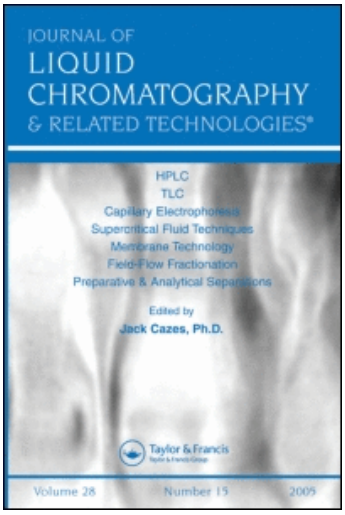

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DETERMINATION OF HALOACETIC ACIDS IN TAP WATER BY CAPILLARY ELECTROPHORESIS WITH DIRECT UV DETECTION

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ABSTRACT

Application of capillary zone electrophoresis with direct ultraviolet (UV) detection for determining the haloacetic acids in tap water is described. The haloacetic acids were monochloroacetic, trichloroacetic, monobromoacetic, dichloroacetic, bromochloroacetic, and dibromoacetic acids. For direct UV detection, the haloacetic acids were treated by liquid-liquid extraction and concentrated up to 2000 times. The analysis was successful with a fused-silica capillary containing 25 m*M* phosphate −0.5 m*M* cetyltrimethyl-ammonium chloride by direct UV detection at 185 nm. This technique can determine haloacetic acids at the 5 μg L^{-1} level in tap water within 7 min, except for trichloroacetic acid.

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INTRODUCTION

Disinfection of drinking water with chlorine results in haloacetic acids (HAAs) due to the reaction of chlorine with natural "humic and fulvic" materials in the source water (1). Since HAAs are carcinogenic even at low concentrations (1,2), a reliable method is required to detect the low parts per billion levels. In the U.S. Environmental Protection Agency's (EPA) Disinfectants/Disinfection By-Products Rule, effective from November 1998, the first stage establishes maximum contaminant levels of 60 μg L^{-1} for the sum of the HAAs (3,4).

As a cleanup method for a water sample, liquid-liquid extraction (LLE) has been the most frequently used technique for the determination of HAA compounds (3,5). Now solid-phase extraction (SPE) and solid-phase microextraction (SPME) are also becoming sample cleanup techniques for the determination of HAAs (6–8). For determination of HAAs in water samples, gas chromatography (GC), with electron capture detection (ECD), and liquid chromatography, with ultraviolet-visible detection (UV), are mostly used (3).

The standard method for the determination of HAAs is LLE followed by derivatization with diazomethane and GC-ECD analysis (9,10). But, this method requires use of diazomethane, which is toxic, carcinogenic, and explosive (6,11). For analysis of HAAs without derivatization with diazomethane, SPME, after acid-catalyzed derivatization of HAAs in water (8), and SPE, followed by acid-catalyzed esterification of HAAs, and GC-ECD analysis have been carried out (6,7). The derivatization makes the method complicated because of the low volatility and high polarity of HAAs.

For direct analysis of HAAs without any derivatization, liquid chromatography has been used. Reversed-phase ion-pair chromatography with indirect UV detection (12) and reversed-phase liquid chromatography with direct UV detection have been applied to detect trichloroacetic acid (13), and anion exchange separation with electrochemical detection was carried out (1,14).

Recently anion exclusion separation and electrospray ionization-mass spectrometry have been used to determinate the HAAs in environmental water (15). However, in liquid chromatography, the analysis time was long and the detection limits were not good (16).

In the determination of haloacetic compounds, capillary electrophoresis (CE) can be a good alternative to the chromatographic methods because it does not require a tedious derivatization step and analysis times can be reduced (3,16). CE has been used to separate various organic acids (17–27). On the other hand, the drawback of CE is its poor detection limits, which lead to a major problem when one is attempting to analyze aliphatic organic acids which lack UV absorbance, particularly those from environmental sources. To avoid poor detection limits, Martínez and co-workers (16) reported the analysis of HAAs using capillary zone electrophoresis (CZE) with indirect UV detection.

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Recently, these researchers (3) have reported the analysis of HAAs using SPE and CZE with indirect UV detection. However, in the indirect UV detection method, the choice of suitable background electrolyte is restricted to substances that have background UV absorbance and co-migrate with the mixture of analytes (20,28). Furthermore, considering some aspects such as stability of the baseline, direct UV detection seems to be more suitable (16,25). Therefore, this work focused on the development of simple and sensitive analysis methods for HAAs using direct UV detection. To overcome the poor limit of direct UV detection in CZE, 200-mL water samples were treated by LLE and concentrated up to 2000 times (10).

EXPERIMENTAL

Chemicals

As the individual haloacetic standards, monochloroacetic acid (MCAA; Chem Service, West Chester, PA, USA), trichloroacetic acid (TCAA; Chem Service), monobromoacetic acid (MBAA; Supelco, Bellefonte, PA, USA), dichloroacetic acid (DCAA; Supelco), bromochloroacetic acid (BCAA; Supelco), and dibromoacetic acid (DBAA; Supelco) were used to identify the unknown peaks.

Standard solutions of six HAAs (EPA 552 haloacetic acids calibration standard, 2000 mg L^{-1} haloacetic acids, 4-8047; Supelco) were used for the calibration. High-performance liquid chromatography grade methyl *tert*-butyl ether (MTBE; Merck, Darmstadt, Germany) was used in the extraction step as an organic phase. Sodium sulfate (Merck) was used to increase the extraction efficiency. Concentrated sulfuric acid (Junsei Chemical Co., Ltd., Tokyo, Japan) was used to adjust the pH of the sample.

Sodium phosphate monobasic (NaH_2PO_4; Merck) was used as the electrolyte. Cetyltrimethylammonium chloride (CTAC, 25 wt.-% water solution; Aldrich Chemical Co., Milwaukee, WI, USA) was used as electroosmotic flow (EOF) modifier. Sodium hydroxide (Aldrich) was used to adjust the electrolyte pH and condition the capillary wall.

Sample Preparation

Water samples were treated, based on U.S. EPA method 552.2 for the determination of HAAs in drinking water, by LLE (10). A 200-mL water sample was transferred to a 500-mL separatory funnel, and the solutions were acidified at pH <0.5 with 10 mL of concentrated sulfuric acid. Then 80 g of muffled (10 h at 450°C) sodium sulfate and 20 mL of MTBE were added, followed by vigorous shaking for 5 min.

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The lower phase was collected in another 500-mL separatory funnel and re-extracted with an additional 10 mL of MTBE in the same way. The organic phase was filtered through a 0.2-μm disposable syringe filter (nylon 66, 25 mm, catalog no. 2040; Alltech Associates, IL), and combined in a 50-mL TurboVap test tube (part 42526; Zymark, Hopkinton, MA, USA) and evaporated to about 50 μL using a TurboVap II evaporator (Zymark).

The extract was transferred to a 300-μL vial insert (part 8030.010; Prince Technologies B.V., Emmen, The Netherlands) quantitatively. Then the solvent was evaporated by nitrogen gas purging, 100 μL of electrolyte (25 m*M* phosphate −0.5 m*M* CTAC) was added to the extracted residue, and the analysis using CZE was carried out.

Electrophoretic Conditions and System Operation

CZE was performed using a Unicam Crystal CE system (Unicam, Madison, WI, USA) equipped with a UV detector (Unicam), and data were collected with an HP integrator (Hewlett-Packard, Avondale, PA, USA). Separation was carried out using fused-silica capillary tubing (75 μm inside diameter × 365 μm outside diameter × 93 cm) obtained from Supelco.

The detection window was prepared by burning off the polyimide coating, at 48 cm from the capillary inlet. Before analysis, the capillary was pretreated for 20 min with 0.1 *M* sodium hydroxide solution, 10 min with deionized water, and 10 min with running buffer until equilibrium was reached.

The carrier electrolyte consisted of 25 m*M* phosphate 0.5 m*M* CTAC, and the pH of solution was adjusted to 7.0 by adding 1 *M* NaOH at 25°C. Buffers were filtered through 0.2-μm disposable syringe filters and degassed in an ultrasonic bath for 10 min.

Injection was performed hydrodynamically at the cathodic side at 50 mbar for 0.07 min, and separation was carried out at −20 kV constant voltage, with a current of 20 μA at 37°C. Direct UV detection at 185 nm was used.

RESULTS AND DISCUSSION

The electrophoretic separation of the haloacetic acids started with 25 m*M* phosphate 0.5 m*M* CTAC at pH 5. The EOF modifier concentration (0.5 m*M* CTAC) was selected from the previous reports (16). As the concentration of the carrier electrolyte is increased from 25 to 50 m*M* the migration time for all HAAs are increased but improvement in resolution was not shown (Table 1).

A high concentration of the carrier electrolyte can lead to relatively high currents so a 25 m*M* concentration of carrier electrolyte was chosen. As the pH is

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Table 1. Effect of pH and Phosphate Concentration on the Migration Time of the Haloacetic Acids

	Migration Time (min)			
			Phosphate Conc.	
Compounds	pH 5	pH 7	25 m*M*	50 m*M*
MCAA	5.2	5.2	5.2	5.8
MBAA	5.3	5.4	5.3	5.9
DCAA	5.5	5.9	5.5	6.1
BCAA	5.8	6.2	5.8	6.2
DBAA	6.2	6.6	6.2	6.6

increased from 5.0 to 7.0, the migration times for all HAAs are increased (Table 1). The improvement of resolution or change of migration time as a function of pH is not too significant. The pK_a values of the haloacetic acids are in the range of 0.63–2.90 (16). So, at pH greater than 5, all HAAs were ionized completely. The changes in capillary temperature can cause variations in resolution and migration time.

As the temperature rose from 20 to 50°C, the migration time was decreased (Fig. 1). This can be explained as temperature increases causing a decrease in viscosity of the running electrolyte, thus, increasing both EOF and electrophoretic mobilities (26). On the other hand, at 50°C the resolution deteriorates due to

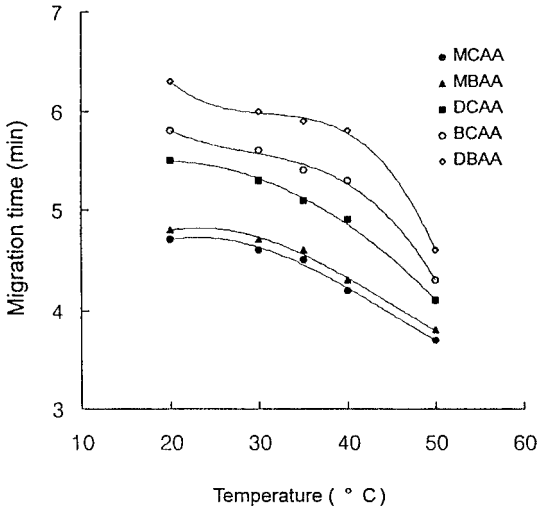

Figure 1. Effect of the temperature on the migration time.

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inefficient dissipation of Joule heating. For the effective separation of HAAs, a capillary temperature of 37°C was chosen as the optimum condition.

HAAs were separated using 25 m*M* phosphate −0.5 m*M* CTAC at pH 5 and 37°C and detected by direct UV detection at 185 nm. Electropherograms of the 10 μg mL^{-1} standard solution, the extracts of the spiked sample (10 μL of 200 μg mL^{-1} HAA mixture was spiked in 400 mL of deionized water and 200 mL of this was extracted), and 200 mL of tap water sample are shown in Figure 2. As can be seen in the electropherogram, the HAAs of monochloroacetic, monobromoacetic,

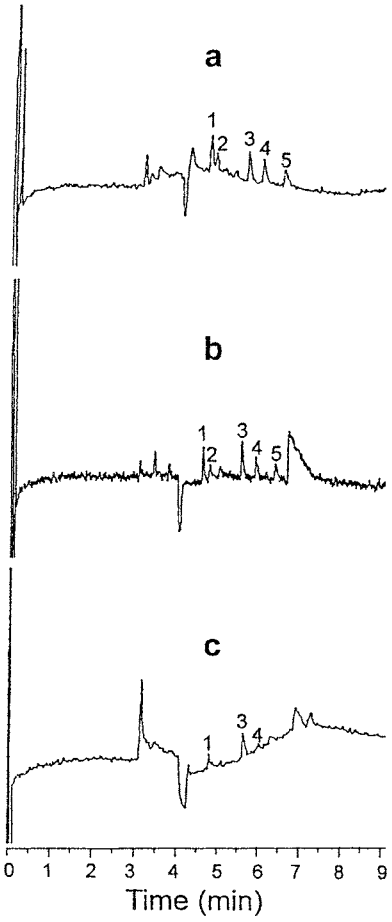

Figure 2. Electropherograms of standards, spiked sample, and tap water. a) standards (10 μg mL^{-1}); b) spiked sample (200 mL of 5 ng mL^{-1} sample was extracted); c) tap water (200 mL was extracted). Peaks: 1) monochloroacetic acid; 2) monobromoacetic acid; 3) dichloroacetic acid; 4) bromochloroacetic acid; 5) dibromoacetic acid.

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Table 2. Calibration and Recovery Data

Compounds	Calibration Curve Range (μg mL^{-1})	r^2	Recovery %	SD[a]	RSD (%)
MCAA	10∼40	0.977	90.2	9.3	10.3
MBAA	10∼40	1.000	88.5	6.1	6.9
DCAA	10∼40	0.994	95.8	9.1	9.5
BCAA	10∼40	0.992	97.2	7.6	7.8
DBAA	10∼40	1.000	90.4	5.5	6.1

[a]Average of 3.

dichloroacetic, bromochloroacetic, and dibromoacetic acids, except trichloroacetic acid, separated well (Fig. 2).

To detect TCAA with a 40-ppm solution of TCAA, various conditions were used such as a change of the buffer from phosphate to borax, or the pH from 5.0 to 7.0, on the wavelength of detection from 185 to 210 nm, but these changes did not improve the detection of TCAA.

In the recovery test, HAAs of interest could be extracted from spiked deionized water samples with 89–97% recovery (Table 2). In the tap water sample three HAA peaks were detected. Comparing the retention times with those of the individual standards, each peak was identified. These identifications were confirmed by adding the individual standards to the sample extracts and by surveying the changes in area, height, width, and shape of the individual peaks after the analysis under the same conditions (in the future, identification by mass spectrometry is needed). The main HAA components in a tap water sample were chlorinated acetic acids (monochloroacetic, dichloroacetic, and bromochloroacetic acids).

The calibration curves were obtained from the peak area of standards and the concentration of standards. Each calibration curve showed a good correlation coefficient of $r^2 = 0.992$–0.999 in the concentration range of 10–40 μg mL^{-1}, which were equivalent to the concentration of each HAA in the final extracts.

The results for the quantitation of the HAAs in tap water samples are shown in Table 3. The analysis method was evaluated by repeated measurement (3 times). The relative standard deviation (RSD) for this method was 8%, which was

Table 3. Concentration of the Haloacetic Acids in Tap Water

Compounds	Concentration (ng mL^{-1})[a]	RSD (%)
MCAA	<5	—
DCAA	5.7 ± 0.5	8.2
BCAA	<5	—

[a]Average of 3.

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satisfactory. Our work demonstrates that the 200-mL tap water sample that has trace HAAs (2–5 ng mL^{-1}) could be analyzed by CZE within 7 min. Further work is required to detect TCAA in tap water.

CONCLUSIONS

CZE was applied to analyze HAAs in tap water. To overcome the poor detection limit of direct UV detection in CZE, 200-mL water samples were extracted using a LLE method for the determination of six HAAs in drinking water and concentrated to 2000 times. With this procedure, we can determine HAAs at the 5 μg L^{-1} level in tap water within 7 min.

To determine the haloacetic compounds in water, CZE can be a good alternative to chromatographic methods because it does not require the tedious derivatization step, and analysis time can be reduced. Furthermore, CZE can be used not only with indirect UV detection but also with direct UV detection for the determination of HAAs.

REFERENCES

1. Akhtar, P.; Too, C.O.; Wallace, G.G. Anal. Chim. Acta **1997**, *341*, 141.
2. Bull, R.J.; Sanchez, I.M.; Nelson, M.A.; Larson, J.K.; Lansing, A.J. J. Toxicol. **1990**, *63*, 341.
3. Martínez, D.; Borrul, F.; Calull, M. J. Chromatogr. A **1998**, *827*, 105.
4. Roberson, J.A.; Cromwell, J.E, III; Krasner, S.W.; McGuire, M.J.; Owen, D.M.; Regli, S.; Summers, R.S. J. AWWA **1995**, *87*, 99.
5. Arora, H.; Lechevallier, M.W.; Dixon, K.L.; J. Am. Water Works Assoc. **1997**, *89*, 60.
6. Benanou, D.; Acobas, F.; Sztajnbok, P. Water Res. **1998**, *32* (9), 2798.
7. Hodgeson, J.W. EPA Method 552.1. In *U.S. EPA Method, Revision 1.0*; U.S. EPA: Cincinnati, 1992.
8. Aikawa, B.; Burk, R.C. Int. J. Environ. Anal. Chem. **1997**, *66* (3), 215.
9. Simpson, K.L.; Hayes, K.P. Water Res. **1998**, *32* (5), 1522.
10. Munch, D.J.; Munch, J.W.; Pawlecki, A.M. EPA Method 552.2. In *U.S. EPA Method, Revision 1.0*; U.S. EPA: Cincinnati, 1995.
11. Xie, Y.; Reckhow, D.A.; Springborg, D.C. J. Am. Water Works Assoc. **1998**, *90* (4), 131.
12. Vichot, R.; Furton, K.G. J. Liq. Chromatogr. **1994**, *17*, 4405.
13. Husain, S.; Narsimha, R.; Alvi, S.N.; Rao, R.N. J. Chromatogr. **1992**, *600*, 316.

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14. Nair, L.M.; Saari-Nordhaus, R.; Anderson, J.M., Jr. J. Chromatogr. A **1994**, *671*, 309.
15. Hashimoto, S.; Otsuki, A. J. High Resolut. Chromatogr. **1998**, *21*, 55.
16. Martínez, D.; Farre, J.; Borrul, F.; Calull, M.; Ruana, J.; Colom, A. J. Chromatogr. A **1998**, *808*, 229.
17. Lalljie, S.P.D.; Vindevogel, J.; Sandra, P. J. Chromatogr. A **1993**, *652*, 563.
18. Chirao, M.; Furuta, R.; Suzuki, S.; Nakazawa, H.; Fujita, S.; Maruyama, T. J. Chromatogr. A **1994**, *680*, 247.
19. Devevre, O.; Putra, D.P.; Botton, B.; Garbaye, J. J. Chromatogr. A **1994**, *679*, 349.
20. Wu, C.H.; Lo, Y.S.; Lee, Y.-H.; Lin, T.-I. J. Chromatogr. A **1995**, *716*, 291.
21. Boden, J.; Darius, M.; Bachmann, K. J. Chromatogr. A **1995**, *716*, 311.
22. Haddad, P.R.; Harakuwe, A.H.; Buchberger, W. J. Chromatogr. A **1995**, *706*, 571.
23. Oehrle, S.A. J. Chromatogr. A **1996**, *739*, 413.
24. Roder, A.; Bachmann, K. J. Chromatogr. A **1995**, *689*, 305.
25. Buchberger, W.; Klampfl, C.W.; Eibensteiner, F.; Buchgraber, K. J. Chromatogr. A **1997**, *766*, 197.
26. Yarabe, H.H.; Shamsi, S.A.; Warner, I.M. Anal. Chem. **1998**, *70*, 1412.
27. Schnierle, P.; Kappes, T.; Hauser, P.C. Anal. Chem. **1998**, *70*, 3585.
28. Klampfl, C.W.; Buchberger, W. Trends Anal. Chem. **1997**, *16* (4), 221.

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