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Trace Analysis of Haloacetic Acids in Water Samples in Maha-Sarakham Province, Thailand

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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 matters in water. It has been causing concern due to potential harmful effect from long-term exposure. Determination of HAAs were performed by using IonPac AS11HC (2x250 mm) ion exchange column, Potassium hydroxide (KOH) as the eluent with the gradient system and conductivity detector. All of HAAs 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 recovery percentages were ranged between 88.27 to 103.39 under 20-fold preconcentration by using 3 mL (200 mg) Lichrolut EN solid-phase. The detection limits of solid–phase extraction were ranged between 0.70 to 30 μgL^{-1} and reproducibility in the range of 1.35-7.62 %RSD. This proposed method was successfully applied to analysis of trace nine HAAs in water resource, tap water and bottled water samples.

Key words: water analysis · Solid-phase extraction · Ion chromatograph · Disinfection by products

INTRODUCTION

Chlorination is the process of adding chlorine to water as disinfectant to destroy microorganism that can cause disease in humans. Disinfection process can be problematic that chlorine can react with natural organic compounds in water to produce some compounds, known as disinfection by-products (DBPs). The major categories of DBPs such as trihalomethanes, haloacetic acids, haloacetonitriles, haloketones, chlorophenols, chloropicrin and chloral hydrate [1, 2]. DBPs in drinking waters have been causing concern due to potential harmful effect from long-term exposure. It was arise upon the discovery of the potential health hazard 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 [3, 4].

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 are 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 [2]. 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 μgL^{-1} [5]. The four unregulated include bromochloro aceticacid (BCAA), tribromoacetic acid (TBAA), bromodichloroacetic acid (BDCAA) and chlorodibromoacetic acid (CDBAA).

Determination of HAAs in drinking waters have several methods for separation and detection, such as gas chromatography (GC) [6-10], high performance liquid chromatography (HPLC) [11, 12], capillary electrophoresis (CE) [13] and ion chromatography (IC) [14]. Liu *et al.* [15] developed IC method for determination of chlorination haloacetic acids: MCAA, DCAA and TCAA by using IonPac AS9HC (4x250 mm) column. Sarzanini *et al.* [16] determined of five HAAs: MBAA, DBAA, TBAA, DCAA and TCAA by reversed-phase ion interaction chromatography with UV detection. Barron and Paull [17] determined MBAA, DBAA, MCAA, DCAA, TCAA, chlorodifluoro- (CDFAA) and trifluoroacetic acids (TFAA) by using two column; AS11HC (2x250 mm) column and AS16 (2x250 mm) column. Simone *et al.* [18]

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developed the post column reaction with nicotanamide to measure the concentration of five regulated HAAs. Sun and Gu [19] used solid phase extraction to determination of HAA5 in hospital wastewater samples. Liu and Mou [20] determined some haloacetic acids and perchlorate in drinking water by ion chromatography with direct injection. In all the above methods, only 3-7 HAAs species were determined, whereas nine HAAs might be contaminated in drinking waters. Therefore, the objective of this research is to develop a simple and rapid method for determination of trace nine HAAs in waters by ion chromatograph. This proposed method was applied to analysis of HAAs in water samples in Maha-Sarakham Province, Thailand.

MATERIALS AND METHODS

Instrumentation: Ion chromatography DX500 (Dionex, USA) consists of a GP50 pump, CD20 conductivity detector complete with ASRS Ultra (2 mm) suppressor was used. Separations were carried out with IonPac AS11HC (2x250 mm) ion exchange column 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 analytical grade and obtained from Aldrich (USA). Standard stock solutions of monobromoacetic acid (MBAA), monochloroacetic acid (MCAA), dibromoacetic acid (DBAA), dichloroacetic acid (DCAA), tribromoacetic acid (TBAA), trichloroacetic acid (TCAA), bromochloroacetic acid (BCAA), dibromochloroacetic acid (DBCAA) and bromodichloroacetic acid (BDCAA) were prepared to a concentration of 5 mgL^{-1} and stable for approximately 2 weeks when stored at 4°C. Working standards were prepared fresh daily using deionized water.

The 3 ml solid phase extraction columns were packed with 200 mg LiChrolut EN (Merck, Germany). The solid phase manifold with the vacuum pump (Supelco, USA) was used.

Optimization of Ion Chromatography 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 Range and Detection Limits: The linearity of mixed standard solution (0-1000 μgL^{-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.

Optimization of Solid Phase Extraction: Prior to extraction, the solid phase extraction (SPE) columns were conditioned with 5 ml methanol under vacuum, following with 3 ml of 200mM sulfuric acid. The 100 ml of acidified spiked sample ($50\mu gL^{-1}$) of each HAAs was carried out by adding concentrated sulfuric acid and subsequently passed through the SPE column. The 10 ml of deionized water was used to cleanup, after that drying the SPE column then eluted with 10 mM potassium hydroxide. The result solution was passed through the OnGaurd IC-Ba and IC-Ag to remove sulfate and chloride ion and then injected into ion chromatograph using the optimum chromatographic conditions.

The detection limits were taken as the lowest concentration of HAAs that could be simultaneously extracted with the optimum condition and yielding good recoveries.

Applications: Haloacetic acids in water samples which collected from the surface water in Mahasarakham university, water treatment plant from provincial waterworks authority, tap water from water supply lines in MahaSarakham province and bottled drinking water samples purchased in MahaSarakham province were analyzed by using the optimization conditions.

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 eluent with stronger affinity [18]. In order to separate the weakly retained anions such as fluoride ion, acetate ion and MCAA, a weak eluent should be used. Therefore, a gradient system of KOH mobile phase was employed. 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 $mLmin^{-1}$ and held for a further 10 min with the flow rate 0.38 $mLmin^{-1}$, as shown in Figure 1. The nine HAAs can be separated with common ions; fluoride, acetate and nitrate ion. The weakly compounds (MCAA, MBAA, DCAA, BCAA and DBAA)

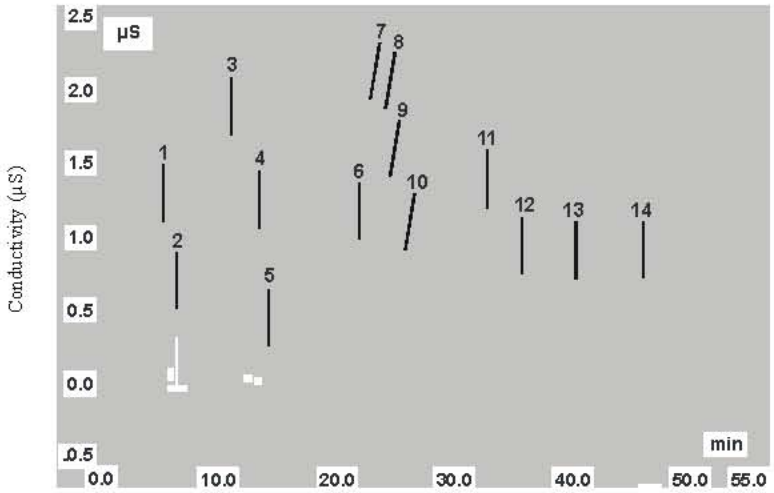

Fig. 1: The chromatogram of nine HAAs standard solutions and common ions on IonPac AS11HC column with KOH gradient system started from 2 mM KOH held for 15 min then increased to 55 mM at 30 min with the flow rate 0.35 $mLmin^{-1}$ and held for a further 25 min with the flow rate 0.38 $mLmin^{-1}$. (1)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

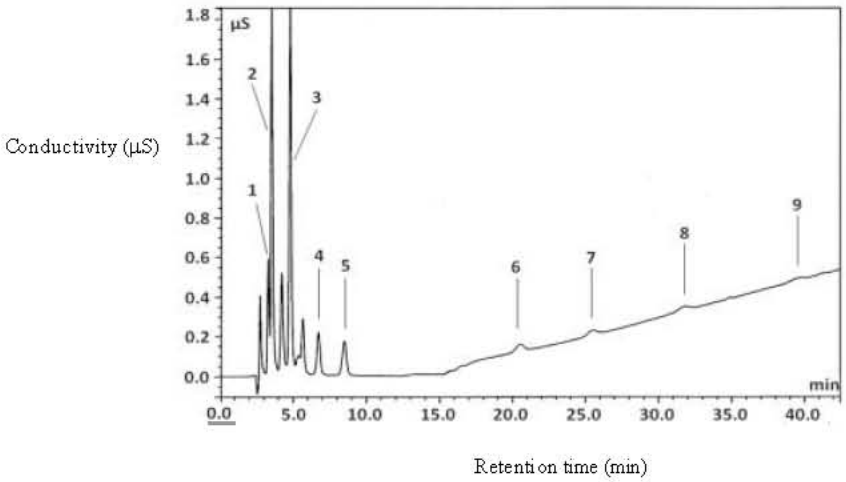

Fig. 2: Chromatogram of nine HAAs standard solutions on IonPac AS11HC column with 20 mM KOH for 10 min with the flow rate 0.35 $mLmin^{-1}$ and increased to 55 mM at 42 min with the flow rate of 0.38 $mLmin^{-1}$ (1) MCAA, (2) MBAA+chloride ion, (3) DCAA+sulfate ion, (4) BCAA, (5) DBAA, (6) TCAA, (7)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

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 $mLmin^{-1}$ and then increased to 55 mM at 42 min with the flow rate 0.38 $mLmin^{-1}$. The results found that the weakly retained ions could not be separated and sulfate ion was overlapped with DCAA, but BCAA can be separated, as shown in Figure 2. For analysis of the real water sample, the eight of HAAs; MCAA, MBAA, DCAA, DBAA, TCAA, BDCAA, CDBAA and TBAA can be analyzed with the first gradient system and BCAA should be individual analyzed with the new gradient system.

Table 1: Analytical performance data for HAAs and detection limits using ion chromatography

HAAs	Linearity (μgL^{-1})	Linear equation	Correlation coefficient (R^2)	Detection limit (μgL^{-1})	Repeatability (%RSD, n=5)
MCAA	7-1000	$y= 1.3x10^{-4}X - 1.4x10^{-4}$	0.9991	7	6.86
MBAA	7-1000	$y= 0.2 x10^{-4}X - 4.7x10^{-4}$	0.9976	7	0.90
DCAA	5-1000	$y= 0.7x10^{-4}X - 2.4x10^{-3}$	0.9871	5	5.93
BCAA	5-1000	$y= 0.7x10^{-4}X + 0.3x10^{-3}$	0.9981	5	7.46
DBAA	10-1000	$y= 0.4x10^{-4}X - 4.6x10^{-4}$	0.9990	10	3.31
TCAA	5-1000	$y= 2.4x10^{-4}X - 2.2x10^{-3}$	0.9977	5	5.41
BDCAA	10-1000	$y= 0.4x10^{-4}X + 8.6x10^{-4}$	0.9980	10	7.42
CDBAA	200-1000	$y= 0.2x10^{-4}X - 4.5x10^{-4}$	0.9982	170	9.57
TBAA	300-1000	$y= 0.2x10^{-4}X + 5.3x10^{-4}$	0.9966	200	6.50

Table 2: The percentage recoveries of SPE method with difference load rate and pH of the sample

	load rate		Effect of pH		
HAAs	1ml/min	2 ml/min	0.5	1	2
MCAA	103.39	6.23	98.60	7.33	8.05
MBAA	104.45	0.00	104.45	0.00	0.00
DCAA	103.60	19.30	103.60	0.00	0.00
BCAA	93.02	10.97	93.02	37.70	31.26
DBAA	103.68	18.75	96.85	28.52	15.10
TCAA	80.58	16.08	80.58	28.44	19.04
BDCAA	90.81	34.55	90.81	31.67	29.24
CDBAA	97.70	25.85	97.70	27.24	11.92
TBAA	78.27	14.39	78.27	21.40	19.77

Table 3: The percentage recoveries and detection limit of solid phase extraction and reproducibility

HAAs	%Recovery ±RSD	Detection limit (μgL^{-1})	Reproducibility (%RSD, n=3 days)
MCAA	98.60±0.12	1.00	4.20
MBAA	96.36±0.06	2.50	3.32
DCAA	103.39±0.01	1.00	3.00
BCAA	93.02±0.01	0.70	3.14
DBAA	88.13±0.16	5.00	1.35
TCAA	93.85±0.12	3.00	7.62
BDCAA	90.81±0.14	1.50	7.62
CDBAA	97.70±0.04	15.00	6.58
TBAA	88.27±0.07	30.00	5.76

Table 4: Haloacetic acids concentration (µg/l ± RSD, n=3) in water sample (August 2009)

Water sample		MCAA	MBAA	DCAA	BCAA	DBAA	TCAA	BDCAA	CDBAA	TBAA
Surface water	1	4.77±0.01	nd	16.64±0.01	nd	8.48±0.18	1.70±0.21	nd	9.65±0.01	2.45±0.01
	2	3.62±0.02	nd	107.99±0.04	nd	4.58±0.68	1.54±0.20	nd	nd	nd
	3	3.03±0.01	nd	11.09±0.03	nd	nd	1.95±0.01	0.23±0.14	6.33±0.25	nd
	4	2.54±.0.07	nd	60.78±0.02	nd	nd	2.14±0.01	nd	12.80±0.07	nd
	5	2.13±0.07	nd	10.47±0.10	3.35±0.05	4.010.16	1.0±90.01	nd	nd	nd
Water treatment plant		0.49±0.07	nd	10.61±0.17	nd	4.54±0.05	6.90±0.22	3.94±1.18	5.30±0.85	50.63±1.10
Tap water	1	1.61±0.02	nd	29.86±1.84	2.96±0.02	nd	nd	22.46±0.44	nd	0.28±0.11
	2	2.05±0.08	nd	13.49±0.05	nd	nd	1.08±0.03	nd	nd	nd
	3	0.66±0.17	nd	14.30±2.71	0.92±0.03	nd	4.81±0.08	nd	9.33±2.16	nd
	4	0.78±0.01	nd	14.34±0.80	nd	6.56±0.94	6.37±0.01	1.98±0.42	3.95±0.71	48.70±5.66
Bottled drinking water	1	1.61±0.01	nd	nd	nd	nd	nd	nd	nd	nd
	2	1.59±0.03	nd	nd	nd	nd	nd	24.31±0.13	nd	0.57±0.90
	3	1.30±0.01	nd	nd	nd	nd	nd	8.48±0.01	nd	7.15±0.04
	4	1.14±0.01	nd	nd	nd	nd	nd	18.43±0.01	nd	nd
	5	1.36±0.01	nd	nd	nd	nd	nd	4.13±0.01	nd	nd
	6	1.62±0.01	nd	nd	nd	nd	nd	9.53±0.01	nd	nd
	7	0.40±0.02	nd	nd	nd	nd	1.04±0.04	nd	nd	nd
	8	0.38±0.05	nd	nd	nd	nd	1.15±0.04	nd	nd	nd
	9	0.33±0.02	nd	nd	nd	nd	1.09±0.02	nd	nd	nd
	10	0.62±0.04	nd	nd	nd	nd	nd	nd	nd	nd

*nd= not detected, lower than detection limit

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 μgL^{-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 μgL^{-1}, respectively. The results are summarized in Table 1. The repeatability (%RSD, n=5) were in the range of 0.90-9.57%.

Optimization of Solid Phase Extraction: As part of optimization of the preconcentration step, it was necessary of assess the effect of sample loading rate upon HAAs recoveries. Barron and Paull [17] prescribed the use of sample load rate of 1 $mLmin^{-1}$. Hence, the load rate of 1 and 2 $mLmin^{-1}$ were investigated. The recoveries were decreased with increasing of the loading rate, as shown in Table 2.

The LiChrolute EN sorbent has a high degree of cross-linking and high porosity [21] and the pKa of HAAs are in the range 0.65-2.86 [19]. Therefore adjust pH of the sample solution was also necessary before loading. The pH of spiked sample solution was achieved at 0.5, 1 and 2. The optimum pH was found at 0.5, as shown in Table 2.

Under the 20 fold preconcentration, the percentage recoveries of HAAs using solid-phase extraction were ranging 78.27-103.39. The detection limits were found in the range of 0.70-30 μgL^{-1} and the reproducibility was ranging 3.14-8.75 %RSD, as shown in Table 3.

Haloacetic Acids Concentration in Water Samples: The optimum SPE method was applied to analysis of water samples which collected from surface water in Mahasarakham university, tap water and drinking water in MahaSarakham province, Thailand, as summarized in Table 4. The MCAA was found in all water samples. The DCAA was the major compounds in water resource samples and tap water samples. The seven HAAs; MCAA, DCAA, DBAA, TCAA, BDCAA, CDBAA and TBAA were found in the water from treatment plant, the regulated HAA5 were found within the regulated values (60 μgL^{-1}). The MBAA was not found in all samples and DCAA, BCAA and CDBAA were also not found in all bottled drinking samples.

CONCLUSION

Determination of nine HAAs were performed by ion chromatograph using IonPac AS11HC column with potassium hydroxide in gradient system as mobile phase. All of nine HAAs could be separated from common ions; fluoride, nitrate, chloride and sulfate ion by using the optimized two gradient system The preconcentration method by using solid-phase extraction provides good recoveries and low detection limit in range of 0.70-30 μgL^{-1} under the 20 fold preconcentration factor. Application of this proposed method was successful to investigation of HAAs in natural water, tap water and drinking water samples. The concentration levels of HAAs obtained were slightly varied from the location of water samples.

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REFERENCES

1. Dojlido, J., E. Zbiec and R. Swietlik, 1999. Formation of the haloacetic acids during ozonation and chlorination of water in warsaw waterworks (Poland). Water Research, 33: 3111-3118.
2. 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.
3. 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., Amercan J. Epidemiol., 141: 850-862.
4. Wright, J.M., J. Schwartz and D.W. Dockery, 2004. The effect of disinfection by-products and mutagenic activity on birth weight and gestational duration. Environmental Health. Perspective, 112: 920-925.
5. US Environmental Protection Agency, 2008. Disinfection Byproducts: A Reference Resource. Available from: URL: http: //www.epa.gov/enviro/html/icr/dbp.html. February 2nd.
6. Malliarou, E., C. Collins, N. Graham and M.J. Nieuwenhuijsen, 2005. Haloacetic acids in drinking water in the United Kingdom. Water Research, 39: 2722-2730.
7. Zhang, X. and R.A. Minear, 2002. Decomposition of trihaloacetic acids and formation of the corresponding trihalomethanes in drinking water. Water Research, 36: 3665-3673.
8. Domino, M.M., B.V. Pepich, D.J. Munch and P.S. Fair, 2004. Optimizing the determination of haloacetic acids in drinking waters. Journal of Chromatography A, 1035: 9-16.

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. Journal of Chromatography A, 859: 159-171.
10. Golfinopoulos, S.K. and A.D. Nikolaou, 2005. Survey of disinfection by-products in drinking water in Athens, Greece. Desalination., 176: 13-24.
11. Wang, X., S. Saridara and S. Mitra, 2005. Microfluidic supported liquid membrane extraction. Anal. ytica Chimica Acta, 543: 92-98.
12. Ghassempour, A., S. Chalavi, A. Abdollahpour and S.A. Mirkhani, 2006. Determination of mono- and dichloro- acetic acids in betaine media by liquid chromatography. Talanta, 68: 1396-1400.
13. 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. Journal of Chromatography A, 808: 229-236.
14. Paull, B. and L. Barron, 2004. Using ion chromatography to monitor haloacetic acids in drinking water: a review of current technologies. Journal of Chromatography A, 1046: 1-9.
15. 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. Journal of Chromatography. A, 1039: 89-95.
16. 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. Journal of Chromatography A, 850: 197-211.
17. Barron, L. and B. Paull, 2004. Determination of bromate and chlorinated haloacetic acids in bottled drinking water with chromatographic methods. Analytica Chimica Acta, 522: 153-161.
18. Simone, P.S., G.T. Anderson and G.L. Emmert, 2006. on the monitoring of μg/l levels of haloacetic acids using ion chromatography with post-column nicotinamide reaction and fluorescence detection. Analytica Chimica Acta, 570(2): 259-266.
19. Sun, Y. and P. Gu, 2007. Determination of haloacetic acids in hospital effluent after chlorination by ion chromatography. J. Environ. Sci., 19(7): 885-891.
20. Liu, Y. and S. Mou, 2003. Determination of trace levels of haloacetic acids and perchlorate in drinking water by ion chromatography with direct injection. Journal of Chromatography A, 997: 225-235.
21. Martinez, D., F. Borrull and M. Calull, 1998 Comparable study of solid-phase extraction system couples to capillary electrophoresis in the determination of haloacetic compounds in tap water. Journal of Chromatography. A, 827: 105-112.