Research Journal of Applied Sciences 4 (2): 80-84, 2009
ISSN: 1815-932X

Evaluation of Headspace Solid-Phase Microextraction and Direct Solid-Phase Microextraction for Analysis of Trihalomethanes in Water Samples

N. Saesim and W. Kanchanamayoon
Department of Chemistry, Faculty of Science, Mahasarakham University,
Kantharawichai, Mahasarakham, 44150, Thailand

Abstract: The chlorination process is one of the water treatment plant used for the disinfection of water. The disinfection by products are trihalomethanes such as chloroform, bromodichloromethane, dibromochloromethane and bromoform. Headspace Solid-Phase Microextraction (HS-SPME) and Direct Solid-Phase Microextraction (DI-SPME) (100 μm polydimethylsiloxane fiber) were studied for analysis of trihalomethanes in water samples. The effect of stirring rate, extraction time, extraction temperature and desorption time on the analysis were investigated. The linearity, detection limit and repeatability were evaluated by using the optimized HS-SPME and DI-SPME techniques. The percentage recoveries by spiking samples with standard solutions of THMs were also examined and compared with the conventional liquid-liquid extraction. The percentage recoveries of HS-SPME and DI-SPME techniques showed no significant difference by using t-test (95% probability). The results can be concluded that HS-SPME technique has a great potential for determination of trihalomethanes with lower limit of detection.

Key words: Solid phase mocroextraction, trihalomethanes, gas chromatography, water analysis

INTRODUCTION

Trihalomethanes (THMs) are the major disinfection by-products, resulted from the reaction of chlorine with naturally occurring organic matter, principally humic acid and fulvic acid (Cho *et al*., 2003). The THMs formed are Chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloro-methane ($CHBr_2Cl$) and bromoform ($CHBr_3$). They are all considered to be possible carcinogen. US-EPA has established maximum contaminant level for total THMs concentration in drinking water at 80 μg L^{-1} (Tor and Aydin, 2006). The analytical methods have been reported for analysis of THMs in water such as liquid-liquid extraction (Golfinopoulos and Nikolaou, 2005), purge and trap method (Zygmunt, 1996), headspace solid-phase microextraction (Stack *et al*., 2001; Cho *et al*., 2003) and headspace liquid phase microextraction (Tor and Aydin, 2006).

The solid-phase microextraction is a solvent free process used for simultaneous extraction and preconcentration of analytes. There are several types of solid-phase microextraction fibers, the selectivity of method depend on the polarity and the film thickness of the coating phase. There are two modes of solid-phase microextraction sampling: Direct Immersed Solid Phase Microextraction (DI-SPME) and Headspace Solid-Phase Microextraction (HS-SPME).

The objective of this study was to evaluation of HS-SPME and DI-SPME conditions for determination of THMs using gas chromatography with electron capture detector. The linearity, limit of detection, percentage recoveries and repeatability were investigated by optimum extraction conditions and compared with conventional standard liquid-liquid extraction.

MATERIALS AND METHODS

Instrumentation: Gas chromatograph is conducted with a varian model CX-3600 equipped with fused silica capillary column was CP Sil 5 CB (100% polydimethyl-siloxane) (15 m × 0.25 mm I.D., 0.25 μm film thickness, varian). The injector temperature was 220°C, electron capture detector temperature was 280°C and the column temperature program. The temperature program was started from 35°C held for 4 min, ramp to 75°C with the rate of 10°C min^{-1} and held 2 min, then ramp to 150°C with the rate of 30°C min^{-1} and held 3.5 min.

Corresponding Author: Wanna Kanchanamayoon, Department of Chemistry, Faculty of Science, Mahasarakham University, Kantharawichai, Mahasarakham, 44150, Thailand

Solid-phase microextraction fiber assembly fitted with 100 μm (nonbond) polydimethylsiloxane (Supelco, USA). The fibers were equilibrated at 250°C for 3 h prier to use and blank desorption.

Chemicals: The purity grade of Chloroform ($CHCl_3$), bromodichloro-methane ($CHBrCl_2$), dibromochloro-methame ($CHBr_2Cl$), bromofrom ($CHBr_3$) were obtained from Fluka (Switzerland). Methanol (Uropeon Union, Spain) and n-pentane (Carlo Erba, Italy) were HPLC grade. The water was ultrapure form MilliQ purification system and sodium chloride from Lab-Scan (Ireland). The standard solutions of each trihalomethane were prepared in methanol. All standard solutions are stable up to 4 weeks when stored at 4°C.

Solid Phase Microextraction (SPME)

Head Space Solid Phase Extraction (HS-SPME): The 1.8 mL ultrapure water was spiked with 1.0 μg L^{-1} of each THMs standard, then placed in a 4 mL amber glass vial, 25% (w v^{-1}) sodium chloride was added. The vial was sealed with a PTFE faced septum cap. The SPME fiber was then exposed to the headspace at various conditions: stirring rate, extraction time and extraction temperature. The extraction process was allowed to the equilibration of analytes between the aqueous phase and the headspace and immediately inserted into the injection port of gas chromatograph of various desorption time at 220°C.

Direct Solid Phase Microextraction (DI-SPME): The 1.8 mL ultrapure water was spiked with 1.0 μg L^{-1} of each THMs standard, then placed in a 2 mL amber glass vial. The vial was sealed with a PTFE-faced septum cap. The SPME fiber was immersed into the sample at various conditions: stirring rate, extraction time and extraction temperature. After sampling time, the SPME fiber was immediately inserted into the GC injection port of gas chromatograph of various desorption time at 220°C.

Extraction recoveries: The 1.8 mL water samples were spiked with 1, 5 and 10 μg L^{-1} of each THMs standard. The percentage recoveries investigated by the optimum extraction conditions for 7 replicates.

RESULTS AND DISCUSSION

A typical chromatogram of THMs is presented in Fig. 1. The retention time of $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$ were 1.305, 1.954, 3.358 and 5.613 min, respectively.

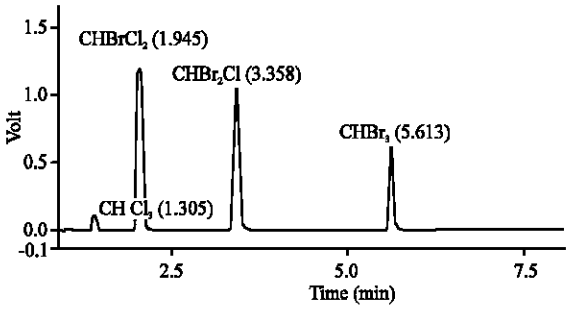

Fig. 1: Chromatogram of 20 μg L^{-1} THMs using a CP Sil 5 CB capillary column

Optimization of solid phase microextraction conditions

Effect of the addition of salt using HS-SPME technique: Addition of salts may result in the change of the partial pressure, solubility and surface tension of analyte enhance the partitioning into the fiber (Cho *et al*., 2003; Zhao *et al*., 2005). The high peak areas were achieved with salt addition compared to unsalt addition, as shown in Fig. 2.

Effect of stirring rate: The effects of stirring rate on the extraction of THMs by both HS-SPME and DI-SPME methods were performed using the extraction time of 6 min under 20°C and the desorption time of 2 min at 220°C. The peak areas obtained were increased with increasing the stirring rate up to 800 rpm for HS-SPME and up to 400 rpm for DI-SPME, as shown in Fig. 3. The result showed agreement with the earlier studies (Cho *et al*., 2003; Tor and Aydin, 2006; Zhao *et al*., 2005). Therefore, the stirring rate of 800 and 400 rpm were used in further experiment for HS-SPME and DI-SPME techniques, respectively.

Effect of extraction time: The effects of extraction time were performed with stirring rate 800 rpm for HS-SPME and 400 rpm for DI-SPME, extraction temperature at 20°C and desorption time 2 min at 220°C. The peak areas obtained were increased with increasing of extraction time up to 6 min for HS-SPME and up to 4 min for DI-SPME, as shown in Fig. 4. The equilibrium times of HS-SPME are found longer than DI-SPME, indicating that the diffusion of the analytes from the liquid phase into the headspace needed longer equilibrium time than direct immersing. The peak areas obtained from HS-SPME are found higher than DI-SPME technique. The optimum extraction times for HS-SPME technique was 6 min and for DI-SPME technique was 4 min.

Effect of extraction temperature: In order to evaluate, the extraction efficiency, the experiment was performed with

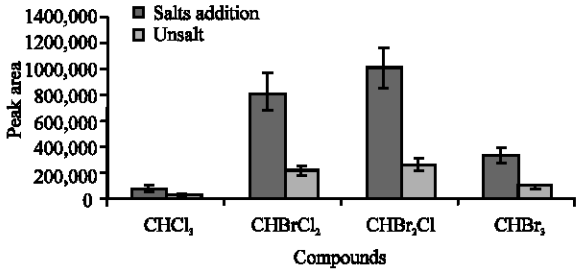

Fig. 2: The effect of salt addition on HS-SPME extraction of 5 μg L^{-1} THMs, stirring rate 600 rpm min^{-1}, extraction time 6 min at ambient temperature, desorption time 2 min at 220°C

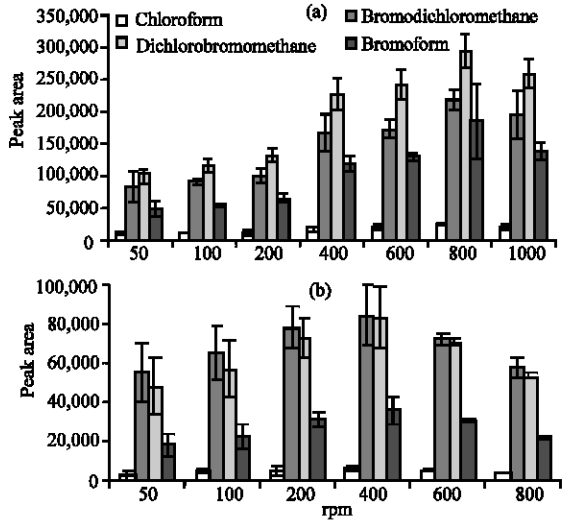

Fig. 3: Effect of stirring rate on extraction of 1 μg L^{-1} THMs: extraction time 6 min at ambient temperature, desorption time 2 min at 220°C (a) HS-SPME, 25% (w v^{-1}) NaCl (b) DI-SPME

the optimum condition of stirring rate and the extraction time, the desorption temperature of 2 min at 220°C. In the headspace mode, increasing the extraction temperature decreased the distribution constants on exothermic process and the amount of analytes adsorbed onto the fiber decreased, the results are agreement with the previous studies (Stack *et al*., 2001). On the other hand, increasing the extraction temperature for DI-SPME showed the absorption of analyte increased, as shown in Fig. 5. The optimum extraction temperature for HS-SPME technique was 20°C and for DI-SPME technique was 40°C.

Effect of desorption time: The appropriate desorption time are also important parameters to ensure that

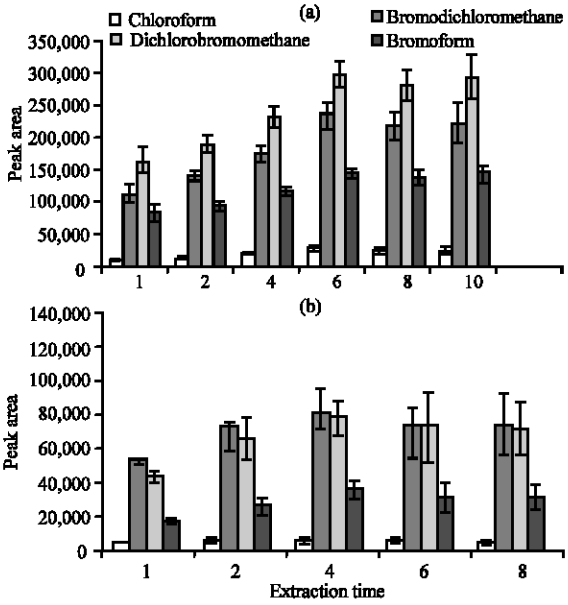

Fig. 4: The effect of extraction time on extraction of 1 μg L^{-1} THMs: extraction temperature at ambient temperature, desorption time 2 min at 220°C (a) HS-SPME: 25% (w v^{-1}) NaCl, stirring rate 800 rpm min^{-1} (b) DI-SPME: stirring rate 400 rpm min^{-1}

analytes are completely desorbed from the fiber. The optimum desorption time of HS-SPME and DI-SPME techniques were 2.5 and 2 min, respectively, as shown in Fig. 6.

Linearity, limit of detection, limit of quantitation and repeatability: The linearities were ranging from 0.1-50 μg L^{-1} for both HS-SPME and DI-SPME with the correlation coefficient of 0.9925-0.9980, except the linear range of chloroform for extraction by DI-SPME was 0.5-50 μg L^{-1}. The Limit Of Detection (LOD) and Limit Of Quantitation (LOQ) were calculated base on 3 and 10σ of noise signal. The LOD and LOQ of all THMs by HS-SPME were found lower than DI-SPME technique. The repeatabilities were ranging 2.72-10.86%. The results are compared with the standard Liquid-Liquid Extraction (LLE) method using n-pentane as extracting solvent, as summarized in Table 1.

Extraction recoveries: The recoveries were obtained by spiking the standard solution of each THMs (1, 5 and 10 μg L^{-1}). The percentage recoveries for HS-SPME and DI-SPME were ranging 86-110 and 82-107 μg L^{-1}, respectively, as shown in Table 2. The results are compared with standard liquid-liquid

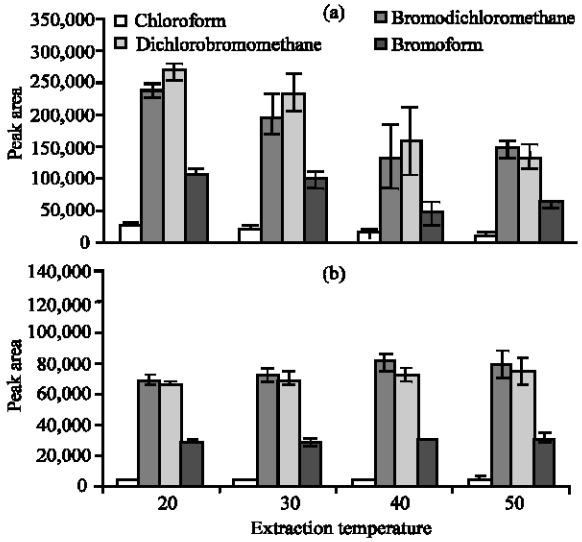

Fig. 5: Effect of extraction temperature on extraction of 1 μg L^{-1} THMs: desorption time 2 min at 220°C (a) HS-SPME: 25% (w v^{-1}) NaCl, stirring rate 800 rpm min^{-1}, extraction time 6 min (b) DI-SPME: stirring rate 400 rpm min^{-1}, extraction time 4 min

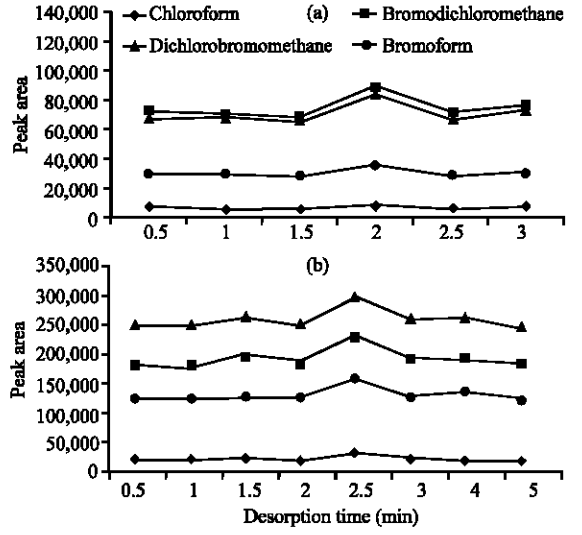

Fig. 6: Effect of desorption time on extraction of 1 μg L^{-1} THMs (a) HS-SPME: stirring rate 800 rpm min^{-1}, extraction time 6 min at 20°C, 25% (w v^{-1}) NaCl (b) DI-SPME: stirring rate 400 rpm min^{-1}, extraction time 4 min at 40°C

extraction. The percentage recoveries of HS-SPME and DI-SPME technique showed no significantly different by using t-test (95% probability).

Table 1: Linearity, correlation coefficient, limit of detection, limit of quantitation for analysis of THMs by gas chromatograph

	Compounds			
Techniques/parameter	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$
HS-SPME				
Linear range	0.1-50	0.1-5	0.1-5	0.1-5
R^2	0.9947	0.9925	0.9948	0.9949
LOD (μg L^{-1})	0.01	0.01	0.01	0.01
LOQ (μg L^{-1})	0.03	0.03	0.03	0.03
RSD (%) (1 ppb)	7.45	6.22	5.69	5.57
RSD (%) (5 ppb)	10.86	8.15	6.32	5.30
RSD (%) (10 ppb)	3.77	2.72	3.03	4.41
DI-SPME				
Linear range	0.5-50	0.1-50	0.1-50	0.1-50
R^2	0.9979	0.9950	0.9965	0.9980
LOD (μg L^{-1})	0.50	0.02	0.02	0.02
LOQ (μg L^{-1})	1.66	0.07	0.07	0.07
RSD (%) (1 ppb)	10.18	9.85	10.20	9.95
RSD (%) (5 ppb)	5.30	4.98	4.38	5.17
RSD (%) (10 ppb)	3.17	2.71	2.79	2.96
LLE				
Linear range	0.5-50	0.1-50	0.1-50	0.1-50
R^2	0.9940	0.9946	0.9958	0.9919
LOD (μg L^{-1})	0.50	0.10	0.10	0.10
LOQ (μg L^{-1})	1.66	0.33	0.33	0.33
RSD (%) (1 ppb)	9.58	8.24	7.71	9.22
RSD (%) (5 ppb)	9.97	6.80	9.62	8.76
RSD (%) (10 ppb)	5.20	5.18	5.43	6.35

R^2 = Correlation coefficient; RSD% = Repeatability

Table 2: Percentage recoveries by SPME compared with the standard liquid-liquid extraction

	Recovery±RSD (%)		
Techniques/compounds	1 (1 μg L^{-1})	5 (1 μg L^{-1})	10 (1 μg L^{-1})
HS-SPME (n = 7)			
$CHCl_3$	98±8	87±7	89±13
$CHBrCl_2$	90±8	86±7	87±10
$CHBr_2Cl$	96±4	102±8	109±9
$CHBr_3$	104±4	107±9	110±8
DI-SPME (n = 7)			
$CHCl_3$	106±4	106±8	82±5
$CHBrCl_2$	91±4	85±7	93±5
$CHBr_2Cl$	101±7	103±8	105±4
$CHBr_3$	99±11	107±9	107±4
LLE (n = 5)			
$CHCl_3$	62±17	109±10	96±3
$CHBrCl_2$	82±5	65±11	80±3
$CHBr_2Cl$	98±13	90±14	94±5
$CHBr_3$	86±12	88±16	94±5

CONCLUSION

Headspace-Solid Phase Microextraction (HS-SPME) technique has a great potential for determination of THMs in water samples with low limit of detection. The optimum conditions of HS-SPME were stirring rate 800 rpm min^{-1}, extraction time 6 min, extraction temperature 20°C, desorption time 2.5 min and desorption temperature 220°C. Application of this technique will be done in real water samples for further study.

ACKNOWLEDGEMENTS

The researcher gratefully acknowledge the support from Center of Excellence for Innovation in Chemistry (PERCH-CIC), Commission on Higher Education, Ministry of Education and thank the Science Center of Rajabhat Mahasarakham University.

REFERENCES

Cho, D.H., S.H. Kong and S.G. Oh, 2003. Analysis of trihalomethanes in drinking water using headspace-SPME technique with gas chromatography. Water Res., 37: 402-408. http://www.sciencedirect.com/science/journal/00431354.

Golfinopoulos, S.K. and A.D. Nikolaou, 2005. Survey of disinfection by-products in drinking water in Athen, Greece. Desalination, 176: 13-24. http://www.sciencedirect.com/science/journal/00456535.

Stack, M.A., G. Fitzgerald, S.O. Connel and K.J. James, 2001. Measurement of trihalomethanes in potable and recreational waters using solid phase microextraction with gas chromatography-mass spectrometry. Chemosphere, 41: 1821-1826. http://www.sciencedirect.com/science/journal/00119164.

Tor, A. and M.E. Aydin, 2006. Application of liquid-phase microextraction to the analysis of trihalomethanes in water. Anal. Chim. Acta, 575: 138-143. http://www.sciencedirect.com/science/journal/00032670.

Zhao, R., W. Lao and X. Xu, 2005. Head space liquid-phase microextraction of trihalomethanes in drinking water and their gas chromatographic determination. Talanta, 62: 751-756. http://www.sciencedirect.com/science/journal/00399140.

Zygmunt, B., 1996. Determination of trihalomethanes in aqueous samples by means of a purge and trap systems on sorbent focusing couples to gas chromatography with electron capture detection. J. Chromatogr. A, 725: 157-163. http://www.sciencedirect.com/science/journal/00219673.