

each sample were analyzed at the time of collection and five replicate aliquots were analyzed at the remaining five time points. The aliquots always were dosed with the same concentration of Cl<sub>2</sub>.

The THMFP of the AR sample changed from values ranging from 129 to 133 µg/L to 143 to 147 µg/L (fig. 2). This is an increase of about 10 percent during a 5-week period. Likewise, the THMFP of the SE sample changed from a range of values from 3,200 to 3,300 µg/L to a range of 3,300 to 3,450 µg/L. This is an increase of about 7 percent during a 6-week period. For both samples, the aliquot analyzed after 3 weeks of aging did not follow the general trend of increasing THMFP with increasing aging. The THMFP of the AR sample remained the same during weeks 2 and 3 then decreased in week 4 before increasing in week 5. The THMFP of the AR sample always remained higher in the subsequent weeks compared with the THMFP level at the initial collection. In contrast, the THMFP of the SE sample increased in week 1 and decreased to the level of the initial sample in week 3, followed by a decrease in week 4 and increases in weeks 5 and 6. The reason for the change in THMFP with sample aging was not investigated in this study. Because DOC concentration was measured only at the time of collection, it is not known whether the changes in THMFP were due to changes in DOC concentration or changes in the chemical structure of the DOC with aging. The amount of Cl<sub>2</sub> consumed did not correlate with sample aging time.



**Figure 2.** Trihalomethane formation potential of aliquots of samples AR and SE analyzed 0–6 weeks after sample collection. THMFP, trihalomethane formation potential.

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A parametric statistical test is not the best test for the small sample size of five; therefore, the Wilcoxon-Mann-Whitney Rank Sum Test, a nonparametric statistical test, was used to determine if there was a significant difference in THMFP concentration (Helsel and Hirsch, 1995). The AR aliquots were significantly different at the 95-percent confidence level from weeks 0 to 1. In contrast, the SE aliquots were different only at the 95-percent confidence interval from weeks 0 to 4 and 0 to 6.

Samples are analyzed as soon after collection as possible to minimize the effects of aging. In the USGS Sacramento Laboratory, samples are dosed as soon as the DOC has been measured, usually within 2 days of arrival.

### Effect of Residual Chlorine Concentration on Trihalomethane Formation Potential

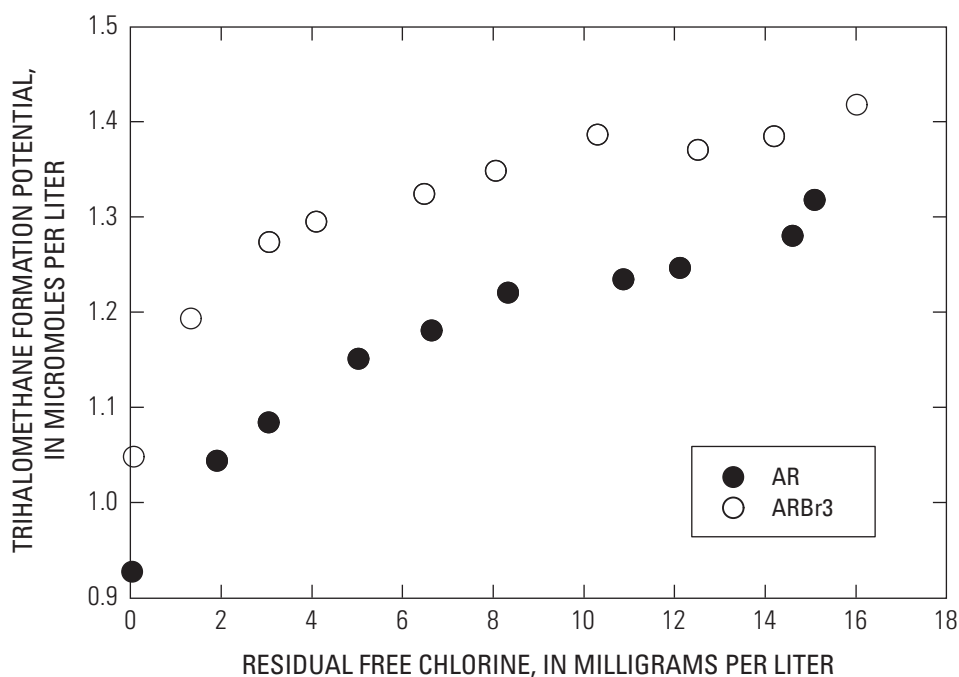
The method specifies that the residual-free  $\text{Cl}_2$  concentrations at the end of the 7-day incubation period must be 2 to 4 mg/L. This range was selected primarily because it is close to the residual  $\text{Cl}_2$  concentrations utilized in the drinking-water-treatment process (Krasner and Scimanti, 1994).

To test the dependence of THMFP on residual  $\text{Cl}_2$  concentration aliquots of the AR and ARBr3, samples were dosed to yield residual-free  $\text{Cl}_2$  concentrations ranging from 0.03 to 16 mg/L. The molar THMFP of AR and ARBr3 increased from 0.93 to 1.33  $\mu\text{mol/L}$  and from 1.05 to 1.42  $\mu\text{mol/L}$ , respectively, as the residual-free  $\text{Cl}_2$  concentration increased (fig. 3). THMFP was plotted in molar units rather

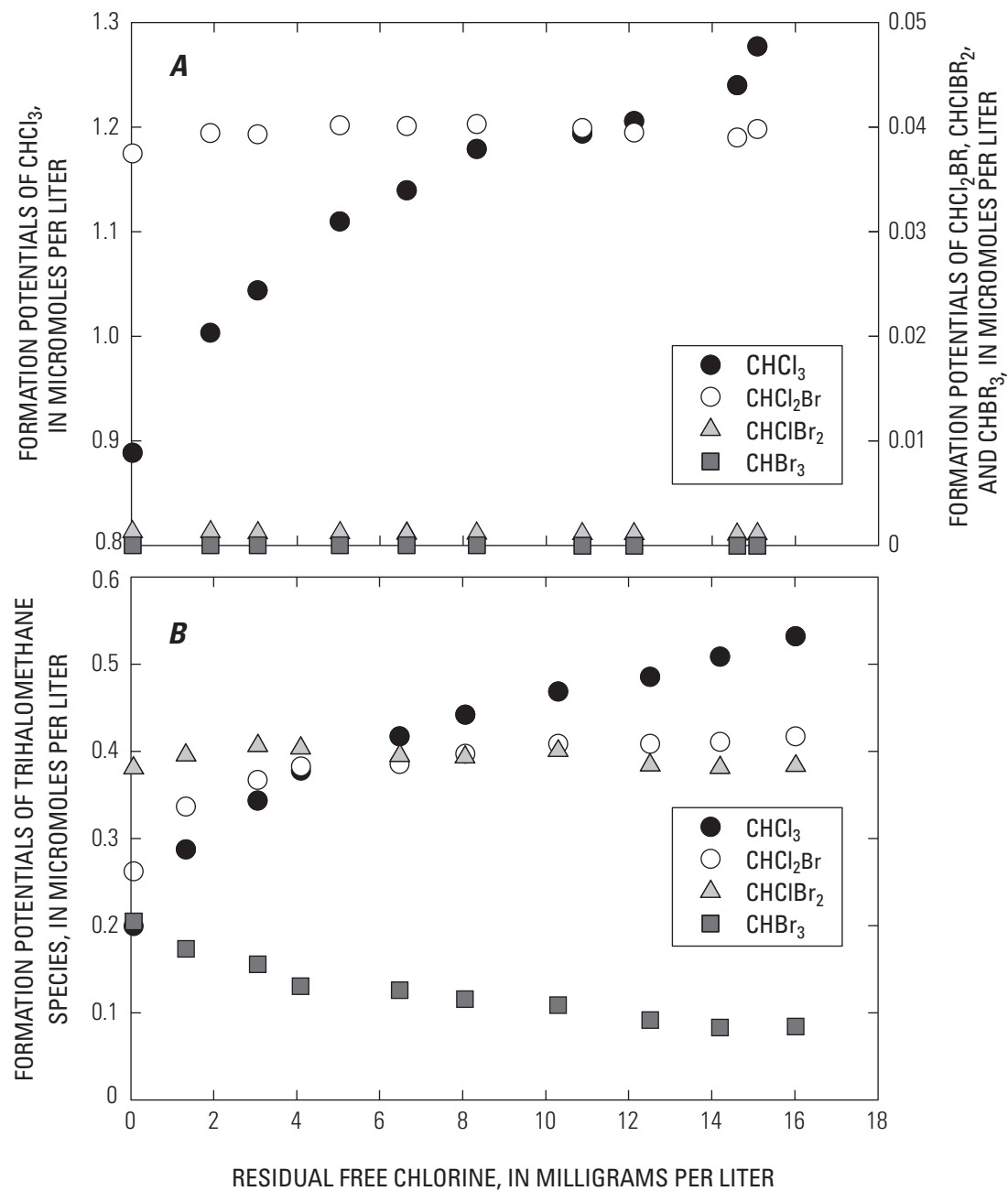
than mass units to unambiguously show the increase in THM formation. The atomic mass of Br is about twice that of Cl, so increases in the relative proportion of brominated species will result in increasing THMFP when expressed in mass units, even if the amount of THM formation remains constant. The rate of increase in THMFP was greatest at low residual  $\text{Cl}_2$  concentrations, but the THMFP value still had not leveled out to a constant value at the highest residual  $\text{Cl}_2$  concentrations investigated.

The increase in THMFP of sample AR entirely was due to an increase in  $\text{CHCl}_3$ ; concentrations of the brominated THM species remained essentially constant as residual  $\text{Cl}_2$  concentration increased (fig. 4A). This supports previous studies showing that oxidation of  $\text{Br}^-$  to HOBr (reaction #3) occurs very rapidly and that HOBr reacts much faster than HOCl to form THMs (Morris, 1978; Symons and others, 1993; Krasner and Scimanti, 1994).

Approximately 45 percent of  $\text{Br}^-$  added to sample ARBr3 was incorporated into the THMs; the remaining  $\text{Br}^-$  probably was incorporated into other DBPs. Samples AR and ARBr3 showed a similar rate of increase of THMFP with increasing  $\text{Cl}_2$  dose, but the THMFP of ARBr3 was 10 to 15 percent higher than the THMFP of AR (fig. 3). This difference is discussed in more detail in the section “Effect of Bromide Concentration on Trihalomethane Formation Potential.” The increase in THMFP as residual  $\text{Cl}_2$  concentration was observed as an increase in  $\text{CHCl}_3$  (fig. 4B). However,  $\text{CHCl}_2\text{Br}$  also increased, and was matched by a decrease in  $\text{CHBr}_3$ .



**Figure 3.** Trihalomethane formation potential of aliquots of samples AR and ARBr3 dosed to yield a range of residual-free chlorine concentrations at the end of the incubation period. THMFP, trihalomethane formation potential.



**Figure 4.** Formation potentials of chloroform, bromodichloromethane, dibromochloromethane, and bromoform in aliquots of samples **(A)** AR and **(B)** ARBr3 dosed to yield a range of residual-free chlorine concentrations at the end of the incubation period.  $\text{CHCl}_3$ , chloroform;  $\text{CHCl}_2\text{Br}$ , bromodichloromethane;  $\text{CHClBr}_2$ , dibromochloromethane;  $\text{CHBr}_3$ , bromoform.

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It is unfortunate that all of the the methods of analyses used for THMFP specify residual-free  $\text{Cl}_2$  concentrations of  $<5$  mg/L because that is the range where the THMFP is strongly dependant on residual- $\text{Cl}_2$  concentration (USEPA 510.1, 0.5 to 1.5 mg/L; Standard method, 3 to 5 mg/L; this method, 2 to 4 mg/L). For the AR sample, the error in THMFP introduced by this range is  $\pm 0.037$   $\mu\text{mol/L}$  ( $\pm 4.5$   $\mu\text{g/L}$ ).

### Effect of Dilution Method on Trihalomethane Formation Potential

Water samples with DOC concentrations greater than approximately 3 mg/L must be diluted with organic-free water to be analyzed by this method. Water samples with greater amounts of DOC generally form concentrations of THMs that are too high for the ECD to measure accurately. The split on the GC already is set at the maximum possible for the instrument, so dilution must be accomplished in other ways. The two dilution methods used are dilution with organic-free water prior to dosing and dilution with organic-free water after the samples are quenched. Dilutions using the Archon autosampler also were tested; however, they were not successful because the sample and dilution water apparently were not mixed thoroughly in the syringe before an aliquot was

transferred to the sparge tube which resulted in THM concentrations that greatly exceeded their expected values, based on the dilution factor.

To test the effect of dilution on the THMFP, the AR and ARBr3 samples were analyzed undiluted, diluted 50 percent after quenching, and diluted 50 percent before dosing (fig. 5). The samples diluted before dosing and after quenching had the same THMFP, and the diluted samples had significantly (p-value for two-sided test is 0.008) lower THMFP than did their respective undiluted samples (Wilcoxon-Mann-Whitney Rank-sum test for significance).

The effect of dilution on THMFP also was tested using sample TW1. This test was more rigorous because the TW1 sample had a higher DOC concentration than the AR sample and, thus, required more dilution. However, this sample could not be analyzed undiluted, so comparisons were made only between the different types of dilutions.

Six types of dilutions were prepared from the TW1 sample. This sample was diluted from an original DOC of 17 mg/L to make aliquots with DOC concentrations equal to 14, 11, 8, 5, and 2 mg/L. The dilutions were made by measuring the sample using a graduated cylinder in volumes of 16 to 123 mL. The graduated cylinders used for dilutions were purchased calibrated “to deliver” with a tolerance of 1 percent. Organic-free water was added to bring the final volume up to 150 mL

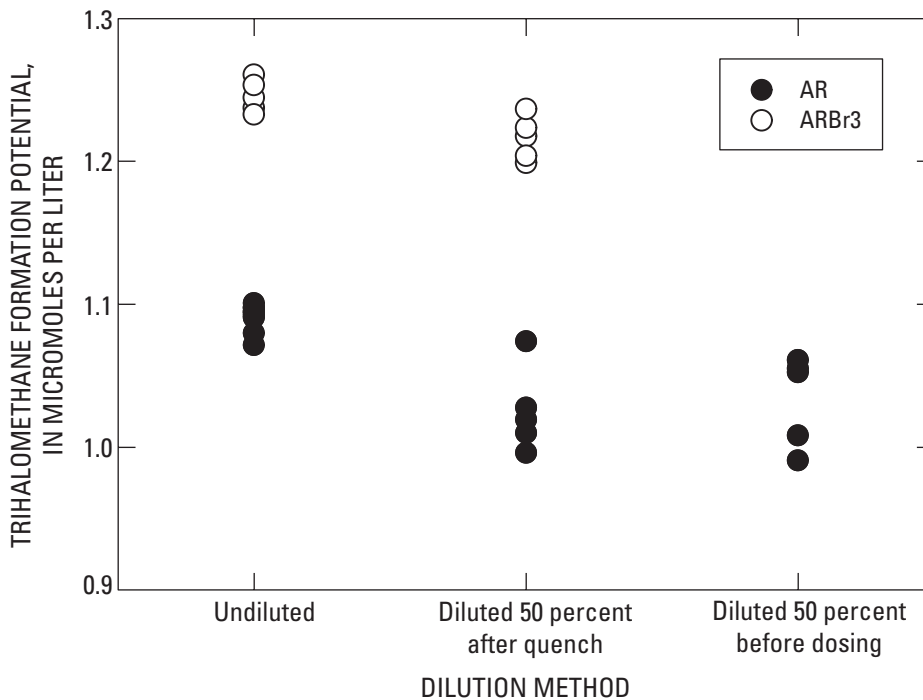


Figure 5. Trihalomethane formation potential of aliquots of samples AR and ARBr3 analyzed using different dilution methods. THMFP, trihalomethane formation potential.

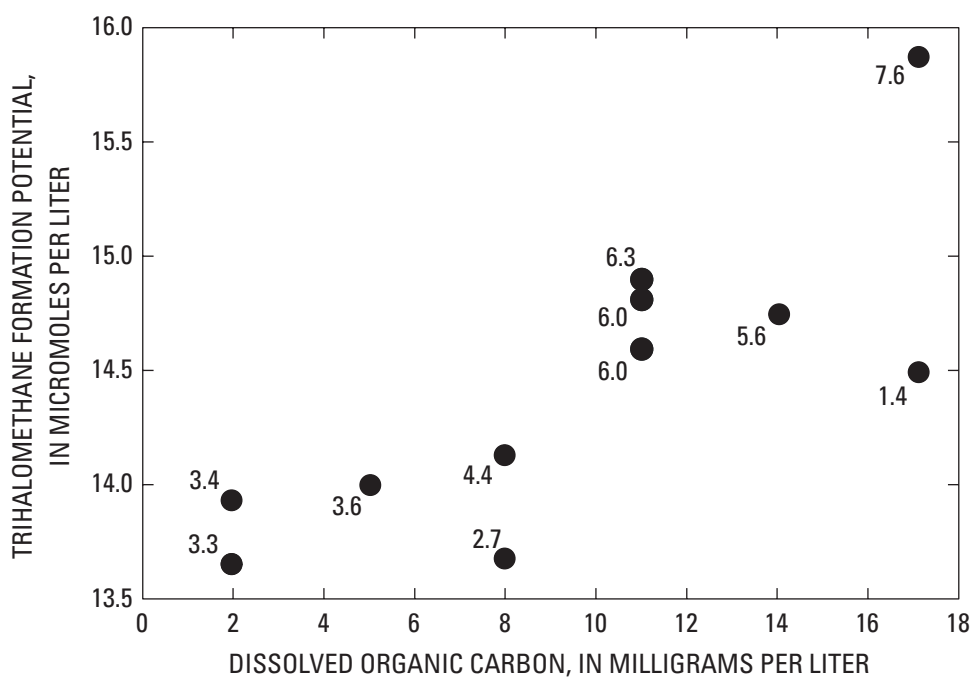
(or 140 mL for the 2 mg/L dilution) using a Wheaton bottle-top dispenser. The samples were dosed and incubated for 7 days. The samples were diluted again after the 7 days to a final DOC of about 1.5 mg/L to be certain that concentrations of all four THM species would be within the standard curve. The final dilutions were made using a pipettor to measure sample volumes from 4 to 20 mL into either a 50 or 100-mL volumetric flask. The 17- and 8-mg/L dilution samples were dosed with two concentrations of  $\text{Cl}_2$  (fig. 6) so that the effect of residual  $\text{Cl}_2$  concentration could be observed. The residual  $\text{Cl}_2$  for the 8-mg/L samples were 2.7 and 4.4 mg/L, and the residual  $\text{Cl}_2$  for the 17-mg/L samples were 1.4 and 7.6 mg/L.

The molar THMFP of sample TW1 increased with the DOC concentration at the time of dosing with  $\text{Cl}_2$  (fig. 6). The residual-free  $\text{Cl}_2$  values for each sample dilution have been included in the graph for comparison because increasing residual  $\text{Cl}_2$  also increases the THMFP (fig. 3). The THMFP of the aliquot dosed at a DOC concentration of 17 mg/L (undiluted) and with a residual-free  $\text{Cl}_2$  concentration of 1.4 mg/L was greater than the THMFP of all the aliquots dosed at a DOC concentration of 2, 5, and 8 mg/L, even though the latter aliquots had higher residual-free  $\text{Cl}_2$  concentrations.

The data show that making dilutions after quenching the samples lowers the measured THM concentration in the sample aliquot. THMFP of the undiluted AR and ARBr3 samples were approximately 5 percent higher than the THMFP of the AR and

ARBr3 samples diluted after quenching and the THMFP of the AR diluted before dosing (fig. 5). Similarly, the  $\text{CHClBr}_2$  concentrations in aliquots of the TW1 sample analyzed with no dilution after quenching were approximately 5 percent higher than the  $\text{CHClBr}_2$  concentrations in aliquots that had the same DOC concentration at the time of dosing, but that were diluted after quenching (not shown). This effect probably occurred with the other three THM species, but only the  $\text{CHClBr}_2$  concentrations were within the range of the standards for the undiluted and diluted aliquots. Making dilutions after quenching requires opening the sample vial and drawing the sample into a pipettor. The volatile THMs begin to escape from the sample during this process.

The observation that molar THMFP increases with the DOC concentration at the time of dosing with  $\text{Cl}_2$  has implications for the comparability of THMFP and STHMFP data from samples having different DOC concentrations. STHMFP was intended to be a measure of the intrinsic reactivity of the DOC in the sample and, therefore, to reflect chemical features of the DOC. The data in figure 6 suggest that the THMFP of sample TW1 decreases by approximately 0.8 mmol/L as the DOC concentration at the time of dosing decreases from 17 to 2 mg/L for a constant residual  $\text{Cl}_2$  concentration. At a residual  $\text{Cl}_2$  concentration of 4 mg/L, this decrease in THMFP corresponds to a decrease in STHMFP from 10.4 to 9.82 millimoles per mole (mmol/mol).



**Figure 6.** Trihalomethane formation potential of aliquots of sample TW1 that were diluted to different dissolved organic carbon concentrations before dosing with chlorine. Numbers next to points indicate residual-free chlorine concentrations, in milligrams per liter. THMFP, trihalomethane formation potential; DOC, dissolved organic carbon.



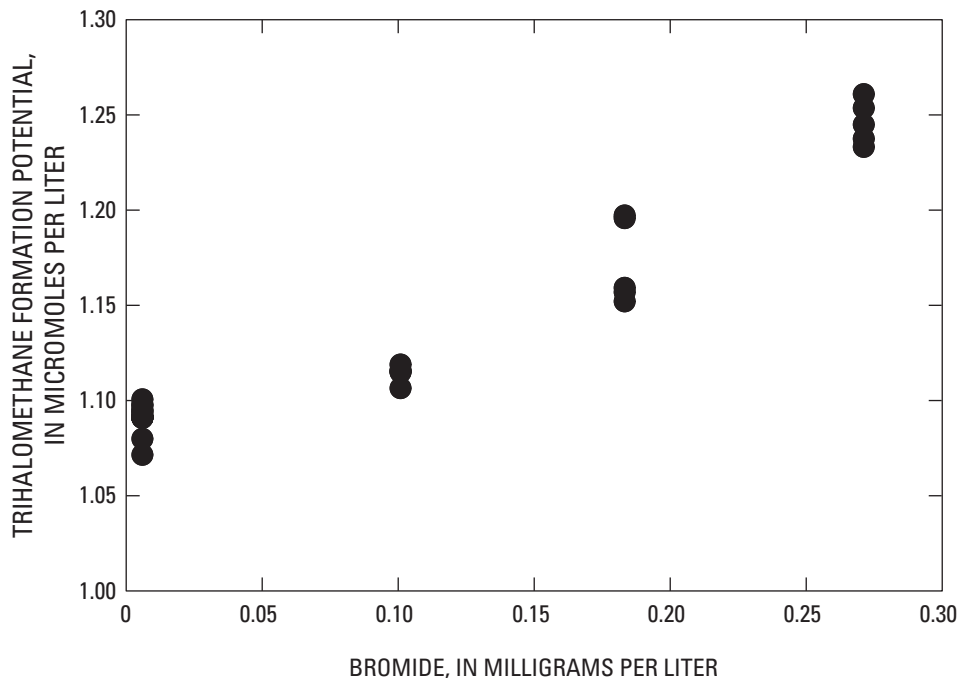
### Effect of Bromide Concentration on Trihalomethane Formation Potential

The effect of Br<sup>-</sup> concentration on THMFP was examined by comparing THMFP of the AR sample to aliquots spiked with NaBr. The presence of Br<sup>-</sup> in the water increased the molar THMFP in the AR samples. THMFP rose by 14 percent (fig. 7) and Cl<sub>2</sub> consumption rose 11 percent (not shown) as the Br<sup>-</sup> concentration increased from 0.006 to 0.27 mg/L. The increase in THMFP is not linear as Br<sup>-</sup> increases (fig. 7).

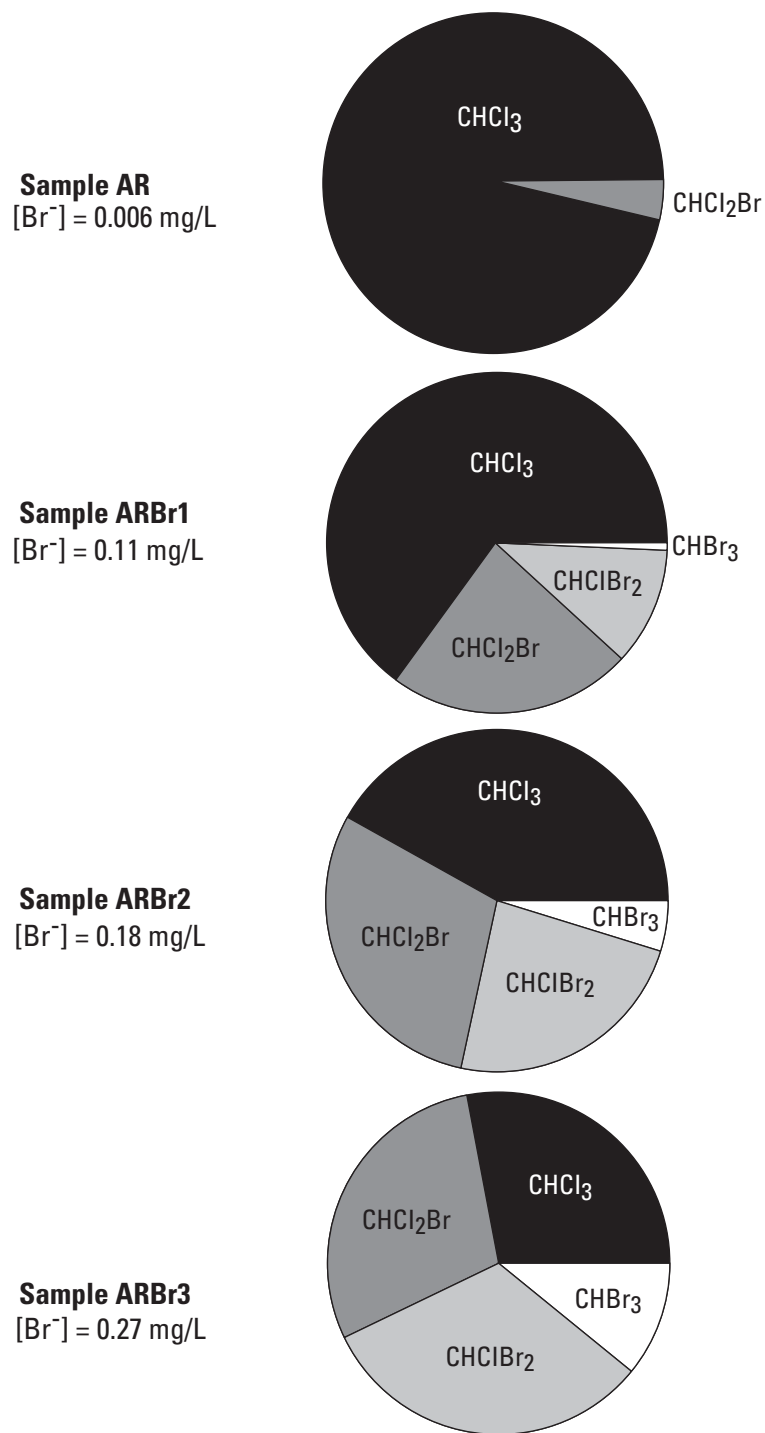
In addition to increasing THMFP, the proportions of the four THM species also changed as the Br<sup>-</sup> concentration increased (fig. 8). CHCl<sub>2</sub>Br was the dominant brominated species in the ARBr1 sample; CHClBr<sub>2</sub> steadily increased in proportion to the decrease in CHCl<sub>3</sub> and was the dominant brominated species in the ARBr3 sample; CHBr<sub>3</sub> also increased steadily in proportion from 0 to 16 percent of the total THMFP as the concentration of Br<sup>-</sup> increased for ARBr1 to ARBr3. These results are in agreement with previous studies (Symons and others, 1993; Chang and others, 2001). Similar experiments utilizing a greater range of Br<sup>-</sup> concentrations showed that the proportions of CHCl<sub>3</sub> and CHCl<sub>2</sub>Br declined with increasing Br<sup>-</sup> concentration, the proportion of CHClBr<sub>2</sub> increased and then decreased, and the proportion of CHBr<sub>3</sub>

increased (Symons and others, 1993; Chang and others, 2001). Symons and others (1993) and Chang and others (2001) concluded that the ratio of the concentrations of free Cl<sub>2</sub> and Br<sup>-</sup> (Cl<sub>2</sub>/Br<sup>-</sup>) controls the speciation of the THMs in water samples that contain Br<sup>-</sup>. Because HOBr reacts much faster than HOCl, the THM speciation also will depend on the ratio of the concentrations of Br<sup>-</sup> and DOC (Br<sup>-</sup>/DOC).

The dependence of THMFP on Br<sup>-</sup> concentration may explain the different conclusions concerning the effect of dilution on THMFP determined during this study compared with that determined in the study by Krasner and Scimanti (1994). Krasner and Scimanti (1994) suggested that THMFP is independent of sample dilution, that is, THMFP does not change with DOC concentration at the time of dosing. Our results contradict those of Krasner and Scimanti. A likely explanation for this contradiction is that Krasner and Scimanti (1994) made their sample dilution aliquots using dilution water containing a concentration of Br<sup>-</sup> equal to that in the undiluted sample whereas we made samples using dilution water containing no Br<sup>-</sup>. However, although the effects on THMFP of increasing Br<sup>-</sup> concentration and of decreasing DOC at the time of dosing are opposite in direction, both effects are nonlinear and, thus, may not necessarily be of equal magnitude in a given water sample.



**Figure 7.** Trihalomethane formation potential of samples AR, ARBr1, ARBr2, and ARBr3 dosed to yield a constant residual-free chlorine concentration. THMFP, trihalomethane formation potential.



**Figure 8.** Proportions of chloroform, bromodichloromethane, dibromochloromethane, and bromoform formation potentials in samples AR, ARBr1, ARBr2, and ARBr3 dosed to yield a constant residual-free chlorine concentration.

## Quality-Control Practices

### Analytical Sequence

The analytical sequence follows the same general pattern for each run. One or two instrument blanks are analyzed first, followed by the calibration standards. An instrument blank is run next in order to monitor carry-over from the highest standard. Then a set of as many as 10 samples is run. After each set of samples is run, two calibration verification standards are analyzed to verify the calibration. Another instrument blank is run after these calibration verification standards. Sets composed of samples, full procedural blanks, duplicates, calibration verification standards, and instrument blanks are run until all the samples have been analyzed. The initial calibration curve may be used for as much as 1 week, providing that gas flows have not been changed.

### Blanks

Two types of blanks are analyzed for the THMFP method, instrument blanks and full procedural blanks. Instrument blanks consist of organic-free water analyzed without dosing or quenching and are used to test for THM contamination in the organic-free water, the surrogate solution, and the purge and trap and GC instruments. Instrument blanks are analyzed at the start of a run and between sets of samples within a run. The measured THM concentration in the instrument blank must be less than half the concentration in the lowest calibration standard. This corresponds to maximum permissible concentrations in the instrument blanks of 0.08- $\mu\text{g/L}$   $\text{CHCl}_3$  and 0.02- $\mu\text{g/L}$   $\text{CHCl}_2\text{Br}$ ,  $\text{CHClBr}_2$ , or  $\text{CHBr}_3$ . Instrument blanks also may be analyzed after the analysis for samples suspected of having concentrations of some THM species that are greater than the concentrations in the highest standard. In this case, the instrument blank serves to prevent contamination of the next sample by removing the compounds that may still be present in the purge and trap or GC column.

If the instrument blanks analyzed at the start of a run or between sets of samples within a run have higher than permitted concentrations of THMs, corrective actions must be taken. To determine the source of the problem, first, an instrument blank is analyzed without the surrogate injection and compared with those analyzed with the surrogate injection. If the surrogate injection seems to be the source of the contamination, it is prepared again. Second, determine if there is carry-over of THMs from one sample to the next; carry-over indicates that either the trap has deteriorated, and thus the THMs are not desorbed efficiently from it, or a cold spot exists in the Tekmar concentrator unit or in the transfer line from the

unit to the GC injection port. The trap may be replaced, and the operation of the heating units is checked. Third, if the source of the contamination is not found in the surrogate solution, the trap, or the instruments, then the resin tanks in the organic-free water Picotech system may be the source and should be replaced.

Full procedural blanks consist of organic-free water that is dosed, incubated, and quenched like a sample. It is dosed to achieve a free- $\text{Cl}_2$  concentration of 3 mg/L. The full procedural blank is used to test for DOC contamination of the organic-free water and the overall cleanliness of sample handling during the dosing and quenching process. If the concentration of  $\text{CHCl}_3$  in the full procedural blank is greater than 1.2  $\mu\text{g/L}$ , then corrective actions must be taken. The organic-free water system may require maintenance and the laboratory glassware cleaning procedures may need to be reviewed.

The THMFP of a full procedural blank is a more sensitive method for measuring contamination of the organic-free water with natural DOC than is direct measurement of DOC concentration. Assuming that natural DOC forms between 1 and 20 mmols of  $\text{CHCl}_3$  per mole of DOC (Oliver and Thurman, 1983; Reckhow and others, 1990; and Fram and others, 1999), a  $\text{CHCl}_3$  concentration of 1.2  $\mu\text{g/L}$  corresponds to a DOC concentration of 0.12 to 0.006 mg/L. For comparison, the method detection limit for analysis of DOC in the USGS Sacramento Laboratory is 0.12 mg/L (Bird and others, 2003). However, contamination with organic solvents that do not react with  $\text{Cl}_2$  to form THMs, such as methanol, is not detected by measuring the THMFP of the organic-free water, therefore, the organic-free water DOC also is monitored by direct analysis of DOC concentration.

### Calibration Verification Standards

Calibration verification standards are used to verify that the calibration is accurate through the entire run. They are prepared by the same method as the calibration standards. A mid-level (63  $\mu\text{g/L}$  of  $\text{CHCl}_3$ ) and a low-level (24  $\mu\text{g/L}$  of  $\text{CHCl}_3$ ) calibration verification standard are run after every set of 10 sample injections. The measured concentrations are compared with the calculated concentrations (eq. 8).

$$\text{difference} = \frac{|C_{\text{meas}} - C_{\text{calc}}|}{C_{\text{calc}}} \times 100 \quad (8)$$

where

$C_{\text{meas}}$  is the measured concentration, and  
 $C_{\text{calc}}$  is the calculated concentration.

Acceptable difference values are 5 percent for all four THM species in the mid-level calibration verification standard,

5 percent for  $\text{CHCl}_2\text{Br}$  and  $\text{CHClBr}_2$  in the low-level calibration verification standard, and 10 percent for  $\text{CHCl}_3$  and  $\text{CHBr}_3$  in the low-level calibration verification standard. These criteria are rarely exceeded, and the most common reason for unacceptable values is operator error (for example, incorrect labeling of vials). If difference values are consistently unacceptable within a run, a new standard curve must be analyzed.

Peak area counts for the five analytes (the four THM species and the surrogate) were tabulated and compared with peak area counts from previous analyses of the same calibration verification standard to monitor the inter-run, long-term performance of the trap. If the peak area for any of the analytes is more than 20 percent different than the peak area of the analyte when the trap was first installed, then the trap has degraded and must be replaced. Since degradation of the trap will affect results for all samples and standards, peak areas, rather than calculated concentrations, are monitored.

### Surrogate Standard

The surrogate,  $\text{CH}_2\text{ClCHBrCH}_3$ , is added to every sample automatically by the Archon auto-sampler to monitor the instrument stability during a run. The measured peak area for the surrogate from each injection of a run is tabulated. The percent RSD (eq. 5) must be less than 2 percent or the instrument is tested to find leaks. If there are no leaks, then matrix effects in individual samples must be considered the cause.

### Retention Time and Peak Shape for Analytes

The retention times for the analytes in all standards, samples, and blanks are monitored. The EZChrom software is configured with a retention time window of  $\pm 0.2$  minutes. Because the column flow rate is set manually at the start of each run, the retention times for the analytes shift slightly between runs.

The chromatograms are monitored for appearance of additional peaks. THMs are the only halogenated volatile organic compounds (VOCs) produced in large quantities during chlorination of natural DOC. Thus, it is extremely rare that additional peaks that could interfere with the analyte peaks are present in the chromatograms. However, additional peaks may occur in samples that have been contaminated with anthropogenic halogenated VOCs. In this case, samples are analyzed for THM concentrations in addition to THMFP. The

chromatograms for the chlorinated and unchlorinated aliquots are compared with each other and with published chromatograms of halogenated VOCs analyzed under similar conditions to estimate the identities of the unknown peaks.

The shapes of the peaks also are monitored. If the peaks become broader, asymmetric, or acquire tails, then the GC requires maintenance. The most common cause of peak shape problems is obstruction of the ECD make-up gas flow. If maintenance of the ECD detector does not improve the peak shapes, then the GC column may need replacement.

### Duplicate Samples

Two full THMFP procedure duplicates are prepared for every 10 samples. The THMFP of the duplicates are compared (eq. 9). The reproducibility of the THMFP procedure duplicates ( $C_{\text{calc}}$ ) is reported as the percent difference between the two duplicates and is calculated as follows:

$$C_{\text{calc}} = \frac{|C_A - C_B|}{(C_A + C_B)/2} \times 100 \quad (9)$$

where

$C_A$  and  $C_B$  are the concentrations in the two duplicates.

If the difference value is greater than 5 percent, then the accuracy of the dilution procedure is examined.

### Instrument Maintenance

Instrument maintenance is performed, as needed, on the Archon autosampler, Tekmar concentrator, and the GC. The syringe barrel and plunger that draws up the sample from the vial must be cleaned or replaced approximately every 6 months, depending on the sample matrix and sample load. Otherwise, the Archon has been very reliable and needs minimal care. The sparge tube on the Tekmar concentrator is changed more frequently, approximately every 2 months. The trap is replaced approximately yearly, depending on how much the instrument has been used. The GC column lasts several years providing that column flow is maintained continuously. The ECD is baked out whenever column flow is interrupted or when the ECD baseline is greater than 150 Hz.

## Summary

This report provides a description of the analytical method and quality-control practices for the determination of trihalomethane formation potential (THMFP) used by the U.S. Geological Survey California District, Sacramento Laboratory. The THMFP of the dissolved organic carbon (DOC) in a water sample is measured by dosing filtered water samples with chlorine ( $\text{Cl}_2$ ) from sodium hypochlorite ( $\text{NaOCl}$ ) under specified conditions of pH, temperature, incubation time, and darkness, and then analyzing the resulting trihalomethanes (THM) by purge and trap/gas chromatography (GC). The appropriate dose of  $\text{Cl}_2$  is calculated from the DOC and ammonia-nitrogen ( $\text{NH}_3\text{-N}$ ) concentrations in the sample and is sufficient to leave a residual-free  $\text{Cl}_2$  concentration at the end of the incubation period of 2 to 4 mg/L. Samples are buffered to pH 8.3 and incubated in the dark at 25°C for 7 days. At the end of the 7 days, the pH and residual-free  $\text{Cl}_2$  are measured and the samples are quenched with sodium sulfite solution to neutralize any remaining free  $\text{Cl}_2$ . The THMs are purged from the sample matrix by bubbling nitrogen through an aliquot of the sample. The THMs are collected on an adsorbent trap and then desorbed thermally into the inlet of a GC. The four THM species chloroform ( $\text{CHCl}_3$ ), bromodichloromethane ( $\text{CHCl}_2\text{Br}$ ), dibromochloromethane ( $\text{CHClBr}_2$ ), and bromoform ( $\text{CHBr}_3$ ) are separated by capillary GC and detected by an electron capture detector.

A number of tests were performed on three different natural water samples to validate the method. The analytical precision is estimated to be 1 percent. The THMFP increases with the ages of the samples; therefore, samples should be analyzed immediately after collection to minimize this effect. The THMFP increased as the residual  $\text{Cl}_2$  concentration increased over the range of concentrations tested. It is unfortunate that all of the THMFP analyses methods specify residual-free  $\text{Cl}_2$  concentrations of <5mg/L because that is the range where the THMFP is strongly dependant on residual- $\text{Cl}_2$  concentration (USEPA 510.1, 0.5 to 1.5 mg/L; Standard method, 3 to 5 mg/L; this method, 2 to 4 mg/L). Samples with DOC concentrations greater than 3 mg/L must be diluted to keep the concentrations of the resulting THM species within the range of the standard curves. However, THMFP decreased with the DOC concentration in samples that were diluted at the time of dosing. THM concentrations also decreased when sample vials were opened to make dilutions after quenching. THMFP increased with the concentration of  $\text{Br}^-$  in the sample and the proportions of the four THM species changed systematically.

Quality-control practices are used to assure that a high level of precision and accuracy of the THMFP analyses is

maintained. Quality-control practices include regular analysis of calibration verification standards, duplicate samples and analysis of a surrogate compound, and two types of blanks. Stringent criteria for acceptable results for the quality-control samples and for instrument calibration curves are maintained. Instrument maintenance and corrective actions are undertaken promptly, as needed.

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