CHAPTER III

EXPERIMENTS

3.1 Instrument and apparatus

3.1.1 Gas chromatograph 6890N with ^{63}Ni microelectron capture detector (GC-μECD) system (Agilent Technologies, USA)

3.1.2 7683 Auto sampler (Agilent Technologies, USA)

3.1.3 Capillary column DB-35MS ((35% diphenyl) dimethyl polysiloxane) 30 m × 0.25 mm i.d., 0.25 μm film thickness (J&W Scientific, USA)

3.1.4 Capillary column DB-1701 ((14% cyanopropyl-phenyl) dimethyl polysiloxane) 30 m × 0.32 mm i.d., 0.25 μm film thickness (J&W Scientific, USA)

3.1.5 Balance model AT 200 (Mettler)

3.1.6 pH meter model 744 (Metrohm)

3.1.7 Thermostated water bath

3.1.8 Oven (Memmert, Germany)

3.1.9 Micro pipettes and micro pipettes tip 100-1000 μL (Brand, Germany)

3.1.10 GC micro syringe 10 and 100 μL (SGC, Australia)

3.1.11 HPLC micro syringe 50 μL (Hamiton Company, Switzerland)

3.1.12 Screw cap headspace vial 10 mL and 20 mL (Alltech, USA)

3.1.13 Magnetic stirring bar (Spinbar)

3.1.14 0.8 × 25 mm o.d. medicine syringe needles (Nipro, Thailand)

3.1.15 Medicine syringe 3 and 5 mL (Becton Dickinson, Singapore)

3.1.16 Crimper and decrimper 11 mm (Agilent Technologies, USA)

3.1.17 2 mL clear wide opening crimp vial (Agilent Technologies, USA)

3.1.18 100 μL pulled point conical glass inserts (Agilent Technologies, USA)

3.1.19 Accurel Q 3/2 polypropylene hollow fiber membrane, inner diameter 600 μm, wall thickness 200 μm, pores size 0.2 μm (Membrana, Wuppertal, Germany)

3.1.20 Vifil 4040 polysulfone hollow fiber membrane, inner diameter approximately 1100 μm, wall thickness approximately 270 μm (via microscope) (Ultrapure, Bangkok, Thailand)

3.1.21 Milli Q, Ultrapure Water Systems, with Millipak® 40 FilterUnit 0.22 μm, model Millipore ZMQS 5 V00Y, Millipore, USA

General glassware in laboratory

Owing to that THMs and HAAs are ubiquitously found in tap water and may contaminate the extraction device, all glassware was thoroughly cleaned using detergent and tap water, rinsed with deionised water and dried in an oven at 150 °C over night before use.

3.2 Chemical reagents

3.2.1 Standard chemicals

A standard mixture solution of 100 μg/mL THMs in methanol was purchased from Supelco (Lot no. LB18343, Bellefonte, PA, USA). The components in the standard solution of THMs and their purities were presented in Table 3.1.

Table 3.1 Purity and concentration of each THMs in the standard mixture solution.

Analyte	Purity (%)	Concentration (μg/mL)
Chloroform ($CHCl_3$)	99.9	97.8
Bromodichloromethane ($CHCl_2Br$)	99.9	103.6
Chlorodibromomethane ($CHClBr_2$)	99.9	100.6
Bromoform ($CHBr_3$)	99.9	99.6

A standard mixture solution of 200-2000 μg/mL HAAs in methyl *tert*-butyl ether (MTBE) were purchased from Supelco (Lot no. LB19486, Bellefonte, PA, USA). The components in the standard solution of HAAs and their purities were presented in Table 3.2.

Table 3.2 Purity and concentration of each HAAs in the standard mixture solution.

Analyte	Purity (%)	Concentration (μg/mL)
Monochloroacetic acid (MCAA)	98.3	611.5
Monobromoacetic acid (MBAA)	99.9	409.5
Dichloroacetic acid (DCAA)	97.5	606.7
Trichloroacetic acid (TCAA)	98.8	207.5
Bromochloroacetic acid (BCAA)	99.9	403.8
Bromodichloroacetic acid (BDCAA)	99.9	418.6
Dibromoacetic acid (DBAA)	97.6	209.5
Chlorodibromoacetic acid (CDBAA)	98.2	1047
Tribromoacetic acid (TBAA)	96.6	2102

A standard mixture solution of 200-2000 μg/mL haloacetic methyl ester in methyl *tert*-butyl ether (MTBE) were purchased from Supelco (Lot no. LB22935, Bellefonte, PA, USA). The components in the standard solution of THMs and their purities were presented in Table 3.3.

Table 3.3 Purity and concentration of each haloacetic methyl ester in the standard mixture solution.

Analyte	Purity (%)	Concentration (μg/mL)
Monochloroacetic acid methyl ester	99.9	578.6
Monobromoacetic acid methyl ester	99.9	396.4
Dichloroacetic acid methyl ester	99.7	602.6
Trichloroacetic acid methyl ester	99.4	199.2
Bromochloroacetic acid methyl ester	99.7	398.1
Bromodichloroacetic acid methyl ester	99.9	381.6
Dibromoacetic acid methyl ester	99.4	199.3
Chlorodibromoacetic acid methyl ester	99.9	1014
Tribromoacetic acid methyl ester	99.9	1988

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3.2.2 Organic solvents

1-Octanol (≥99.5%), Dihexyl ether (≥97%) and Dodecane (≥90%) were purchased from Fluka (Steinheim, Germany). Methanol (ACS reagent grade) and acetone were obtained from J.T. Baker (Phillipsburg, NJ, USA).

3.2.3 Other chemicals

98% Sulfuric acid (GR for analysis) was obtained from Merck (Darmstadt, Germany). Sodium sulfate (AR grade) was purchased from Fisher scientific (Leicestershire, UK). Helium (99.999%) and Nitrogen (99.999%) for gas chromatographic were obtained from TIG (Chacherngsow, Thailand).

All blank and standard solutions were prepared using Milli-Q water, which was boiled for 1 hour.

3.3 Preparation of stock solutions

3.3.1 The THMs stock solution

The stock solution of 5 μg/mL THMs in methanol was prepared by pipetting 100 μL of the standard mixture solution of 100 μg/mL THMs into a 2-mL clear vial that contained 1.9 mL methanol. The vial was immediately closed with aluminum crimp cap and stored in the freezer.

3.3.2 The HAAs stock solution

The stock solution of 10-100 μg/mL HAAs in water was prepared by pipetting 100 μL of the standard mixture solution of 200-2000 μg/mL HAAs into a 2-mL clear vial that contained 1 mL water. Subsequent, the MTBE layer was blown off with a gentle stream of air. After that, another 1 mL of water was pipetted into the same vial. The vial was immediately closed with aluminum crimp cap and stored at 4 ^{o}C in the refrigerator. The final volume of HAAs stock standard solution was 2 mL.

3.3.3 The haloacetic methyl ester stock solution

The stock solution of 200-2000 μg/L haloacetic methyl ester in dodecane was prepared by pipetting 100 μL of standard mixture solution of 200-2000 μg/mL haloacetic methyl ester into a 2-mL clear vial that contained 1.9 mL MTBE. The 40

μL of this mixture solution was once again diluted into 2-mL clear vial that contained 1.96 mL dodecane. The vial was immediately closed with aluminum crimp cap and stored at 4 °C in the refrigerator.

3.4 Gas chromatographic conditions

Analysis of THMs and HAAs was performed using GC-μECD. The GC condition of THMs and HAAs was shown in Table 3.4 and Table 3.5, respectively.

Table 3.4 The gas chromatographic conditions for analysis of THMs.

GC Parameters	GC condition
Carrier gas	Helium, 1 mL/min
Injector	Spit mode; split ratio 10:1, 270 °C
Analytical column	DB-35MS ((35% diphenyl) dimethyl polysiloxane) 30 m × 0.25 mm i.d., 0.25 μm film thickness
Oven	40 °C for 1 min, increased to 100 °C at 5 °C/min, then a final increase to 270 °C at 20 °C/min to eliminate any residual
Detector	Electron capture detector, 300 °C
Make up gas	Nitrogen, 60 mL/min

Table 3.5 The gas chromatographic conditions for analysis of HAAs.

GC Parameters	GC condition
Carrier gas	Helium, 1 mL/min
Injector	Spit mode; split ratio 10:1, 270 °C
Analytical column	DB-1701 ((14% cyanopropyl-phenyl) dimethyl polysiloxane) 30 m × 0.32 mm i.d., 0.25 μm film thickness
Oven	40 °C for 1 min, increased to 100 °C at 5 °C/min, then a final increase to 270 °C at 15 °C/min and maintained at 270 °C for 20 min to eliminate any residual
Detector	Electron capture detector, 300 °C
Make up gas	Nitrogen, 60 mL/min

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3.5 Determination of immobilized organic solvent volume in the pores of the hollow fiber membrane

Before extraction by LPME, hollow fiber membrane was impregnated in an organic solvent to immobilize organic solvent in the pores. The volume of the organic solvent in fiber preparation may have varied and therefore the consistence of organic solvent volume in the pores was investigated.

First, the empty hollow fiber membrane was weighed (W_i). Then, the pores of the hollow fiber membrane were filled with an organic solvent (1-octanol was used for this study) by dipping the hollow fiber membrane in the organic solvent for impregnation. Because the hollow fiber was porous hydrophobic membrane, the organic solvent was automatically filled into the pores of hollow membrane by the capillary force. The organic solvent in the lumen of the fiber was removed by blown with a 5-mL syringe. The organic solvent filled hollow fiber membrane was weighed (W_f). The mass of organic solvent immobilized within the pores of the fiber was determined by the difference of the weight of the fiber before and after dipped in the organic solvent. The volume of the immobilized solvent was calculated by adjusting for solvent density as follow:

$$V_p = \frac{W_f - W_i}{D} = \frac{m}{D} \tag{3.1}$$

Where V_p is volume of organic solvent in the pores. D is specific density of organic solvent. m is mass of organic solvent immobilized in the pores. The experiment was repeated several times. Standard deviation was using to represent the consistence of the volume of organic solvent in the pores. The results were shown in Section 4.2.

3.6 Liquid-phase microextraction procedure for THMs extraction

The objective of this procedure was to develop a simple, inexpensive and environmental friendly method using liquid-phase microextraction for the determination of trihalomethanes in water samples. Simple conditions such as extraction at room temperature, no stirring and no salt addition were attempted. The extraction procedure for THMs can be briefly described as follows:

Before use, polypropylene hollow fiber membrane was sonicated in acetone for several minutes to remove any contaminants, whilst polysulfone hollow fiber membrane was sonicated in methanol. The fiber was removed and allowed to

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completely dry. The configuration of liquid-phase microextraction system was adopted from Pedersen-Bjergaard and Rasmussen [52] as illustrated in Figure 2.6. Both ends of the fiber were attached to two conventional medical syringe needles that pierced through the septum lined screw cap of the headspace vial. The fiber was initially immersed into the extracting organic solvent for several seconds to ensure that the pores of the hollow fiber membrane were filled with the extracting solvent. After the solvent impregnation, the solvent in the lumen of fiber was removed using an air blow from a 5-mL syringe and the predetermined amount of extracting solvent was carefully injected into the lumen of the fiber using a micro syringe. The impregnated and filled fiber with screw cap was then reattached to the headspace vial containing sample solution for immediate extraction. Both open ends of the medical syringe needles were connected to the syringe bodies to prevent the solvent loss during extraction. With this set up, there was no microsyringe, clamp or stand required for the support; in addition, several samples can be extracted simultaneously. The extraction was carried out in a 10-mL vial filled with 10 mL of sample solution without addition of salt and stirring. After extraction for a predetermined period of time at room temperature, one end of the fiber was detached from the medical syringe needle and the extracting solvent was flushed by an air blow from a 5-ml syringe into a 100-μl micro insert placed in a 2-ml PTFE/rubber septum crimp GC vial. The extract was ready for analysis by the GC-μECD; otherwise, it was kept in the refrigerator at 4 °C until analysis. The 1 μL was injected into the GC system for the final analysis. The GC condition was show in Table 3.4.

3.7 Liquid-phase microextraction optimization for THMs extraction

3.7.1 Study of extraction efficiency on difference membrane

Physical nature of membrane may be affected on extraction efficiency. In order to study, two different types of hollow fiber membranes were used. One was Accurel Q 3/2 polypropylene hollow fiber membrane. The length of 8.5 cm with an extracting phase volume of 25 μL was used for this fiber. The other one was Vifil 4040 polysulfone hollow fiber membrane. The length of 7 cm with an extracting phase volume of 40 μL was used for this fiber. The characteristics of both membranes

were shown in Table 3.6. From use these volume, the extracting phase of both membranes were approximately the same.

Table 3.6 Properties of membrane.

Property	Membrane	
	Polypropylene	Polysulfone
Inner diameter (μm)	600	1100[a]
Outer diameter (μm)	1000	1640[a]
Wall thickness (μm)	200	270[a]
Porosity (%)	66[b]	30[b]
Contact area (mm^2)	187	65[c]
Organic solvent in pores (μL)	28	15[c]
Organic solvent in lumen (μL)	25	40
Total volume of organic solvent (μL)	53	55

[a] Calculated from microscope.

[b] Estimated by calculation.

[c] Calculated from height of solvent in lumen.

Both membranes were used for direct extraction of spiked water samples THMs with 10 μg/L at 35 °C for 30 min using 1-octanol as extracting solvent. The peak area of each analyte was used to compare extraction efficiency. The results were shown in Section 4.3.1.

3.7.2 Study of organic solvent

Selection of organic solvent for extraction is the key in solvent extraction techniques. For LPME the organic solvent should be based on several considerations. First, the organic solvent should be compatible with the fiber and low solubility in water to prevent dissolution into the aqueous phase. Second, the solvent should also have low volatility to prevent evaporation during extraction. Finally, the solvent should extract analyte well and be separated from the analyte peaks in the chromatogram. Based on these criteria, three organic solvents, i.e., dodecane, 1-octanol and dihexyl ether were used in this study. From the result in Section 3.7.1, one could either choose polypropylene hollow fiber membrane or polysulfone hollow fiber membrane. In this section, the experiment was performed on direct extraction of

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spiked water sample with 10 μg/L THMs at 35 °C (control temperature) at 30 min extraction time. The peak area of each analyte was determined to compare extraction efficiency. The results were shown in Section 4.3.2.

3.7.3 Study of extraction mode

In the case of extraction of THMs that are volatile, two sampling modes, i.e., direct extraction and headspace extraction, can be performed. In direct extraction mode, the membrane is inserted directly into the sample. In headspace mode, the membrane is hanged above the sample solution. The technique set up for direct extraction and headspace extraction was shown in Figure 3.1.

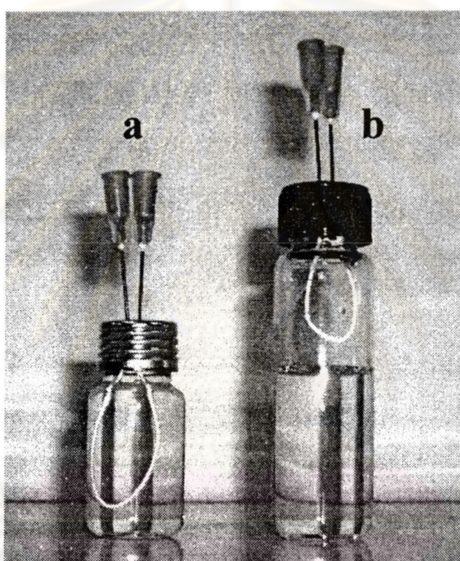

Figure 3.1 Liquid-phase microextraction set up (a) direct extraction; (b) headspace extraction.

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From the result in Section 3.7.1 and Section 3.7.2, the hollow fiber membrane and the solvent for the method can be achieved. In this section, the sampling modes were studied because of the influences on amount of analytes in extracting solvent and speed of extraction. Water sample of 10 mL was pipeted into 10-mL and 20-mL vial for direct extraction and headspace extraction, respectively. The extraction of spiked water sample with 10 μg/L THMs was performed in direct and headspace modes at 35 °C for 30 min extraction time. The peak area of each analyte was determined to compare extraction efficiency. The results were shown in Section 4.3.3.

3.7.4 Study of extraction time

In the theory of LPME, the amount of extracted analyte is expected to increase with extraction time. The optimal extraction efficiency is obtained when equilibrium is established. From the results in Section 3.7.1, 3.7.2 and 3.7.3, the hollow fiber membrane, organic solvent and extraction mode for the method were obtained. In this section, the extraction time was studied to determine the optimal exposure time of the membrane. The extraction was performed with spiked water sample with 10 μg/L THMs at 35 °C. The extraction time profiles were examined by monitoring the mass extracted with extraction time in the range 10-60 minute. The results were shown in Section 4.3.4.

3.7.5 Study of sample volume on enrichment factor

Since the enrichment factor *(EF)* for the analyte is related to the sample volume (V_d) and the extraction efficiency (*EE*), which is also related to the distribution constant ($K_{org/d}$) as described in the equations 2.15. As the volume of the organic solvent is the same, the enrichment factor might be influenced by the volume of the sample. In this study, two sample volumes of 10 mL and 20 mL were examined the influence of sample volume on enrichment. The experiment was performed on direct extraction of spiked water sample with 5 μg/L THMs at 35 °C for 30 min extraction time using 1-octanol in polypropylene as extracting device. The enrichment factor, which is defined as the ratio of the analyte concentration in the organic solvent to that in the initial water sample, was calculated from respond proportions of THMs in GC after extraction and that before extraction with LPME. The respond of THMs before extraction was determined by directly injection of standard solution of 200 μg/L THMs into GC. The results were shown in Section 4.3.5.

3.8 Method evaluation of trihalomethanes

From the result in Section 3.7, the optimum extraction conditions were obtained. In this section, LPME for the determination of THMs was evaluated.

3.8.1 Calibration curves

The calibration curves were constructed and used for quantitative determination of analytes in the samples. The calibration curves were prepared by adding the mixture of THMs into the 10 mL blank solutions. The added volumes and

concentrations of THMs were showed in Table 3.7. The spiked solutions were extracted with developed method and injected into the GC under condition in Table 3.4. The calibration curves were plotted by peak area versus concentration of each THMs. For calibration linearity, correlation coefficient should be greater than 0.99. The summary of linear range and correlation coefficient (R^2) were shown in Section 4.4 and calibration curve was shown in the APPENDIX A.

Table 3.7 The pipetted volume and concentration of each THMs for calibration curve.

The volume of THMs stock standard solution (μL)	Concentration (μg/L)			
	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$
0.4	0.2[a]	0.2	0.2	0.2
2	1	1	1	1
10	5	5	5	5
20	10	10	10	10
40	20	20	20	20
100	50	50	50	50
160	80	80	80	80
200	100	100	100	100

[a] This concentration is not used for calibration plot.

3.8.2 Method detection limit (MDL) and method quantification limit (MQL)

The method detection limit (MDL) and the method quantification limit (MQL) were defined by the concentrations of THMs in water that provide the signal to noise (S/N) of 3 and 10, respectively. The MDL and MQL were determined by injection of extracting solvent of spiked water sample with 0.2 μg/L THMs into GC. The results were shown in Section 4.4.

3.8.3 Study of accuracy and precision

Accuracy is the difference between the average value determined for the analyte of interest and the accepted true value or known level actually present. Precision is the repeatability of measurement. The term commonly used to measure of precision is the relative standard deviation (RSD). The accuracy and precision was

performed by analyzing THMs spiked water samples several times. The accuracy was accomplished by calculating the average of recovery. The precision was accomplished by calculating the RSD. The experiment was performed on direct extraction of spiked water sample with 1, 5, 10 and 50 µg/L THMs at 35 °C for 30 min extraction time. The results were shown in Section 4.4.

3.9 Liquid-phase microextraction procedure for HAAs extraction

Analysis of HAAs with GC consisted of two steps; i.e., extraction with organic solvent and derivatization to methyl esters [18]. In this study, HAAs were directly derivatized in water without evaporation to their volatile methyl ester and directly extracted by headspace LPME. The general extraction procedure was described below.

Polypropylene and polysulfone hollow fiber membranes were studied in Section 3.7.1 and the result showed that polypropylene provides higher extraction efficiency. So, polypropylene was applied to use in this section. The 6.5 cm of polypropylene hollow fiber membrane was dipped in organic solvent. After impregnation, air was flushed through the hollow fiber with 5-mL syringe to remove excess organic solvent from inside of the fiber. Subsequently, the needle was inserted into the two end of hollow fiber. Next, 20 µL of same organic solvent was injected into the lumen of the hollow fiber with a microsyringe. The fiber membrane was placed and sealed with screw caps in a 20-mL headspace vial that contained 10 mL of water sample. The sample was adjusted to pH < 0.5 by adding 1 mL 98% sulfuric acid. After the solution was cooled down to room temperature, methanol was pipetted in the sample. The vial was swirled and the HAAs were derivatized in thermostatized water bath. After extraction, the organic solvent in the lumen was flushed into a 100-µL insert vial for the GC by applying a small pressure with a 5-mL syringe on the inlet needle to the hollow fiber. The 1 µL was injected into the GC system for the final analysis. The GC condition was shown in Table 3.5.

3.10 Liquid-phase microextraction optimization for HAAs extraction

3.10.1 Study of organic solvent

In this study three types of solvents, i.e., 1-octanol, dihexyl ether and dodecane, were studied. The experiment was performed in spiked water sample with 30-90 μg/L HAAs. The methanol volume, extraction temperature and extraction time were fixed at 1 mL, 50 °C and 60 min, respectively. The peak areas of each analyte were used to compare extraction efficiency. The results were discussed in Section 4.5.1.

3.10.2 Study of extraction temperature

Temperature has a significant effect on both kinetics and thermodynamics of the sorption process. Moreover, based on the derivatization condition study by Domino *et al.*, derivatization temperature has also an effect on methylation efficiency [18]. In order to study the effect of the temperature on the extraction efficiency, difference extraction temperatures between 40-65 °C were investigated. The best extracting solvent in Section 3.10.1 was used in this section. The experiment was performed in spiked water sample with 30-90 μg/L HAAs. The methanol volume and extraction time were fixed at 1 mL and 60 min, respectively. The peak areas obtained for each analytes with different extraction temperature were used to compare extraction efficiency. The results were discussed in Section 4.5.2.

3.10.3 Study of methanol volume on in-situ derivatization

In acidic methanol technique, the reaction can be driven towards ester formation by the adding of a large molar excess of methanol. In this section, the effect of methanol volume was studied between 0.5-1.25 mL. The best extracting solvent and temperature in Section 3.10.1 and Section 3.10.2 were used in this section. The experiment was performed in spiked water sample with 30-90 μg/L HAAs. The extraction time was fixed at 60 min. The peak areas of each analyte were used to compare extraction efficiency. The results were shown in Section 4.5.3.

3.10.4 Study of extraction time

In the principle of LPME, the amount of extracted analyte is expected to increase with enhancing the exposure time. Maximum sensitivity is attained when

equilibrium is established. From the results in Section 3.10.1, 3.10.2 and 3.10.3, the organic solvent, extraction temperature and methanol volume for the method were obtained. In this section, the extraction time profiles were examined by monitoring the mass extracted with extraction time between 10-180 minutes. The experiment was performed in spiked water sample with 30-90 μg/L HAAs. The results were shown in Section 4.5.4.

3.10.5 Study of salting out effect

Depending on the nature of the target analytes, addition of salt to the sample may have several effects on extraction. Increasing of ionic strength in the aqueous may enhance, not influence or even limit extraction [57]. In order to investigate the effect of ionic strength, a series of spiked samples with various concentration of sodium sulfate in the range of 0-20 % w/v (saturated Na_2SO_4) were studied. Na_2SO_4 was used in this study because other salts such as NaCl has high bromide impurity, which reacts with residual chlorine and NOM to form brominated DBPs [67]. The best extraction condition from Section 3.10.1-Section 3.10.4 were used in this section. The experiment was performed in spiked water sample with 30-90 μg/L HAAs. The peak areas obtained for each analytes with different concentration of Na_2SO_4 were used to compare salting out effect. The results were discussed in Section 4.5.5.

3.10.6 Study of magnetic stirring

Stirring of the sample may accelerate mass transfer of analyte in the aqueous phase into the headspace. The effect of stirring and non stiring on the extraction was studied. The experiment was performed in spiked water sample with 30-90 μg/L HAAs with stirring and without stirring. The best extraction conditions from Section 3.10.1 - Section 3.10.5 were used in this section. The peak areas of each analyte were used to compare effect of stirring. The analytical significance of the mean values was studied statistically using the Student's *t*-test at the 95% confidence level. The results were discussed in Section 4.5.6.

3.11 Method evaluation of haloacetic acids

From the result in Section 3.10, the optimum extraction conditions were obtained. In this section, in-situ derivatization using LPME for the determination of HAAs was evaluated.

3.11.1 Calibration curves

The calibration curves were prepared by adding the mixture of HAAs into the 10 mL blank solutions. The added volumes and concentrations of HAAs were shown in Table 3.8. The spiked solutions were extracted with developed method and injected into the GC under the condition in Table 3.5. The calibration curves were plotted by peak area versus concentration of each HAAs. The summary of value of slope, intercept and correlation coefficient (R^2) were shown in Section 4.6 and calibration curve was shown in the APPENDIX A.

Table 3.8 The pipetted volume and concentration of each HAAs for calibration curve.

The volume of HAAs stock standard solution (μL)	Concentration (μg/L)						
	MCAA	MBAA	DCAA	TCAA	BCAA	BDCAA	DBAA
1	3[a]	2[a]	3[a]	1[a]	2	2[a]	1
3	9[a]	6	9	3	6	6	3
5	15[a]	10	15	5	10	10	5
10	30[a]	20	30	10	20	20	10
20	60	40	60	20	40	40	20
30	90	60	90	30	60	60	30
40	120	80	120[a]	40	80	80	40
60	180	120[a]	180[a]	60	120[a]	120[a]	60
80	240	160[a]	240[a]	80	160[a]	160[a]	80
100	300	200[a]	300[a]	100[a]	200[a]	200[a]	100[a]

[a] This concentration is not used for calibration plot.

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3.11.2 Method detection limit (MDL) and method quantification limit (MQL)

The method detection limit (MDL) and the method quantification limit (MQL) were defined by the concentration of HAAs in water that provide the signal to noise

ratio (S/N) of 3 and 10, respectively. The MDL and MQL were determined by injection of extracting solvent of spiked water sample with 1-3 μg/L HAAs into GC. The results were shown in Section 4.6.

3.11.3 Study of accuracy and precision

The accuracy and precision was obtained from measure HAAs spiked water sample several times. The accuracy was accomplished by calculating the average of recovery. The precision was accomplished by calculating the RSD. The experiment was performed in spiked water sample with 5-15 μg/L HAAs. The methanol volume, extraction temperature and extraction time were fixed at 1 mL, 50 ^{o}C and 60 min, respectively. The results were shown in Section 4.6.

3.12 The determination of THMs and HAAs in drinking water

The developed methods were applied to analyze THMs and HAAs in water samples. All bottled water and tap water were bought and collected in Chulalongkorn University, Thailand. Samples for determination of THMs were collected in March 2005. Samples for determination of HAAs were collected in November 2005. Tap water samples were collected in plastic bottles with screw cap no headspace. Tap water was sampling after flushing at least 2 minutes. Ammonium chloride, dechlorinating agent to preserve the samples by converting free chlorine to monochloramine, was not added because the analysis was performed immediately after sampling. The results were shown in Section 4.7.

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