Measurement of Trihalomethanes and Methyl Tertiary-Butyl Ether in Tap Water Using Solid-Phase Microextraction GC–MS*

Frederick L. Cardinali[1,†], David L. Ashley[1], John C. Morrow[1], Deborah M. Moll[2], and **Benjamin C. Blount[1]**

[1]Division of Laboratory Sciences, National Center for Environmental Health, Centers for Disease Control and Prevention, Atlanta, GA 30341 and [2]Division of Environmental Hazards and Health Effects, National Center for Environmental Health, Centers for Disease Control and Prevention, Atlanta, GA 30333

Abstract

The prevalence of water disinfection byproducts in drinking water supplies has raised concerns about possible health effects from chronic exposure to these compounds. To support studies exploring the relation between exposure to trihalomethanes (THMs) and health effects, we have developed an automated analytical method using headspace solid-phase microextraction coupled with capillary gas chromatography and mass spectrometry. This method quantitates trace levels of THMs (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) and methyl tertiary-butyl ether in tap water. Detection limits of less than 100 ng/L for all analytes and linear ranges of three orders of magnitude are adequate for measuring the THMs in tap water samples tested from across the United States. THMs are stable for extended periods in tap water samples after quenching of residual chlorine and buffering to pH 6.5, thus enabling larger epidemiologic field studies with simplified sample collection protocols.

Introduction

The quality of household tap water is a public health issue of increasing concern. Potentially harmful chemicals in tap water can originate either from contaminated source water [e.g., methyl tertiary-butyl ether (MTBE) leaking into ground water] or be formed as byproducts of the water disinfection process. Although water disinfection inactivates potentially pathogenic microorganisms, the process can lead to the formation of byproducts such as trihalomethanes (THMs). THMs are halogenated organic compounds formed by the reaction of chlorine with naturally occurring organic matter in the water. Chloroform, bromodichloromethane (BDCM), dibromochloromethane (DBCM), and bromoform are the primary THMs found in United States (U.S.) tap water. Significant exposure to these compounds results from ordinary daily activities such as bathing and showering (1,2). Long-term exposure to water disinfection byproducts, including THMs, may increase risk for bladder cancer (3), spontaneous abortion (4), and birth defects (5,6). The widespread and ongoing exposure to these potentially harmful chemicals merits further research.

Measuring the internal dose is often the best method for assessing human exposure to environmental toxicants (7). To better assess human exposure, we developed methods for measuring THMs and MTBE in human blood (8). Tap water probably is the most significant nonoccupational source of exposure to THMs. Assessment of the role of tap water as an exposure medium required the development of new methods of sample collection and analysis because current methods for measuring THMs and MTBE in water were not adequately sensitive and rapid. U.S. Environmental Protection Agency (EPA) methods 502 (9), 524 (10), and 551 (11) define the analysis of volatile constituents of water for regulatory purposes. These EPA methods specify restrictions on water sample storage time and temperature and preservation techniques. Additionally, EPA methods 502 and 524 use purge-and-trap, and EPA method 551 uses liquid–liquid extraction for recovery of a variety of chemicals from water; these extraction techniques can be cumbersome and can lead to reduced sample throughput. Furthermore, MTBE is the recommended primary extraction solvent for EPA method 551 (although pentane can be used), which limits its usefulness for measurement of MTBE in tap water samples. For our work, assessing the role of tap water as an exposure medium for THMs and MTBE, we desired a simple, rapid, and sensitive method. We also wished to investigate alternative sample preservation techniques and the effects of elevated temperature on the integrity of the THMs and MTBE in tap water samples to determine whether we could implement a more flexible sample collection and storage protocol than those specified in the EPA methods for regulatory compliance.

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† Author to whom correspondence should be addressed: Frederick L. Cardinali, 4770 Buford Hwy MSF47, Atlanta, GA 30341. Email: fcardinali@cdc.gov.

Solid-phase microextraction (SPME) offers a simpler extraction technique than purge-and-trap and liquid–liquid extraction. Stack et al. (12) used SPME in conjunction with gas chromatography mass spectrometry (GC–MS) to analyze high levels of THMs in tap and swimming pool water. The low µg/L limits of detection (LODs) of this method were not adequate for quantitating THMs in many tap water samples. Cho et al. (13) used SPME in conjunction with a GC equipped with an electron-capture detector (ECD) to analyze THMs in tap water. Although this method has detection limits of between 0.005 and 0.01 µg/L, the lack of specificity inherent in an ECD, as well as the inability to use this detector to identify unknowns, prevented us from using this method for our research. Therefore, we developed an improved SPME–GC–MS method to quantitate trace levels of THMs and MTBE in tap water. Application of this method will help to support studies exploring the relation between exposure to THMs/MTBE and health effects.

Experimental

Materials

Purge-and-trap-grade methanol purchased from Burdick and Jackson (Muskegon, MI) was used to prepare all standards and rinse glassware. High-performance liquid chromatography (HPLC)-grade water was purchased from J.T. Baker (Phillipsburg, NJ). Because the level of THMs, especially chloroform, varies widely between production lots, a sufficient quantity of water was purchased so that the same lot was used to prepare all solutions, blanks, standards, and quality control (QC) material during these experiments. Residual THMs in this water were removed by helium sparging and distillation (14). Sodium hydrogen phosphate (98%) and sodium dihydrogen phosphate (99%) were purchased from Aldrich (Milwaukee, WI). Sodium thiosulfate was purchased from Chem Service (West Chester, PA). Stainless steel needles (18 gauge, Luer-Lok) were purchased from Becton Dickinson (Franklin Lakes, NJ). Reaction vials (10 mL, serum type), septa (20 mm, Teflon-faced–silicone), and seals (aluminum, open center) were purchased from Supelco (Bellefonte, PA).

Standards

Chloroform, BDCM, DBCM, bromoform, and MTBE were purchased as neat compounds (> 99%, Supelco) in flame-sealed ampoules and stored at –20ºC to minimize degradation. Stable isotope-labeled analogues chloroform ($^{13}C_1$), BDCM ($^{13}C_1$), DBCM ($^{13}C_1$), bromoform ($^{13}C_1$), and MTBE ($^{2}H_{12}$) were purchased as neat compounds (> 99% chemical and isotopic purity, Cambridge Isotope Labs, Andover, MA) in flame-sealed ampoules and stored at –20ºC. Standards and labeled analogues were prepared from neat chemicals and diluted with methanol (purge-and-trap grade) to intermediate stock solution concentrations. These stock solutions were sealed in glass ampoules and stored at –60ºC. On the day of use, stock solutions of standards were further diluted in helium-sparged/distilled water (14). Solutions of labeled analogues were prepared by further dilution with methanol (purge-and-trap grade), and 40.0 µL was added to each blank, standard, unknown, or QC sample being analyzed. Positive displacement pipettors and glass capillary tips were used for all liquid transfers in the µL range (15).

Buffer-quench solution

Tap water samples typically contain sufficient chlorine residual to discourage the growth of potentially pathogenic microorganisms. This chlorine residual can react further with other sample components to alter the levels of THMs during sample shipment and storage. To minimize any artifactual formation or loss of THMs or MTBE, all water samples were buffered to pH 6.5 and residual chlorine levels quenched using a buffer-quench solution. The buffer-quench solution is based on a previously described phosphate buffer-quench solution (16), except for the use of sodium thiosulfate as the dechlorinating agent. The buffer-quench solution was prepared by adding sodium dihydrogen phosphate (3.00 g), sodium hydrogen phosphate (3.60 g), and sodium thiosulfate (0.40 g) in HPLC-grade water to a final volume of 25.0 mL. The buffer-quench solution was prepared fresh and aliquoted (125 µL) into each vial before tap water sample collection. The use of buffer-quench solution also offered a safer alternative to the concentrated acid used for stabilizing samples as part of EPA methods 502 and 524.

The stability of buffer-quench solution was assessed to insure that an appropriate shelf life was assigned to water-collection vials awaiting sampling in the field. These vials contained a small volume of buffer-quench solution; if this solution lost its efficacy for quenching residual chlorine, then samples collected into these vials would be rejected. Therefore, we periodically sampled laboratory tap water of known chlorine residual (0.6–0.8 mg/L) using water vials that had been prepared with buffer-quench solution (125 µL) previously. After filling with 12 mL of tap water, the initial concentration of the sodium thiosulfate was 167 mg/L. This large molar excess of sodium thiosulfate ensured that even if substantial degradation accrued over time, enough sodium sulfate would remain to neutralize any chlorine residual present in the tap water samples. The water vials were stored at room temperature (23–25ºC) for up to one year. We found no loss in the ability of the buffer-quench solution to quench residual chlorine in tap water, even after the sample collection vials had been stored for one year. On the basis of these results, we assigned buffer-quench solution (and therefore prepared water collection vials) a shelf life of one year.

Water collection vial preparation

Water samples were collected into borosilicate glass vials (12 mL, screw cap, Wheaton, Millville, NJ) that were prerinsed with methanol and heated overnight at 150ºC in a vacuum oven (~100 kPa). After the oven cooled to room temperature, ultrahigh-purity nitrogen was used to equilibrate the oven to atmospheric pressure. After adding buffer-quench solution, the vial was sealed with an open-top cap (15–425 black plastic, Wheaton) containing a Teflon-faced septum (Wheaton). To minimize the risk of breakage, the vial was placed inside a polypropylene tube (50 mL conical, Becton Dickinson, Franklin Lakes, NJ). However, use of these polypropylene tubes can lead to MTBE contamination of the sample and is, thus, not recommended. Water samples were collected from nonaerated, cold water tap. Following a 3-min cold-water flush, the tap water flow was decreased to a trickle, the

water vial filled to the top, the vial immediately sealed, and the sample stored in the refrigerator.

Water sample collection QC

We assessed the integrity of field-collected water samples using a number of QC tests. Upon receipt, sample vials were inspected for air bubble volume. A properly collected sample contained little air into which the volatile analytes could partition. For the 12-mL sample vials used, air bubbles of up to 2 mL did not lead to significant loss of THMs and MTBE ($\leq$ 5% loss). Samples with air bubbles of > 2 mL were rejected because of analyte loss into this headspace.

We evaluated the efficacy of the buffer-quench solution by measuring pH and free chlorine levels in the water samples. Approximately a 0.3-mL sample was transferred from the sample using a Pasteur pipette and applied to a pH indicator strip (EM-Reagents, Gibbstown, NJ) and allowed to develop for 10 min. Acceptable samples ranged from pH 6 to 8. We rejected samples with pH values outside this range because of concerns about analyte stability during transit and storage. A free chlorine test strip (Industrial Test Systems, Rock Hill, SC) was placed in the vial previously tested for pH and gently agitated for 45 s. The test strip was subsequently removed and visually inspected for color change indicative of free chlorine. Any trace of free chlorine resulted in sample rejection because of possible artifactual formation/loss of THMs during sample transit and storage.

MTBE contamination can occur if a water sample contacts certain types of plastics. Specifically, the polypropylene 50-mL tubes included as sample transit containers proved to be a potential source of contamination if used improperly. If tap water was collected into this polypropylene tube and then decanted into the water vial, MTBE and other components from the plastic contaminated the water sample. Because of this potential contamination, we do not recommend the use of these polypropylene tubes as sample transit containers.

Water sample analysis

The tap water vials were removed from refrigerated storage (8–10ºC) and allowed to equilibrate to room temperature before analysis. Immediately after removing the vial cap, we removed the water (5.0 mL) using a precleaned gas-tight syringe (10 mL, glass, Unimetrics, Shorewood, IL) and transferred it into a 10-mL SPME headspace vial. Labeled analogue solution (40.0 µL) was added to the sample using a positive displacement pipettor (VWR Scientific, West Chester, PA), and the SPME vial immediately was crimp-sealed using a Teflon-lined septum. Blanks, standards, and QC samples were all processed in a similar manner. Samples were prepared and analyzed in daily batches of 22 unknowns, 7 calibrators, 2 QC, and 1 blank.

Instrumentation

The high-throughput SPME-GC–MS method was developed on a ThermoFinnigan TraceMS (ThermoFinnigan, Austin, TX) attached to a Trace 2000 GC equipped with a split/splitless injector and operated in the splitless mode. An SPME injection port liner was used (0.75-mm i.d.). A cryo-trap (model 961, Scientific Instrument Services, Ringoes, NJ) cryofocused volatile compounds at the head of the GC column. With liquid nitrogen as the coolant, the cryo-trap was maintained at –55ºC for the first 3 min of analysis. The trap was then heated ballistically to 220ºC to begin chromatographic separation on a VRX capillary column (20-m × 0.18-mm i.d. × 1.0-µm film, Restek, Bellefonte, PA). The GC oven was equipped with a liquid nitrogen coolant valve to enable a subambient initial oven temperature (20ºC). Helium (UHP grade, 99.999%, Airgas South, Atlanta, GA) served as the carrier gas with a constant flow of 1.5 mL/min. The GC was held at an initial temperature (20ºC) for 3 min, followed by a linear thermal gradient of 30ºC/min to 200ºC. Automated sampling was done using a CombiPAL autosampler (CTC Analytics AG, Zwingen, Switzerland) equipped with a 75-µm carboxen/polydimethylsiloxane (PDMS) SPME fiber assembly (Supelco, Bellefonte, PA). The carboxen/PDMS fiber is very robust. A thousand or more samples are routinely run per fiber. Before each sample set was run, the carboxen/PDMS SPME fiber was preconditioned by exposing it for 6 min to the headspace above an SPME vial containing 5 mL helium-purged distilled water. Subsequently, the fiber was inserted into the GC inlet, which was set to split mode and desorbed for 30 min. Any desorbed chemicals were cleared from the GC column by maintaining the GC oven at 200ºC during this initial instrument preparation procedure.

After preparation, samples were queued in a Peltier cooled rack (15 $\pm$ 1ºC) before analysis. We began sample analysis by moving the active sample to a heated agitator station (50ºC). Following preincubation (10 s), the SPME fiber was inserted into the vial headspace and the sample extracted (8 min, 500 rpm). This nonequilibrium extraction did not compromise quantitation because stable isotope analogues compensate for variability in extraction efficiency. The extraction time of 8 min was selected to balance the need for maximum analyte extraction against adsorbing too much water vapor from the headspace. Excessive water vapor causes problems because the water vapor can coelute with MTBE. This results in suppression of the MTBE signal and poor reproducibility. The fiber was promptly desorbed by insertion into the hot GC inlet (200ºC). The SPME fiber remained in the GC inlet for the remainder of the GC run to ensure complete analyte desorption and minimize contamination from laboratory air.

The MS was equipped with an electron-impact source and run in the selected ion monitoring (SIM) mode (Table I). As each analyte eluted from

Table I. MS Parameters for the Analysis of THMs and MTBE in Household Tap Water

Compound (label configuration)	Labeled standard (*m/z*)	Analyte mass (*m/z*)	Confirmation mass (*m/z*)	Dwell time per mass (ms)	Photomultiplier detector setting (V)
MTBE ($^2H_{12}$)	82	73	74	50	300
Chloroform (^{13}C)	84	83	85	50	225
BDCM (^{13}C)	84	83	85	50	300
DBCM (^{13}C)	130	129	127	50	300
Bromoform (^{13}C)	174	173	171	50	350

the GC column; the MS measured three ions, one each for quantitation, confirmation, and the labeled analogue. Quantitation ions were selected as the most abundant ion in the MS that did not compromise the specificity of the analysis. We determined the retention time for each compound by analyzing known standards in full-scan mode and adjusting the SIM windows accordingly. The cycle time per sample was 21 min.

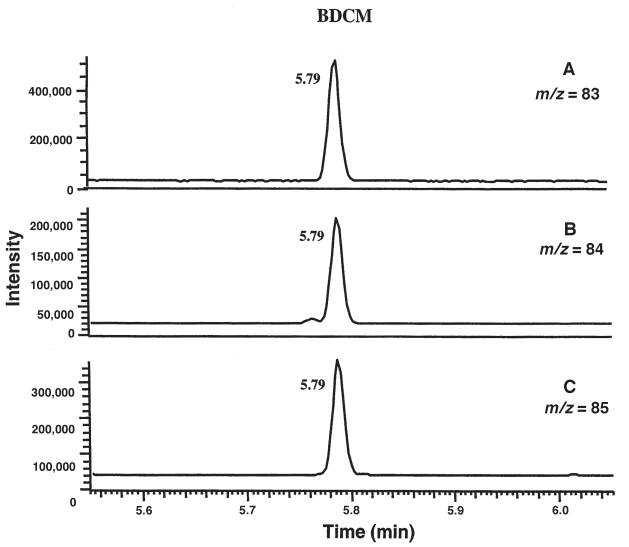

Figure 1. SIM trace resulting from GC of analyte (*m/z* 83), confirmation (*m/z* 85), and labeled analogue (*m/z* 84) ions for BDCM in tap water.

Table II. Assay Precision and Theoretical Concentration vs. Mean Concentration of QC Pools

Analyte	QC pool	Analyte level (µg/L)	CV*	LOD (µg/L)	Recovery†
BDCM	High QC	11.30	4.0%	0.05	94%
BDCM	Low QC	1.25	3.8%	0.05	96%
Bromoform	High QC	7.11	3.6%	0.10	95%
Bromoform	Low QC	0.81	4.3%	0.10	101%
Chloroform	High QC	28.31	4.0%	0.12	94%
Chloroform	Low QC	3.09	4.5%	0.12	95%
DBCM	High QC	13.77	3.8%	0.10	94%
DBCM	Low QC	1.52	4.4%	0.10	96%
MTBE	High QC	9.83	6.4%	0.10	103%
MTBE	Low QC	1.04	11.5%	0.10	102%

* Coefficient of variation.
† Recovery of calculated theoretical concentration, based on dilution of neat standard materials.

Table III. Average Finished Drinking Water Parameters from WTPs

WTP	pH	Alkalinity (ppm)	Temperature (°C)	TOC* (ppm)	Bromide (ppm)	Ammonia (ppm)
Southeast A	7.02	25.9	19.2	2.52	0.02	0.10
Southeast B	9.10	19.6	18.3	0.89	0.01	0.01
Southeast C	8.00	36.0	11.0	1.40	ND†	ND
Southwest A	8.00	135.6	24.6	3.96	0.38	0.02
Southwest B	7.64	132.6	27.7	1.91	0.07	0.06

* Total organic carbon.
† Not detectable.

Quantitation

Xcalibur Quan software (ThermoFinnigan) was used for peak integration, calibration, and quantitation. Peak integrations were performed with the interactive chemical information system (ICIS) integrator software and confirmed by visual inspection. Relative response factors were calculated on the basis of relative peak areas of analyte quantitation and labeled analogue ions. The set of seven calibrators analyzed with each set of samples was used to generate the calibration curve for that day. These calibration curves were linear ($r^2 \geq 0.99$) and spanned three orders of magnitude. Calibration curves were adjusted for ion cross contamination between native analytes and isotopic analogues according to Colby and McCaman (17). The lowest calibrators ranged from 30 to122 ng/L. The LOD was calculated as three times the standard deviation at zero concentration ($3S_0$). If $3S_0$ was less than the lowest standard, then the lowest standard served as the LOD (18).

Quality assurance

Data were subjected to rigorous QC procedures using a custom laboratory information management system constructed in Microsoft Access. Before analysis of samples, the MS was tuned against perfluorotri-*N*-butylamine calibration gas using the autotune function to ensure proper mass calibration. Contamination was evaluated both qualitatively and quantitatively. Laboratory air was extracted using SPME for 8 min and then desorbed into the GC–MS as described previously. The resulting chromatograms were qualitatively reviewed for the presence of gross contamination of THMs or MTBE. The analysis of a water sample free of volatile organic compounds was used to quantitate any trace contamination of analyte. Following sample analysis and the visual inspection of every integrated peak, additional QC parameters were evaluated. Adequate labeled analogue response was evaluated on the basis of absolute peak area signal, as well as signal-to-noise ratio. We further evaluated the identity of the analyte ion by comparing the confirmation ion ratio in unknown samples with that for reference standards. Each batch of data also was judged against blind QC samples.

QC samples

Two QC samples were processed and analyzed with each batch of samples. We prepared these aqueous samples from concentrated standards in purge-and-trap-grade methanol and stored them at –60°C as aliquots in flame-sealed glass ampoules. On the day of use, we further diluted these stock solutions in helium-sparged and distilled water, and the QC material was sampled as though it was an unknown. Two QC pools were prepared (high and low levels) and characterized

by 15 separate determinations. Blind QC samples were evaluated by an independent QC officer according to Westgard QC rules (19). If a QC sample exceeded QC limits for an analyte, then all results for that analyte on that day were rejected.

Blank analysis

Volatile organic compounds such as chloroform and MTBE are ubiquitous in a typical laboratory; rigorous technique is required to minimize sample contamination from laboratory air. Potential sources of contamination include chlorinated water, common household cleaning products, laboratory solvent usage, and oxygenated fuel usage. Volatile contaminants from these sources and others easily can spread through laboratory air to samples during preparation (sample handling) or analysis (SPME fiber). Contamination was minimized by removing sources of THMs and MTBE from the laboratories where samples were prepared and analyzed. A blank water sample was used to test for contamination. Blank water was prepared by helium sparging, distillation, and flame sealing in glass ampoules. On the day of use, a water blank was removed from an ampoule, spiked with labeled analogue, and run with each batch of unknowns. If the blank contained analyte levels of at least half of the LOD, the run was then flagged as contaminated. Additionally, an SPME fiber sampling of laboratory air was run to qualitatively assess airborne contaminants.

Results and Discussion

Method validity

Figure 1 shows GC traces resulting from the analysis of a tap water sample for BDCM. The quantitation (*m/z* 83), confirmation (*m/z* 85), and labeled analogue (*m/z* 84) ions were well resolved from potential interfering compounds. These data are typical of the analysis of the other THMs and result from the combination of a selective detector, chromatographic resolution, and relatively simple matrix.

Assay precision was evaluated by analyzing QC samples of known composition (Table II). During nine months of analysis, the QC results varied 4–6% from the characterized levels, with the exception of MTBE (11% in the low QC pool). Daily calibration was used to prevent calibration curve drift from compromising quantitation; however, no evidence of calibration curve drift was observed during 9 months of analysis. Interday variability of daily calibration curves was minimal; the relative standard deviation of calibration curve slopes over 6 months of analysis ranged from 2.6% to 7.6%, depending on the analyte.

Over a 2-year period, this method was used to analyze 1420 tap water samples from a geographically diverse U.S. population. The reported values for these samples encompassed the following ranges: MTBE, < LOD–25.4 µg/L; chloroform, < LOD–233 µg/L; BDCM, < LOD–39.3 µg/L; DBCM, < LOD–36.2 µg/L; and bromoform, < LOD–48.3 µg/L. The linear calibration range used for the analysis was MTBE, 0.038–38.4 µg/L; chloroform, 0.122–122 µg/L; BDCM, 0.049–48.6 µg/L; DBCM, 0.059–59.1 µg/L; and bromoform, 0.030–30.1 µg/L. Samples with analyte concentrations above the highest calibrator were diluted and reanalyzed. As a measure of the accuracy of this method, we used the calculated theoretical concentrations of the low and high QC and compared these values with the mean QC values generated by this method. Good agreement existed between the calculated theoretical and mean concentrations for both the high and low QC (Table II).

The optimization of this method led to SPME extraction techniques that do not recover the majority of analyte in the sample. This potential problem was minimized by the use of stable isotope dilution for quantitation; thus, variation in absolute signal did not significantly alter quantitative accuracy. The limited recovery of analytes during SPME extraction had the advantage of allowing for multiple extractions of a prepared water sample. Samples with punctured septa could be stored frozen for several weeks at –4ºC with minimal loss of analytes. For reanalysis of these samples, the frozen samples were thawed at room temperature and then analyzed. Absolute recovery of analytes decreased with each SPME headspace extraction of a sample; however, the quantitated amount remained constant because of proportional loss of the stable isotope-labeled analogue. As predicted by partitioning coefficients, THM levels decreased more than MTBE with each re-extraction.

Extraction with SPME is an excellent method for sampling volatile compounds, such as THMs and MTBE, in an aqueous matrix. Nonetheless, some problematic interfering compounds can also be extracted in the process. Trimethylsilanol is ubiquitous in the laboratory environment and easily extracted from air or water onto a carboxen/PDMS SPME fiber. Trimethylsilanol elutes a few seconds before MTBE and fragments to produce a large *m/z* 75 ion. The $^{13}C_3$ analogue of MTBE also fragments to produce a base peak at *m/z* 75. The large tailing trimethylsilanol peak at *m/z* 75 can fully conceal the $^{13}C_3$ MTBE peak and, thus, prevent quantitation of MTBE in the sample. The trimethylsilanol contamination was traced to a new supplier of Teflon-faced/silicone rubber septa and the problem resolved. To prevent a reoccurrence of interference from trimethylsilanol, the $^{13}C_3$ analogue of MTBE was replaced by $^{2}H_{12}$ MTBE.

THMs temperature stability study

EPA methods 502, 524, and 551 impose storage temperature (< 4ºC) and holding time (< 14 days) constraints for the analysis of volatile compounds in tap water samples. These constraints are probably imposed because of the instability of other analytes also measured by these multianalyte methods; the stability of THMs and MTBE in quenched and buffered tap water should allow for less restrictive shipping and storage parameters. The ability to ship quenched and buffered water samples in nonchilled containers and to store samples for longer than 14 days widens the scope of field studies possible; therefore, we studied the stability of THMs under different shipping and storage conditions.

Water samples were collected from five geographically diverse water treatment plants (WTP) located in the U.S. The sampling sites were chosen to reflect a variety of water quality parameters related to the formation of THMs (Table III). Each type of water was treated with buffer-quench solution, aliquotted into water collection vials, and stored at 45ºC. Periodically, triplicate samples were removed, allowed to equilibrate to room temperature, and analyzed. These samples were stored for up to 30 days at 45ºC to simulate a worst-case scenario for shipping unrefrigerated sam-

ples from collection sites to the laboratory (Figure 2). In general, at 45ºC over 30 days, we found the THMs to be stable at elevated temperatures. We noted one exception where chloroform and bromoform levels increased slightly (1–2 µg/L) following 2 days of storage at 45ºC. After this initial increase, the values stabilized for the remainder of the 30-day storage period.

The temperature-dependent increase in THM concentration for certain tap water samples probably resulted from the instability of precursor molecules formed during water disinfection. THMs are decomposition products of unstable halogenated organic compounds formed by the reaction of disinfectant with a complex mixture of naturally occurring organic material in untreated water (20). Although the reaction mechanisms for some groups of compounds have been studied (21), the exact reaction pathways, molecular composition, and stability of these halogenated organic intermediates are not well understood. Additional studies have been performed on five classes of these unstable precursor molecules: dihaloacetonitriles (DHANs), trihaloacetic acids, trichloroacetones, trichlorophenols, and halopropionic acids. Nikolaou et al. (22) studied the decomposition of DHANs at three different temperatures over a 96-h time course. They observed that DHANs decompose rapidly into THMs at 35ºC, and this rate was increased substantially by the presence of sodium thiosulfate. When sodium thiosulfate was present, all DHANs disappeared after 24 h. The decomposition of DHANs was slower at 21ºC, and almost no reaction occurred at 4ºC. Takahashi et al. (23) investigated the formation of THMs from halopropionic acids, trichloroacetones, trihaloacetonitriles, and trihaloacetic acids in aqueous solutions at various pH and temperatures. The water samples were heated over a range of 40–80ºC for up to 45 min. The water samples also were tested at pHs ranging from 1.0–9.2. The halopropionic acids and trichlorophenols did not form THMs under these experimental conditions. However, trichloroacetones, trihaloacetonitriles, and trihaloacetic acids formed THMs. Temperature, pH, and time of contact had an effect but were not the limiting factors. The experiments by Nikolaou et al. (22) and Takahashi et al. (23) give a likely explanation for the THM increases observed in the water samples heated to 45ºC. The use of sodium thiosulfate as a dechlorinating agent in the buffer-quench solution would accelerate decomposition of any DHAN in WTP samples and would be complete after 24 h (22). Large variation in water disinfection processes and the physical/chemical characteristics of raw water leads to formation of varying amounts of halogenated organic intermediates during the disinfection process. Thus, minor changes in tap water THM levels are expected during even short storage periods. The same water samples that showed increased THMs with storage at 45°C for 2 days also showed increased THM levels after refrigerated storage (4ºC) for 1 week. The increases observed at both temperatures are likely to be lower than the variation from other sources (e.g., residence time, season, and time of day of sample collection).

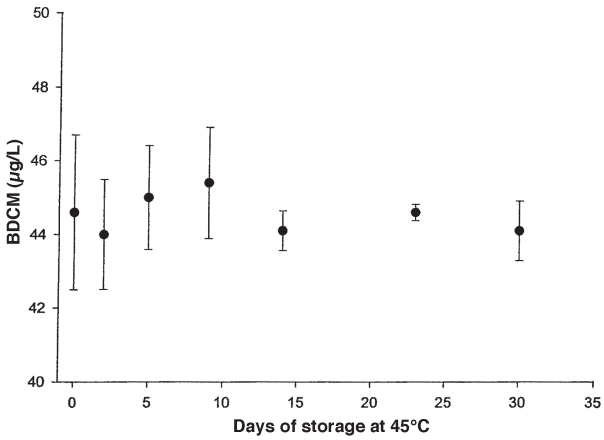

Figure 2. BDCM levels in quench-buffer-treated tap water stored for 30 days at 45°C. Each point is the average of three samples (± standard deviation).

Given the change in THM levels observed at 45ºC in water from one of five water treatment plants tested, we recommend shipping drinking water samples with some type of temperature control. The addition of a cold pack (4–25ºC) should prevent the sample from reaching temperatures that would result in significant THM formation during transit. Temperature control also would reduce the possibility of water samples freezing and shattering during winter transit. Sample overheating during shipping can be easily monitored by including an inexpensive maximum temperature indicator along with the water samples.

We also investigated the long-term stability of THMs and MTBE

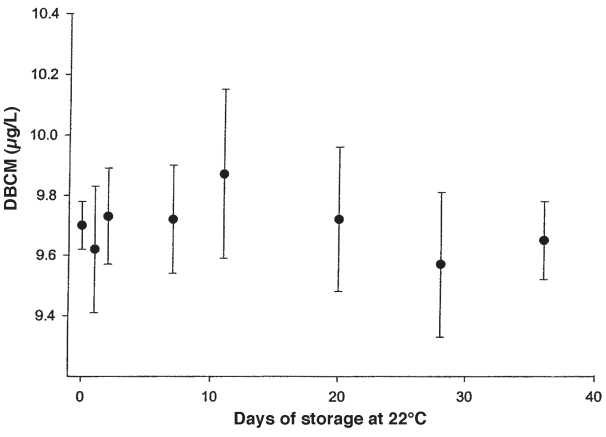

Figure 3. DBCM levels in quench-buffer-treated tap water stored for 28 days at 22°C. Each point is the average of three samples (± standard deviation).

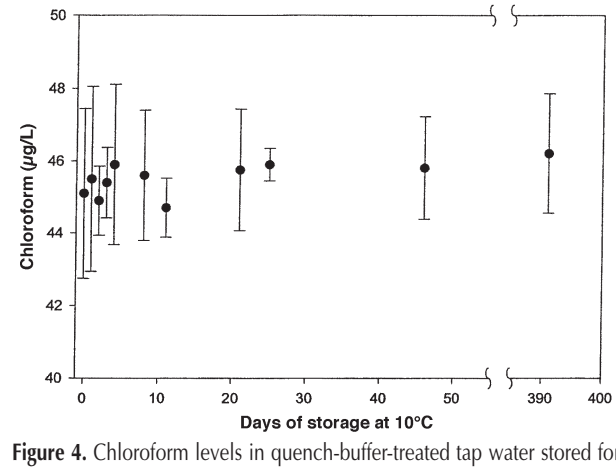

Figure 4. Chloroform levels in quench-buffer-treated tap water stored for 391 days at 10°C. Each point is the average of three samples (± standard deviations).

in water samples at 22ºC to approximate storage at room temperature. Periodically, triplicate samples of quench-buffer-treated water were removed, allowed to equilibrate to room temperature, and analyzed (Figure 3). At 22ºC over 28 days, the THMs and MTBE were stable throughout the entire time period. These results were confirmed with a water sample from a second WTP in a different region of the country.

The stability of THMs and MTBE in drinking water samples during refrigerated storage (10ºC) also is an important parameter. We evaluated the long-term stability of THMs and MTBE in quench-buffer-treated aliquots of spiked tap water by analyzing aliquots stored at 10ºC for up to 1 year. Periodically, triplicate samples were removed, allowed to equilibrate to room temperature, and analyzed (Figure 4). At 10ºC over 391 days, the THMs and MTBE were stable throughout the entire time period. The ability to store quench-buffer-treated samples for longer than 14 days before analysis provides the laboratory with additional analysis flexibility.

Applicability to real water samples

The suitability of the method for detecting THMs and MTBE in 1420 tap water samples from the National Health and Nutrition Examination Survey was evaluated. The water samples were collected from geographically diverse regions around the U.S. during 2000–2002 and analyzed as described. In these tap water samples, the method measured detectable levels (> LOD) of chloroform (86% of the total samples), BDCM (87% of the total samples), DBCM (86% of the total samples), bromoform (64% of the total samples), and MTBE (26% of the total samples). The data showed that the method can successfully quantitate THMs in the majority of U.S. tap water samples and, thus, would be useful in quantitating exposure to these potentially harmful chemicals.

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