GC Analysis of Trihalomethanes in Drinking Water — A Rapid and Direct Quantitative Method

The determination of disinfection by-products such as trihalomethanes has become extremely important because of the current regulatory testing requirements of the U.S. Environmental Protection Agency. The difficulties and expenses involved in regulatory testing require a low-cost, simple, quantitative test for these compounds. The authors developed a gas chromatography method using electron-capture detection for measuring trihalomethanes in drinking water without solvent extraction or concentration steps. The assay allowed the determination of chloroform, dichlorobromomethane, chlorodibromomethane, and bromoform.

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Trihalomethanes are small organic compounds similar in structure to methane, but they have three hydrogen atoms substituted with chlorine or bromine. They are formed in water when disinfectants such as the chlorine used in water-treatment plants react with organic matter; for example, humic acids, which are found in the source water, especially in case of surface waters. Humic acids are the organic portion of soil formed by the decay of leaves, wood, and other plant materials. Disinfectants reduce the levels of microbes in the water supply; however, as the use of disinfectants in water increases, the risk of formation of trihalomethanes increases. Thus, trihalomethanes can be found in most disinfected drinking water supplies.

The most important trihalomethanes in disinfected water are chloroform, dichlorobromomethane, chlorodibromomethane, and bromoform. Among other factors, the levels of trihalomethanes are dependent upon the specific conditions of chlorine dosage and concentration, pH, and the quantities of organic carbon in the source water.

The negative effect of trihalomethanes has not been fully elucidated yet. Studies of human populations have indicated a slightly higher incidence of bladder and colon cancers in areas where the drinking water has been chlorinated (1). Other studies show the association of waterborne chloroform in drinking water with low birth weight, prematurity, and intrauterine growth retardation (2). Animal studies have found possible relationships between oral exposure to various trihalomethanes and fetotoxicity and sperm abnormalities (3,4).

The U.S. Environmental Protection Agency (EPA) has published the Stage 1 Disinfectants–Disinfection By-products Rule to regulate total trihalomethanes at a maximum allowable annual average level of 80 ppb. In December 2001, this standard replaced the 100-ppb maximum allowable annual average level for large surface water public water systems. The standard will become effective for small surface water and all ground water systems in December 2003 (http://www.epa.gov/enviro/html/icr/gloss_dbp.html#tthm). Additionally, some bottled water producers in California and Florida have adopted a 10-µg/L total trihalomethane limit, which is a standard recommended by the International Bottled Water Association (IBWA) (see "Bottled Water, Pure Drink or Pure Hype?" Natural Resources Defense Council, http://www.nrdc.org).

Different analytical methods have been developed to analyze trihalomethanes in drinking water. The most widely used are

based on gas chromatography (GC) with electron-capture or mass spectrometry detection and use extraction with organic solvents such as pentane and hexane (5,6) or purge-and-trap techniques (7).

As the basis of this study, we evaluated the concept of a chromatographic method without solvent extraction from application notes (8,9). The present study reflects a method development based upon major modifications and changes a basic concept to improve reliability and accuracy of the method. Furthermore, we performed reproducibility studies. Finally, we compared our method with the current official Standard Method 6232 for the Examination of Water and Wastewater of the American Public Health Association (APHA), American Water Works Association (AWWA), and Water Environmental Federation (WEF), which is based upon solvent extraction. The most important differences in methodology are the use of 1,3-dichloropropane as an internal standard, the elimination of the deactivated retention gap, and the replacement of the original oven temperature program with isothermal operation (Figure 1).

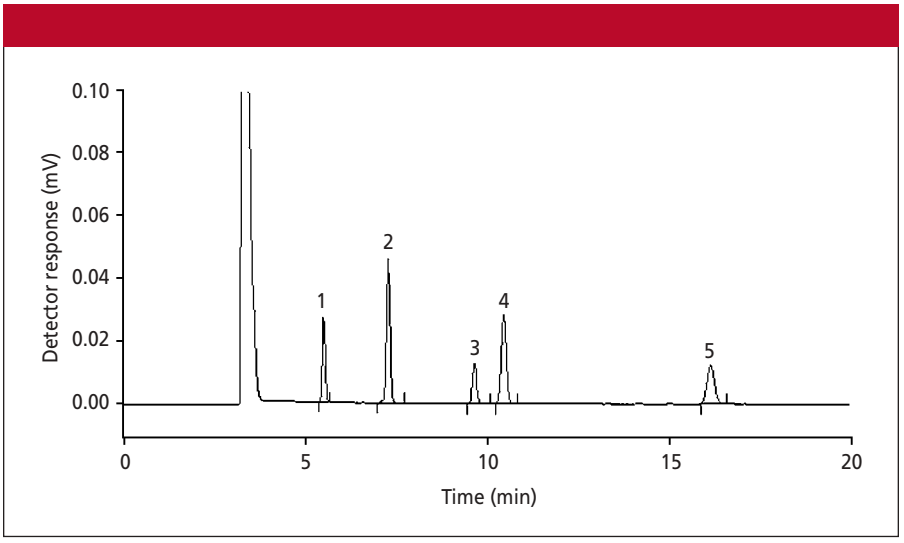

Figure 1: Gas chromatogram of standard trihalomethanes (40 µg/L) obtained using the evaluated direct method. Column: 30 m × 0.53 mm, 2.65-µm d_f HP-1 (Agilent Technologies); carrier gas: helium at a constant inlet pressure of 15 kPa; makeup gas: 95:5 argon–methane at 60 mL/min; injector temperature: 93 °C; oven temperature: 90 °C; detector temperature: 300 °C. Peaks: 1 = chloroform, 2 = dichlorobromomethane, 3 = internal standard, 4 = chlorodibromomethane, 5 = bromoform.

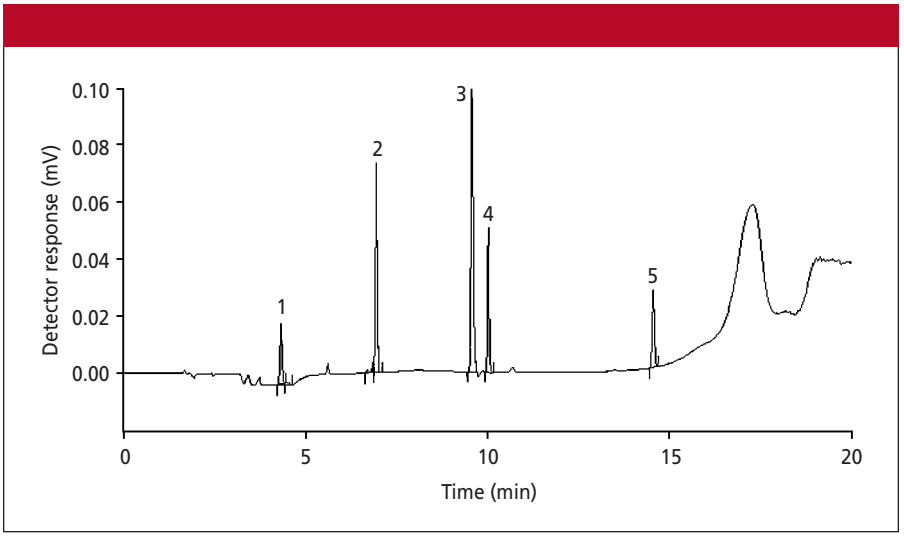

Figure 2: Gas chromatogram of standard trihalomethanes (40 µg/L) obtained using method 6232 (Standard Methods AWWA). Column: 30 m × 0.32 mm, 1.0-µm d_f HP-5 (Agilent Technologies); column head pressure: 10 psi; makeup gas: 95:5 argon–methane at 60 mL/min; injector temperature: 200 °C; oven temperature: 35 °C for 5 min, 35–70 °C at 10 °C/min, then 70–200 °C at 20 °C/min; detector temperature: 300 °C. Peaks: 1 = chloroform, 2 = dichlorobromomethane, 3 = internal standard, 4 = chlorodibromomethane, 5 = bromoform.

Experimental

Reagents: *Reagent water:* We used purified water that contained no measurable quantities of the analytes or any other interfering species. Distilled water that has been charcoal-filtered also would be suitable. For this study, we boiled tap water for 15 min and maintained it at 90 °C while purging a contaminant-free inert gas (nitrogen) through the water at 100 mL/min for 1 h.

Solvents: We used methanol that was demonstrated to be free of analytes for organic trace analysis.

Internal standard: The internal standard was 1% (v/v) 1,3-dichloropropane in methanol. We kept the flask tightly closed and the temperature lower than 5 °C.

Stock standard solutions: We obtained trihalomethanes calibration mix stock standard solutions from Supelco (Bellefonte, Pennsylvania) as 100 µg/mL in methanol.

Apparatus: We used 100- and 500-µL micropipettes, 10- and 50-µL microsyringes, and 10- and 50-mL volumetric flasks. The gas chromatograph was a model 5890 series II system (Agilent Technologies, Inc., Wilmington, Delaware) that was equipped with an electron-capture detector and cool on-column injection system. We used a 30 m × 0.53 mm, 2.65-µm d_f HP-1 capillary column (Agilent Technologies).

Operating conditions: The helium carrier gas was maintained at a constant 15-kPa inlet pressure. The makeup gas was 95:5 (v/v) argon–methane with a flow rate of 60 mL/min. The injector temperature was 93 °C in the oven track mode. The oven temperature was 90 °C, and the detector temperature was 300 °C.

Method of analysis: *Calibration of standard solutions:* To prepare 5-, 10-, 20-, 40-, and 60-µg/L calibration standards, we added an appropriate volume of a stock standard solution (2.5, 5, 10, 20, or 30 µL) to 45-mL aliquots of the reagent water in 50-mL volumetric flasks. We added 25 µL of internal standard solution and diluted it to volume with reagent water and mixed it well. We made sure that the drops from the standard solution fell directly into the water without contacting the neck of the flask. We injected 1 µL of the solution into the injector and drew an additional 1 µL of air into the syringe.

When we stored the aqueous standards in headspace-free sample storage vials, we were able to use them for 24 h.

Sample collection and storage: We collected samples according to EPA Method 502.2 on sample collection, preservation, and storage (10).

Sample preparation: We filled a 50-mL volumetric flask with 45 mL of sample water and added 25 µL of the internal standard. Then we filled the flask to the mark with the same sample water and mixed the solution well.

Sample analysis: We injected 1 µL of each aqueous solution into the injector and drew an additional 1 µL of air into the syringe.

Results and Discussion

The direct injection procedure proved to be very reliable for quantifying trihalomethanes in drinking water. Avoiding the extra step of solvent extraction produced no visible matrix effects (Figure 1). In contrast, using extraction solvents such as hexane or pentane frequently leads to the occurrence of several interfering organic compounds (6) (see Figure 2).

It was unnecessary to use a deactivated retention gap. The isothermal GC operation yielded excellent chromatographic separation (8) (Figure 1).

The internal standard 1,3-dichloropropane was well suited as an internal standard, because it was water soluble, was stable in aqueous solutions during a period of more than three months, usually was absent in water samples, and did not interfere with any of the trihalomethanes peaks (see Figure 1).

Our results showed an excellent linearity for each component (R^2 = 0.998) (Figure 3). We performed linearity checks using standard solutions, and the response of the GC system was linear within the 1–60 µg/L concentration range of trihalomethanes.

We calculated the limits of detection, defined as the concentration of the analyte that provides a signal equal to three times the standard deviation of the blank (11), from the calibration plot data (Figure 3). For all trihalomethanes, the limits of detection obtained were lower than 1 µg/L. The limits of detection for this method were higher than those of the standard AWWA methods (0.1 µg/L), but considering the 80-µg/L maximum contaminant level for trihalomethanes in drinking water given by EPA (see http://www.epa.gov/safewater/mcl.html), this value is absolutely acceptable. In addition, the detection limit of AWWA method 6232 is highly dependent upon the characteristics of the GC system used and upon the interferences arising from the solvent.

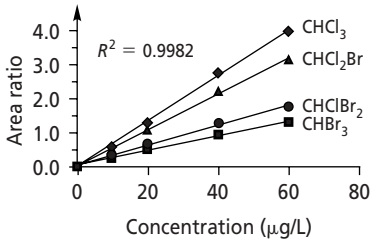

Figure 3: Trihalomethanes calibration plot. Area ratio is defined as the peak area of the respective compound divided by the peak area of the internal standard.

Table I: Repeatability of analysis at different trihalomethane concentrations using relative standard deviation method

Concentration (µg/L)	Chloroform (% RSD)	Dichlorobromomethane (% RSD)	Chlorodibromomethane (% RSD)	Bromoform (% RSD)
5	0.91	1.02	1.50	1.42
10	2.00	1.26	1.61	1.51
20	0.82	0.94	1.57	1.88
30	0.90	0.68	0.53	0.76
40	0.95	0.58	0.77	0.90

Table II: Average results of trihalomethanes in water samples using method 6232 (AWWA Standard Methods) and evaluated direct method

Target Concentration (µg/L)	Method	Chloroform (µg/L)	Dichlorobromomethane (µg/L)	Chlorodibromomethane (µg/L)	Bromoform (µg/L)
1	AWWA method 6232	1.3	1.2	0.9	0.9
1	Direct injection	1.2	1.1	0.8	0.8
5	AWWA method 6232	5.6	4.0	4.0	5.0
5	Direct injection	5.4	3.6	3.6	4.1
9	AWWA method 6232	9.5	7.8	7.6	8.5
9	Direct injection	9.4	6.7	7.0	8.0
10	AWWA method 6232	11.1	9.8	9.8	11.0
10	Direct injection	11.8	8.6	9.0	10.6
12	AWWA method 6232	12.4	11.1	11.1	13.4
12	Direct injection	12.8	11.1	12.3	14.0
15	AWWA method 6232	16.3	15.7	15.7	17.5
15	Direct injection	17.0	16.7	16.1	17.1
20	AWWA method 6232	19.6	20.0	20.0	21.6
20	Direct injection	21.0	21.0	20.6	21.0
26	AWWA method 6232	26.0	27.4	27.4	26.5
26	Direct injection	26.3	27.6	27.0	27.0
30	AWWA method 6232	29.0	29.3	29.4	30.2
30	Direct injection	28.5	31.0	30.0	29.5
35	AWWA method 6232	36.3	37.0	38.0	36.2
35	Direct injection	36.1	38.0	36.0	34.2
40	AWWA method 6232	39.3	42.0	43.0	41.0
40	Direct injection	39.0	42.0	40.3	37.2

Table III: Correlation coefficient and confidence limit of slope and intercept with a confidence interval of 95%

Value	Chloroform	Dichlorobromomethane	Chlorodibromomethane	Bromoform
Concentration interval (µg/L)	1–40	1–40	1–40	1–40
x axis	Method 6232	Method 6232	Method 6232	Method 6232
y axis	Direct injection*	Direct injection	Direct injection	Direct injection
Intercept	0.3802 ± 0.7424	−0.4486 ± 0.9515	0.3841 ± 0.9124	0.2035 ± 1.1187
Slope	0.9899 ± 0.0340	1.0343 ± 0.0420	0.9649 ± 0.0400	0.9593 ± 0.0497
Correlation coefficient	0.9960	0.9971	0.9959	0.9980

*Direct injection = evaluated direct injection method.

We analyzed five concentrations (5, 10, 20, 30, and 40 µg/L) using six injections at each concentration. Table I lists the results of each trihalomethane species. The repeatability was satisfactory, with a maximum 2.0% relative standard deviation (RSD) for chloroform, and was lower for the other trihalomethanes. We compared the method using water samples with 11 trihalomethane concentrations ranging from 1 µg/L to 40 µg/L. We analyzed each of 10 replicates and compared them with method 6232 for the examination of water and wastewater (APHA, AWWA, and WEF) (6). The results indicated no significant differences from the results of both methods, which demonstrated very good comparability for the concentration range used (see Table II). Furthermore, the obtained values closely matched the target values, which were obtained by calculating a dilution series from the concentrations given by the supplier of the calibration mix.

We calculated regression graphs for each trihalomethane by comparing both methods (see Figure 4); therefore, the random errors in the values for the slope and intercept were important. Table III lists the confidence limits for the slope and intercept of the regression line with 95% confidence level and nine degrees of freedom (11). From these results, it is clear that the calculated slopes and intercepts do not differ significantly from the ideal values of 1 and 0, respectively, and thus the data show no evidence of systematic differences between the two sets of results (11).

Finally, when comparing this method with the conventional method, we found the proposed method was much less labor-intensive and generated fewer contaminants.

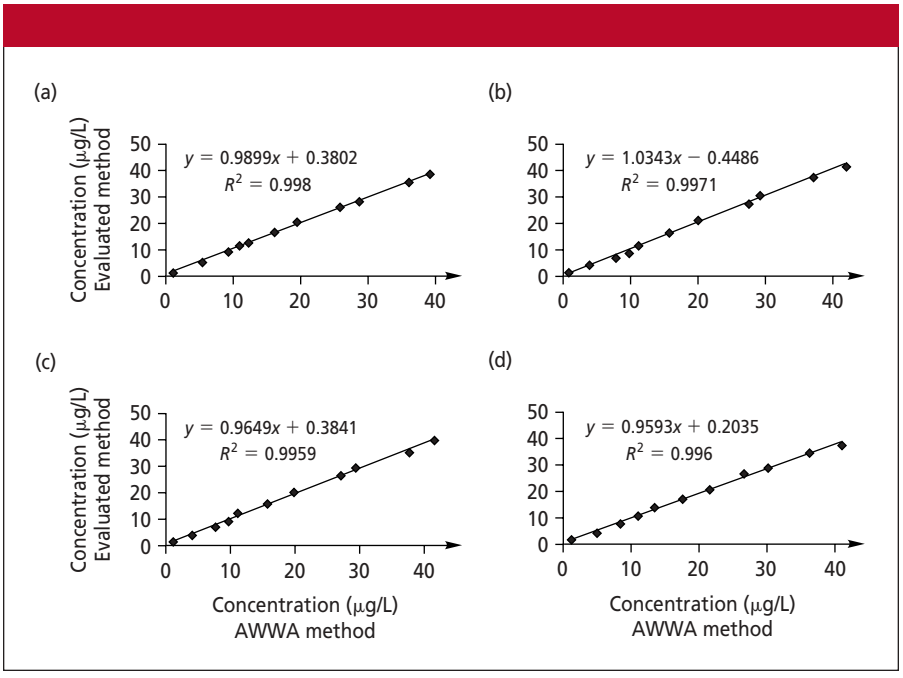

Figure 4: Regression graphs obtained using two methods for trihalomethanes (a) chloroform, (b) dichlorobromomethane, (c) chlorodibromomethane, and (d) bromoform.

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