Journal of Applied Sciences

ISSN 1812-5654

science alert

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Journal of Applied Sciences 10 (1): 75-78, 2010
ISSN 1812-5654

Separation of Nine Haloacetic Acids in Water Samples by Ion Chromatography

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Abstract: Haloacetic acids (HAAs) are by-products from disinfection process in water treatment plant by the interaction of chlorine or other disinfectants with naturally occurring organic and inorganic matters in water. It has been causing concern due to potential harmful effect from long-term exposure. Separation of nine HAAs in water samples was developed by suppressed ion chromatography. The conditions were performed by using IonPac AS11HC (2×250 mm) ion exchange column, Potassium hydroxide (KOH) as the eluent with the gradient system and conductivity detector. All of analytes could be separated from fluoride, nitrate, chloride and sulfate ion, which commonly anions occur in drinking water, by using the two optimized gradient systems. The linearity of MCAA, DCAA, TCAA, MBAA, DBAA, TBAA, BCAA, BDCAA and DBCAA were 7-1000, 5-1000, 5-1000, 7-1000, 10-1000, 300-1200, 5-1000, 10-1000 and 200-1000 μg L^{-1}, respectively, with the correlation coefficient in the range of 0.9871-0.9991. The detection limits were 7, 5, 5, 7, 10, 200, 5, 10 and 170 μg L^{-1}, respectively. The repeatabilities of the peak area (%RSD, n = 5) were found in the range of 0.90-4.57% and the reproducibility in the range of 1.35-7.62%RSD.

Key words: Organic pollutant, haloacetic acid, disinfection by product, ion chromatography

INTRODUCTION

Disinfection is an important step in ensuring that water is safe to drink. Disinfectants system is used to destroy microorganism that can cause disease in humans. During disinfection processes, water treatment leads to the formation of Disinfection by-Products (DBPs). The major categories of DBPs such as trihalomethanes, haloacetic acids, haloacetonitriles, haloketones, chlorophenols, chloropicrin and chloral hydrate (Dojlido *et al*., 1999). The DBPs in drinking waters have been causing concern due to potential harmful effect from long-term exposure. It was arised upon the discovery of the potential health hazards associated with the formation of trihalomethanes during chlorination. These compounds lead to other DBPs such as the haloacetic acids (HAAs), which may pose similar long-term health risk to human and animal (Bove *et al*., 1995; Wright *et al*., 2004).

Haloacetic acids (HAAs) are carboxylic acids in which a halogen atom takes place of hydrogen atom in acetic acid. HAAs are a group of chemicals that formed along with other disinfection by-products when chlorine or other disinfectants used to control microbial contaminants in drinking water reacted with naturally occurring organic and inorganic matter in water. Some of HAAs like dichloroacetic acid is classified as probable carcinogens (Clark and Boutin, 2001). There are nine haloacetic acids, five of them (HAA5) are regulated including monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA) and dibromoacetic acid (DBAA). The current drinking water maximum contaminant level for HAA5 was regulating at 60 μg L^{-1} (US Environmental Protection Agency, 2008). The four unregulated include bromochloroacetic acid (BCAA), tribromoacetic acid (TBAA), bromodichloroacetic acid (BDCAA) and chlorodibromoacetic acid (CDBAA).

Determination of HAAs in drinking waters have several methods such as gas chromatography (Sarrion *et al*., 1999; Zhang and Minear, 2002; Domino *et al*., 2004; Golfinopoulos and Nikolaou, 2005; Malliarou *et al*., 2005), high performance liquid chromatography (Wang *et al*., 2005; Ghassempour *et al*., 2006), capillary electrophoresis (Martinez *et al*., 1998) and Ion Chromatography (IC) (Liu and Mou, 2003; Paull and Barron, 2004). Liu *et al*. (2004) developed IC method for determination of chlorination haloacetic acids: MCAA, DCAA and TCAA by using IonPac AS9HC (4×250 mm) column. The detection limits were 0.06, 0.14 and 0.85 μg L^{-1}, respectively. Sarzanini *et al*. (1999) determined of five HAAs: MBAA, DBAA, TBAA, DCAA and TCAA by reversed-phase ion interaction chromatography with UV detection. The result showed

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good detection limits range from 25-207 μg L^{-1} for ion interaction-based method couple with suppressed conductivity, and the detection limits range from 7-40 μg L^{-1} for non-suppressed conductivity. Barron and Paull (2004) determined MBAA, DBAA, MCAA, DCAA, TCAA, chlorodifluoroacetic acid (CDFAA) and trifluoroacetic acids (TFAA) by using two column; AS11HC (2×250 mm) and AS16 (2×250 mm) column. In all the above methods, only 3-7 HAAs species were determined, but nine HAAs might be contaminated in drinking waters. Therefore, the objective of this research is to develop a method for the separation of nine HAAs and some common ions by ion chromatograph.

MATERIALS AND METHODS

Instrumentation: Ion chromatography DX500 (Dionex, Sunnyvale, CA, USA) consist of a GP50 pump, CD 20 conductivity detector complete with ASRS Ultra (2 mm, Dionex) suppressor was used. Separations were carried out with IonPac AS11HC (2×250 mm) ion exchange columns and potassium hydroxide as mobile phase. The injector loop volume was 200 μL. Instrument control data acquisition and analysis were carried out with Chromeleon Version 6.60 software (Dionex).

Chemicals: All chemicals used were of analytical grade and obtained from Aldrich (Milwaukee, USA). Standard stock solutions of MBAA, MCAA, DBAA, DCAA, TBAA, TCAA, BCAA, DBCAA and BDCAA were prepared to a concentration of 5 mg L^{-1} and were stable for approximately 2 weeks when stored at 4°C. Working standards were prepared fresh daily using deionized water.

Optimization for separation of HAAs: A mixture of nine HAAs standard solution were injected into ion chromatograph. The various concentration of potassium hydroxide eluent and the flow rate were optimized.

Linearity ranges and detection limits: The linearity of mixed standard solution (0-1000 μg L^{-1}) of nine HAAs were examined by using the optimum conditions of ion chromatography. The detection limits were taken as the lowest concentration of HAAs that could be determined.

RESULTS AND DISCUSSION

HAAs were analyzed by the IonPac AS11HC column with conductivity detection. The strongly retained anions such as CDBAA and TBAA have intensive affinity on the column, which must be used stronger affinity eluent

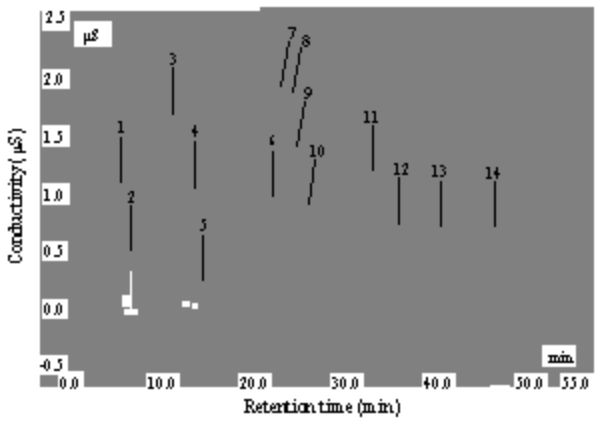

Fig. 1: The chromatogram of nine HAAs standard solutions and common ions on IonPac AS11HC column with KOH gradient system started from 2 mM KOH for 15 min then increased to 55 mM at 30 min with the flow rate 0.35 mL min^{-1} and held for a further 25 min with the flow rate 0.38 mL min^{-1}. (1) fluoride ion, (2) acetate ion, (3) MCAA, (4) MBAA, (5) chloride ion, (6) unknown, (7) nitrate, (8) DCAA, (9) BCAA+sulfate ion, (10) DBAA, (11) TCAA, (12) BDCAA, (13) CDBAA, (14) TBAA

(Liu and Mou, 2003). In order to separate the weakly retained anions such as fluoride ion, acetate ion and MCAA, a weak eluent should be used (Sun and Gu, 2007). Therefore, a gradient system of KOH mobile phase was employed, the result found agreement with the previous study (Barron and Paull, 2004). The condition of mobile phase for separated of nine HAAs were started from 2 mM held for 15 min then increased to 55 mM at 30 min with the flow rate 0.35 mL min^{-1} and held for a further 25 min with the flow rate 0.38 mL min^{-1}. The chromatogram is showed in Fig. 1, nine HAAs can be separated with common ions; fluoride, acetate and nitrate ion. The weakly compounds (MCAA, MBAA, DCAA, BCAA and DBAA) were eluted in 26 min and the tightly bond BDCAA, CDBAA and TBAA were strong retained in the column, therefore low intensity of two compounds were obtained. The peak signal of BCAA was overlapped with the sulfate ion, so the new gradient system was carried out to separate. The concentration of KOH started from 20 mM and held for 10 min with the flow rate 0.35 mL min^{-1} and then increased to 55 mM at 42 min with the flow rate 0.38 mL min^{-1}. The results found that the weakly retained ions could not be separated and sulfate ion was overlap with DCAA, but BCAA can be separated, as shown in Fig. 2. For analysis of the real water sample that, the eight of HAAs; MCAA, MBAA, DCAA, DBAA, TCAA, BDCAA, CDBAA and TBAA can be analyzed

Table 1: Analytical performance data for HAAs and detection limits

HAAs	Linearity range (μg L^{-1})	Linear equation	Correlation coefficient (R^2)	Detection limit (μg L^{-1})	Repeatability (%RSD, n = 5)	Reproducibility (%RSD, n = 3)
MCAA	7-1000	$y = 1.3\times10^{-4}X - 1.4\times10^{-4}$	0.9991	7	6.86	4.20
MBAA	7-1000	$y = 0.2\times10^{-4}X - 4.7\times10^{-4}$	0.9976	7	0.90	3.32
DCAA	5-1000	$y = 0.7\times10^{-4}X - 2.4\times10^{-3}$	0.9871	5	2.93	3.00
BCAA	5-1000	$y = 0.7\times10^{-4}X + 0.3\times10^{-3}$	0.9981	5	3.46	3.14
DBAA	10-1000	$y = 0.4\times10^{-4}X - 4.6\times10^{-4}$	0.9990	10	3.31	1.35
TCAA	5-1000	$y = 2.4\times10^{-4}X - 2.2\times10^{-3}$	0.9977	5	2.41	7.62
BDCAA	10-1000	$y = 0.4\times10^{-4}X + 8.6\times10^{-4}$	0.9980	10	3.42	7.62
CDBAA	200-1000	$y = 0.2\times10^{-4}X - 4.5\times10^{-4}$	0.9982	170	4.57	6.58
TBAA	300-1000	$y = 0.2\times10^{-4}X + 5.3\times10^{-4}$	0.9966	200	3.50	5.76

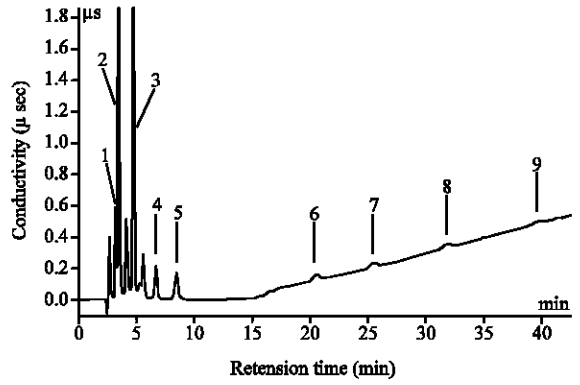

Fig. 2: Chromatogram of nine HAAs standard solutions on IonPac AS11HC column with 20 mM KOH for 10 min with the flow rate 0.35 mL min^{-1} and increased to 55 mM at 42 min with the flow rate of 0.38 mL min^{-1} (1) MCAA, (2) MBAA+chloride ion, (3) DCAA+sulfate ion, (4) BCAA, (5) DBAA, (6) TCAA, (7) BDCAA, (8) CDBAA, (9) TBAA

with the first gradient system and BCAA should be individual analyzed with the new gradient system.

Linearity ranges and detection limits: The linearities of nine HAAs: MCAA, MBAA, DCAA, BCAA, DBAA, TCAA, BDCAA, CDBAA and TBAA were 7-1000, 7-1000, 5-1000, 5-1000, 10-1000, 5-1000, 10-1000, 200-1000 and 300-1000 μg L^{-1}, respectively. The correlation coefficients were ranging from 0.9871-0.9991. The detection limits were 7, 7, 5, 5, 10, 5, 10, 170 and 200 μg L^{-1}, respectively. The results are summarized in Table 1. The repeatability (%RSD, n = 5) were in the range of 0.90-4.57% and reproducibilities were in the range of 1.35-7.62% RSD.

CONCLUSION

Separation of nine HAAs were performed by ion chromatograph using IonPac AS11HC column and potassium hydroxide as mobile phase. All of analytes could be separated from fluoride, nitrate, chloride and sulfate ion, which commonly anions occur in drinking water, with the two optimized gradient systems. The first optimum gradient system for separation of eight HAAs, fluoride, nitrate, chloride ion was started from 2 mM KOH for 15 min then increased to 55 mM at 30 min with the flow rate 0.35 mL min^{-1} and held for a further 10 min with the flow rate 0.38 mL min^{-1}. The second gradient system for separation of BCAA and sulfate ion was started from 20 mM and held for 10 min with the flow rate 0.35 mL min^{-1} and then increased to 55 mM at 42 min with the flow rate 0.38 mL min^{-1}. The advantage of this method is simple which can direct injection without sample preparation, high precision with the relative standard deviation of 0.90-4.57% and showed high reproducibility with the relative standard deviation in the range of 1.35-7.62%.

The optimum chromatographic conditions were applied to analysis of water samples which collected from tap water and bottled drinking water in Maha-Sarakham province, Thailand. The HAAs were not found in all samples, it might be that HAAs content in water samples were less than the detection limits. Therefore, preconcentration method is necessary to develop in the further study.

ACKNOWLEDGMENT

This research has been financially support from Center of Excellence for Innovation in Chemistry (PERCH-CIC), Commission on Higher Education, Ministry of Education and research grant from Mahasarakham University.

REFERENCES

Barron, L. and B. Paull, 2004. Determination of bromate and chlorinated haloacetic acids in bottled drinking water with chromatographic methods. Anal. Chim. Acta, 522: 153-161.

Bove, F.J., M.C. Fulcomer, J.B. Klotz, J. Esmart, E.M. Dufficy and J.E. Savrin, 1995. Public drinking water contamination and birth outcomes. Am. J. Epidemiol., 141: 850-862.

Clark, R.M. and B.K. Boutin, 2001. Controlling Disinfection By-Products and Microbial Contamination in Drinking Water. National Center for Environmental Assessment, Office of Research and Development, US EPA, Ohio, USA.

Dojlido, J., E. Zbiec and R. Swietlik, 1999. Formation of the haloacetic acids during ozonation and chlorination of water in warsaw waterworks (Poland). Water Res., 33: 3111-3118.

Domino, M.M., B.V. Pepich, D.J. Munch and P.S. Fair, 2004. Optimizing the determination of haloacetic acids in drinking waters. J. Chromatogr. A., 1035: 9-16.

Ghassempour, A., S. Chalavi, A. Abdollahpour and S.A. Mirkhani, 2006. Determination of mono-and dichloroacetic acids in betaine media by liquid chromatography. Talanta, 68: 1396-1400.

Golfinopoulos, S.K. and A.D. Nikolaou, 2005. Survey of disinfection by-products in drinking water in Athen, Greece. Desalination, 176: 13-24.

Liu, Y. and S. Mou, 2003. Determination of trace levels of haloacetic acids and perchlorate in drinking water by ion chromatography with direct injection. J. Chromatogr. A., 997: 225-235.

Liu, Y., S. Mou and D. Chen, 2004. Determination of trace-level haloacetic acids in drinking water by ion chromatography-inductively coupled plasma mass spectrometry. J. Chromatogr. A., 1039: 89-95.

Malliarou, E., C. Collins, N. Graham and M.J. Nieuwenhuijsen, 2005. Haloacetic acids in drinking water in the United Kingdom. Water Res., 39: 2722-2730.

Martínez, D., J. Farré, F. Borrull, M. Calull, J. Ruana and A. Colom, 1998. Capillary zone electrophoresis with indirect UV detection of haloacetic acids in water. J. Chromatogr. A., 808: 229-236.

Paull, B. and L. Barron, 2004. Using ion chromatography to monitor haloacetic acids in drinking water: A review of current technologies. J. Chromatogr. A., 1046: 1-9.

Sarrion, M.N., F.J. Santos and M.T. Galceran, 1999. Solid-phase microextraction coupled with gas chromatography-ion trap mass spectrometry for the analysis of haloacetic acids in water. J. Chromatogr. A., 859: 159-171.

Sarzanini, C., M.C. Bruzzoniti and E. Mentasti, 1999. Use of temperature programming to improve resolution of inorganic anions, haloacetic acids and oxyhalides in drinking water by suppressed ion chromatography. J. Chromatogr. A., 850: 197-211.

Sun, Y. and P. Gu, 2007. Determination of haloacetic acids in hospital effluent after chlorination by ion chromatography. J. Environ. Sci., 19: 885-891.

US Environmental Protection Agency, 2008. Disinfection byproducts: A reference resource. http://www.cummingutilities.com/Disinfection_Byproducts_and_THMs_2005.pdf.

Wang, X., S. Saridara and S. Mitra, 2005. Microfluidic supported liquid membrane extraction. Anal. Chim. Acta, 543: 92-98.

Wright, J., J. Schwartz and D.W. Dockery, 2004. The effect of disinfection by-products and mutagenic activity on birth weight and gestational duration. Environ. Health Perspect., 112: 920-925.

Zhang, X. and R.A. Minear, 2002. Decomposition of trihaloacetic acids and formation of the corresponding trihalomethanes in drinking water. Water Res., 36: 3665-3673.