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Supported liquid membrane microextraction with high-performance liquid chromatography–UV detection for monitoring trace haloacetic acids in water

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Abstract

Supported liquid membrane microextraction (SLMME) with high-performance liquid chromatography (HPLC)–UV detection has been developed for the extraction, preconcentration, and determination of all the nine haloacetic acids (HAAs) in water. The HAAs are extracted into a supported liquid membrane, and then back-extracted into few microliters of an acceptor solution. The extract was directly analyzed by HPLC–UV with a 15-min run. Enrichment factors in the range of 300–3000 were obtained in a 60-min extraction, and detection limits were at low to sub-μg/L level with R.S.D. values between 1.5 and 10.8%. The parameters that affected analyte enrichment were studied. This approach offers an attractive alternative to the current US Environmental Protection Agency standard methods for HAA analysis, which require complex sample preparation and derivatization prior to analysis by gas chromatography. SLMME can also be used in conjunction with other analytical schemes, such as, ion chromatography and capillary electrophoresis.
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Keywords: Haloacetic acid; Membrane extraction; Microextraction; Supported liquid membrane

1. Introduction

1.1. Haloacetic acids

The presence of disinfection by-products (DBPs) in chlorinated drinking water has been an important issue since the 1970s when they were first identified. DBPs are generated through the reaction of chlorine with natural organic matter (humic and fulvic compounds) and bromide (if present) in the source water. Trihalomethanes (THMs) are the major volatile DBPs, while haloacetic acids (HAAs) make up the main non-volatile components [1]. There are nine HAAs, whose names and acronyms are given in Table 1. In addition to drinking water, HAAs have also been found in swimming pools [2], rainwater [3], surface water [4,5], and seawater [6].

In recent years, the adverse effects of HAAs on human health and the environment have been increasingly recognized. These compounds are toxic to humans, plants, and in particular to algae [7]. The US Environmental Protection Agency (EPA) has classified DCAA as a group B2 compound (probable human carcinogen), and TCAA as a group C compound (possible human carcinogen). Furthermore, decarboxlyation of HAAs contributes to the formation of THMs [4], which are also carcinogens. According to the current EPA regulations [8], the maximum concentration limit (MCL) for the total of five HAAs (MCAA, MBAA, DCAA, BCAA, and DBAA) in drinking water is 60 μg/L. The EPA information collection rule (ICR) requires water utilities to monitor the concentration of six HAAs (the five HAAs mentioned above plus TCAA). The determination of the remaining three HAAs is voluntary yet strongly encouraged by ICR.

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Table 1
Names, abbreviations, and properties of haloacetic acids[a]

Full name	Abbreviation	pK_a	$\log P$
Monochloroacetic acid	MCAA	2.87	0.22
Dichloroacetic acid	DCAA	1.26	0.92
Monobromoacetic acid	MBAA	2.89	0.41
Bromochloroacetic acid	BCAA	1.39	1.14
Dibromoacetic acid	DBAA	1.47	1.693
Trichloroacetic acid	TCAA	0.51	1.33
Bromodichloroacetic acid	BDCAA	1.09	2.31
Dibromochloroacetic acid	DBCAA	1.09	2.907
Tribromoacetic acid	TBAA	2.13	3.459

[a] The pK_a and $\log P$ values of MCAA, MBAA, DCAA, and TCAA are from [30]; the values of the other HAAs were calculated using Advanced Chemistry Development (ACD) Software Solaris V4.67.

1.2. Analysis of HAAs

The importance of HAAs calls for sensitive and reliable methods for their determination. The EPA Method 552 and Standard Method 6251 involve liquid–liquid extraction and derivatization, prior to analysis by gas chromatography with electron-capture detection (GC–ECD) [9,10]. Low detection limits are attained at the cost of lengthy, cumbersome extraction–derivatization procedures. The derivatization reagent is diazomethane, which is not only toxic and carcinogenic, but also explosive. The EPA Method 552.1 employs ion-exchange derivatization, followed by GC analysis. It uses less solvent, but interference from anions cannot be prevented without sample dilution, which increases the detection limits [11]. The above methods can only analyze six HAAs (MCAA, MBAA, DCAA, BCAA, DBAA, and TCAA). The EPA Method 552.2 uses acidic methanol instead of diazomethane for derivatization, and can be applied to the determination of all nine HAAs [12]. However, it still involves the liquid–liquid extraction–derivatization approach. The overall sample preparation is lengthy and complicated (3 h), and the GC run time is approximately 50 min.

In light of the limitations of the EPA methods, considerable efforts have gone into developing alternative techniques. Some of these, such as the GC–MS-based methods, still require derivatization prior to analysis [13]. A few studies on derivatization–SPME followed by GC analysis have also been reported [2,14]. Methods that do not require derivatization include liquid chromatography (LC) [15,16], ion chromatography (IC) [17–19], capillary electrophoresis (CE) [20], and electrospray ionization mass spectrometry (ESI-MS) [21,22]. ESI-MS provides excellent sensitivity and selectivity, but high cost precludes its widespread use. With the reported sample preparation techniques, the detection limits of the LC, IC and CE methods are significantly higher than the GC methods. Most of the alternative methods have been used for only five or six HAAs, although a few have been reported for all the nine species [2,13,18,21]. A recent report pointed out that the three HAAs (BDCAA, DBCAA, and TBAA) made up a significant portion of the total HAAs and should not be overlooked [23]. At present, there is a need for a simple, inexpensive, and sensitive method for the analysis of all nine HAAs that do not require derivatization or large amounts of organic solvents. The objective of this research was to develop such a technique.

1.3. Support liquid membrane

Supported liquid membranes (SLM) have been used for the extraction of charged and ionizable compounds [24,25]. The membrane liquid is a small amount of organic extractant held by capillary force in the micropores of a porous membrane. The water sample on the donor side of the membrane is maintained at a certain pH, such that the analytes are in their uncharged, molecular form, and can be extracted into the membrane liquid. On the accepter side is an aqueous solution at a different pH, into which the analytes are extracted. This technique offers high analyte enrichment, excellent selectivity, and has been used in large-scale separations.

In this study, an approach referred to as the support liquid membrane microextraction (SLMME) has been developed for the extraction/preconcentration of HAAs. Somewhat similar methods have been reported for the extraction of basic drugs from biological fluids, and phenols from wastewater [26–28], where enrichment factors in the range of 75–380 were possible. The present method was aimed at providing much higher enrichment (a few thousand folds) to obtain μg/L–ng/L level detection of HAAs.

The advantage of HPLC analysis of HAAs is that no derivatization is necessary. Reversed-phase liquid chromatography has been used for the determination of six HAAs [15,16]. In this study, an HPLC–UV method was developed to separate and detect all the nine HAAs. As mentioned before, the detection limits of the previously reported LC methods (as well as IC and CE) have been too high to be used for monitoring HAAs in drinking water. It was anticipated that the sensitivity would be significantly enhanced by combining SLMME with HPLC–UV.

2. Experimental

A schematic diagram of the SLMME system is shown in Fig. 1, which is similar to the setup in [27]. Two syringes were used to hold the membrane in place. One was used to inject the acceptor into the membrane, while the other was used to withdraw the extract. The liquid membrane was placed in a bottle that contained the water sample (the donor), which was acidified by adding concentrated sulfuric acid (H_2SO_4). The effect of adding salt, sodium sulfate, into the sample to increase the ionic strength was evaluated. A magnetic stir plate (Nuova II, Thermolyne, IA, USA) was used to agitate the sample during extraction. After extraction, the acceptor solution was drawn into the syringe and transferred into a vial insert for HPLC analysis.

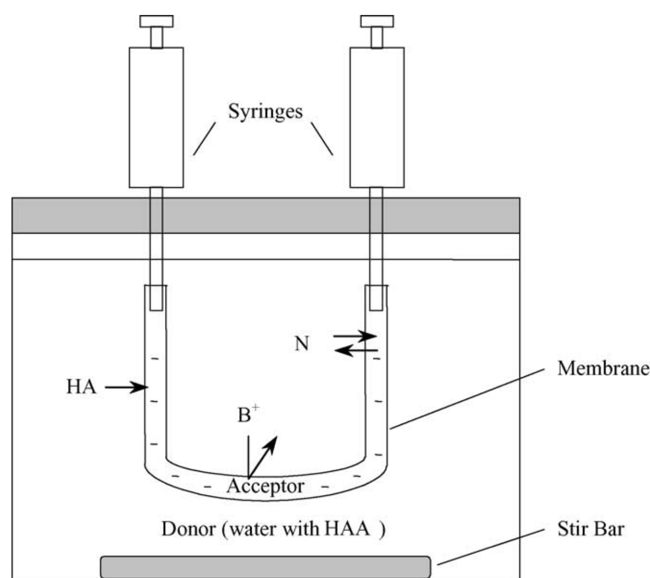

Fig. 1. The schematic diagram of SLMME. HA, N, and B^+ represent acids, neutral species, and bases, respectively.

2.1. Supported liquid membranes

The supported liquid membrane (SLM) used in this study was made by impregnating a segment of microporous hollow fiber with a membrane liquid for a period of 10 s. The membrane pores were automatically filled with the liquid. The excessive liquid was replaced by injecting microliters of the acceptor (NaOH or buffer solution) into the membrane lumen. Two types of polypropylene microporous hollow fiber membranes were used to make the SLM. One was Celgard X20 (Hoechst Celanese, Charlotte, NC, USA). It had an i.d. of 400 μm and an o.d. of 460 μm, with an average pore size of 0.03 μm and porosity of 40%. The other was Accurel PP Q 3/2 (Membrana, Wuppertal, Germany). It had an i.d. of 600 μm and an o.d. of 1000 μm, with an average pore size of 0.2 μm and porosity of 75%. The membrane liquids tested were di(2-ethylhexyl) phosphate (DEHPA) and dihexyl ether (DHE). The effect of adding trioctylphosphine oxide (TOPO) into DHE on the extraction was also investigated.

2.2. Reagents and instrumentation

Nine standard solutions were purchased from Supelco (Supelco Park, PA, USA), each of which contained an individual HAA. All other chemicals used in this study were ACS reagent grade (Sigma, St. Louis, MO, USA). Deionized water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). The microsyringes were from Hamilton (Reno, NV, USA). The 150-μl glass vial inserts were bought from Fisher Scientific (Pittsburgh, PA, USA).

A Hewlett-Packard 1050 HPLC system with an autosampler was used for the analysis. The HPLC column was a 150 mm × 4.6 mm i.d. YMC ODS-A C_{18} column with 3 μm packing (Waters, Milford, MA, USA). A Waters 486 tunable absorbance UV detector was used for the analysis, and the detection wavelength was 210 nm. The HPLC mobile phase was 15 mM KH_2PO_4/H_3PO_4 buffer at pH 2.2–acetonitrile (95:5, v/v) at flow rate of 1.0 mL/min. Minichrom V. 1.62 (VG Data Systems) software was used for data acquisition and analysis.

3. Results and discussion

As shown in Fig. 1, the HAAs in their undissociated, molecular form first diffused from the bulk donor solution to the surface of the membrane, and then partitioned into the membrane liquid. After migrating across the membrane, they were extracted into the acceptor via deprotonation, where they were ionized and could not re-enter the membrane. The two processes occurred simultaneously, and the overall extraction was highly efficient. The concentrations of the neutral compounds remained unchanged on both sides, which implied no enrichment. Basic compounds were in the charged form in the donor and were not extracted. Therefore, the SLMME in this study provided both high enrichment and high selectivity for the acidic compounds.

At equilibrium, the mass balance in SLMME can be written as:

$$C_I V_D = C_W V_D + C_M V_M + C_A V_A \quad (1)$$

C_I is the initial analyte concentration in the donor prior to extraction; C_W, C_M, and C_A are the equilibrium analyte concentrations in the extracted sample, membrane, and acceptor, respectively. V_D, V_M, and V_A are the volumes of the donor, membrane, and acceptor, respectively.

K_D is the partition coefficient between the membrane and the donor, and K_A is the partition coefficient between the membrane and the acceptor:

$$K_D = \frac{C_M}{C_W \alpha_D} \quad (2)$$

$$K_A = \frac{C_M}{C_A \alpha_A} \quad (3)$$

K_D and K_A are of the same order if the ionic strengths in the donor and the acceptor are not significantly different, and α_D and α_A are the fractions of analyte in the undissociated form in the donor and the acceptor phases. It is desirable to have α_D close to 1, and α_A to be a very small number. For the extraction of weak acids, the donor pH must be at least 2 pH units lower than the pK_a of the acid, so that $\alpha_D > 0.99$. To achieve $\alpha_A < 0.0005$, the acceptor must be at least 3.3 pH units higher than the pK_a value [29].

The extraction efficiency (EE) is defined as the fraction of analytes extracted, and is given as:

$$\mathrm{EE} = \frac{C_A V_A}{C_I V_D} \quad (4)$$

The enrichment factor (EF) is defined as the ratio of the analyte concentration in the acceptor to that in the initial water sample:

$$EF = \frac{C_A}{C_I} = EE\left(\frac{V_D}{V_A}\right) \quad (5)$$

When V_D/V_A is fixed, according to Eq. (5), EF is proportional to EE. Combining Eqs. (1)–(4), the EE at equilibrium can be written as:

$$EE = \frac{1}{(\alpha_A V_D K_A)/(\alpha_D V_A K_D) + (\alpha_A K_A V_M)/V_A + 1} \quad (6)$$

Combining Eqs. (1)–(3) and (5), the EF at equilibrium can be written as:

$$EF = \frac{1}{(\alpha_A K_A)/(\alpha_D K_D) + (\alpha_A K_A V_M)/V_D + V_A/V_D} \quad (7)$$

Because α_D is approximately 1, and if K_A and K_D are assumed to be similar, Eqs. (6) and (7) can be simplified to obtain maximum enrichment and extraction efficiency as:

$$EE_{max} = \frac{1}{(\alpha_A V_D)/V_A + (\alpha_A K_A V_M)/V_A + 1} \quad (8)$$

$$EF_{max} = \frac{1}{\alpha_A + (\alpha_A K_A V_M)/V_D + V_A/V_D} \quad (9)$$

Eq. (8) indicates that in order to achieve a high EE, α_A should be small. The maximum possible EE is 1 (100%). According to Eq. (9), a small α_A is also necessary for a high EF. EF decreases with the increase in V_A, and increases with the increase in V_D. The maximum possible EF equals V_D/V_A.

Higher EF is desired to obtain lower detection limits. Therefore, the extraction should be optimized to provide the highest EF. The time required to reach the maximum enrichment depends on several factors [29]. The overall mass transfer resistance is the sum of mass transfer resistance in the bulk donor solution, the donor–membrane boundary layer, the membrane, the membrane–acceptor boundary layer, and the acceptor. For compounds that have a large K_D, the mass transfer in the donor phase is the rate-limiting step. For compounds that have a small K_D, the extraction speed is controlled by the mass transfer in the membrane. When donor conditions are the same, extraction is faster for compounds with a larger K_D.

3.1. The effect of the donor and the acceptor

Concentrated sulfuric acid (H_2SO_4) was added to the water sample to lower its pH to a level at which the HAAs were in the uncharged, molecular form. The pK_a values of the HAAs are listed in Table 1. When 6.0 mL of concentrated H_2SO_4 was added to 100 mL water, the sample pH dropped to about −0.3, which was only one unit below the pK_a value of most HAAs. Further addition of H_2SO_4 improved the EF, because at lower pH, α_D was closer to 1 and more HAAs existed in the extractable form. The EF almost doubled when the amount of H_2SO_4 added to 100 mL water was doubled to 12.0 mL.

The "salting-out effect" has been used in liquid–liquid extraction. It refers to increasing the ionic strength of an aqueous solution to lower the solubility of organic compounds in water. This increases the partition coefficient (K_D). In this research, sodium sulfate was added to the water to "salt out" the HAAs. Salt concentrations from 0 to 40% (w/w; Na_2SO_4 in water) were tested. At 40%, the salt solution was near saturation. It was found that increasing the salt concentration resulted in higher EF. Fig. 2 shows that the EF increased two to six times (compound dependent), when the salt concentration increased from 0 to 40%.

Stirring was found to improve extraction efficiency, because it increased the mass transfer coefficient in the donor phase. When the stirrer setting (arbitrary units) increased from 0 to 5, EF increased in the range of two to nine times, with more increase for HAAs with higher hydrophobicity (as indicated by the log P values in Table 1). This is in agreement with the analysis that compounds with higher K_D (more hydrophobic) are more sensitive to the mass transfer in the donor phase. The enrichment factor was also a function of the donor volume. A larger volume sample contained more analytes, and resulted in higher EF. Under similar conditions, the EF obtained with a 210 mL sample was approximately three times that with a 60 mL sample. Sample availability is generally not an issue in tap water analysis, and a larger volume can be used to obtain higher EF and lower detection limits.

The enrichment factor was directly related to the acceptor volume. The smaller the volume, the higher was the EF. An acceptor volume of 30 μL was adequate for a 20 μL HPLC injection. Acceptor volume of 10 μL was also used in some experiments, and the extract was then diluted to 30 μL for HPLC analysis. When NaOH solution was used as the acceptor, the concentration in the range of 0.002 and 0.2 M

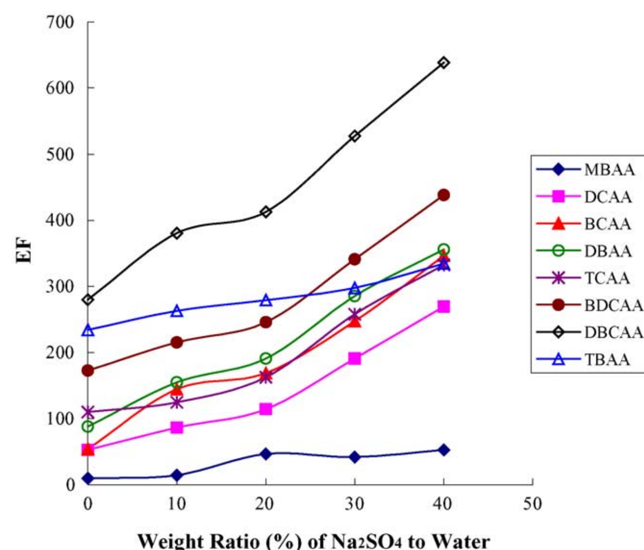

Fig. 2. Enrichment factor as a function of Na_2SO_4 concentration. A 8.5 cm of X20 membrane was used; the donor was 20 mL of water containing 40–400 μg/L HAAs; the acceptor was 10 μL of 0.01 M NaOH; and the extraction time was 30 min at stirring setting 3.

had little effect on the EF. This was because the pH at the lowest concentration was more than 3.3 units above the pK_a values of the HAAs, and the corresponding α_A was smaller than 0.0005. However, when the analyte concentrations are high, the pH of the acceptor solution may drop as the analytes accumulate in the acceptor. To increase the reservoir capacity of the acceptor solution, higher NaOH concentration is preferable. However, concentration higher than 0.2 M might damage the HPLC column and was therefore avoided. A 0.05 M Tris buffer at pH 10 was also tested as the acceptor solution. It was found to have more capacity than NaOH solution, and the linear dynamic range was broader with the Tris buffer.

3.2. The supported liquid membrane

Two types of microporous membranes were tested in this study. Under the same conditions used in our experiments, where extractions did not reach equilibrium, the EF of HAAs with the Celgard X20 membrane was found to be nearly twice that with the Accurel PP Q 3/2. When the acceptor volume was 30 μL, the contact area between the membrane and the aqueous phases was approximately 130 mm^2 for a 25 cm X20 membrane, and 200 mm^2 for a 12.5 cm Q 3/2 membrane. The higher EF with X20 was attributed to its thinner walls, where mass transfer was faster. Therefore, the thinner membrane was preferable for faster extraction. However, the thicker membrane was mechanically stronger, less susceptible to bending, and was easier to work with, especially when a larger acceptor volume required a longer membrane.

Dihexyl ether and di(2-ethylhexyl) phosphate were tested as the membrane liquid. The enrichment factors for HAAs with DHE were an order of magnitude higher than those with DEHPA, so DHE was used in the rest of the study. It had been reported that the addition of trioctylphosphine oxide into the membrane liquid could increase the EE of polar analytes [31]. Fig. 3 shows that the EF increased significantly when the TOPO concentration was increased from 0 to 5%. The level of increase depended upon the polarity of the HAAs. A more polar compound showed a larger increase in EF. When TOPO concentration increased from 5 to 10%, the EF of the more polar (DCAA, BCAA, and DBAA) compounds continued to increase, while the EF of less polar compounds (TCAA, BDCAA, DBCAA, and TBAA) decreased. Moreover, interferences in the chromatogram increased when TOPO concentration was higher than 5%. Therefore, 5% was chosen to be the optimum TOPO concentration in the membrane liquid.

The presence of TOPO significantly changed the behavior of the membrane. As mentioned before, the EF was not affected by the acceptor NaOH concentration in the range of 0.002–0.2 M, when a pure DHE membrane was used. However, when the membrane contained 5% TOPO, no HAAs could be extracted at a NaOH concentration lower than 0.05 M. With 10% TOPO in the membrane, the minimum NaOH concentration needed was 0.2 M. In other words, higher TOPO concentration in the membrane required higher

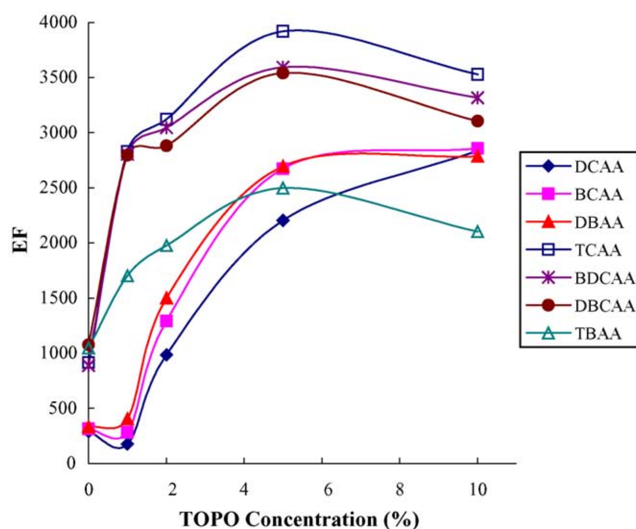

Fig. 3. Enrichment factor as a function of TOPO concentration in the membrane. A 12.5 cm of PP Q membrane was used; the donor was 230 mL of water containing 5 μg/L HAAs; the acceptor was 30 μL of 0.2 M NaOH; and the extraction time was 60 min at stirring setting 9.

NaOH concentration in the acceptor. This can be explained by the fact that TOPO is an effective hydrogen-bonding reagent. A certain OH^- concentration was necessary to break the hydrogen bond between TOPO and the HAAs, so that the acids could be released into the acceptor. Another interesting phenomenon was that with TOPO in the membrane, adding salt to the donor not only failed to increase the enrichment factor, but also had a negative effect. For example, when the membrane contained 5% TOPO and the acceptor NaOH concentration was 0.2 M, increasing the Na_2SO_4 concentration in water to 40% (w/w) decreased the EF to 50% of what was obtained without any salt. Another impact of TOPO was that with 1% of TOPO in the membrane, the EF remained unchanged when the ratio of sulfuric acid to water in the donor was doubled from 6:100 (v/v). This was also contrary to the observations when a pure DHE membrane was used. These behaviors of the membrane with TOPO are yet to be understood.

The enrichment factor increased with the extraction time. The increase was almost linear. Fig. 4 shows that the EF increased two to four times, when the extraction time increased from 30 to 90 min. Sixty minutes extraction was accepted as a compromise between a high enrichment and a relatively short extraction time.

3.3. Analytical performance

An isocratic HPLC method was developed for the separation of all the nine HAAs within 15 min. It was observed that the purity of the membrane liquid was critical for the precision and accuracy of the analysis. Initially, DHE of 98.9% purity was used, and the SLMME of the blank (reagent water) contained two large interfering peaks. Since DHE is insoluble in water, one possibility was that the interferences were caused by the impurities in DHE. When DHE of 99.1% pu-

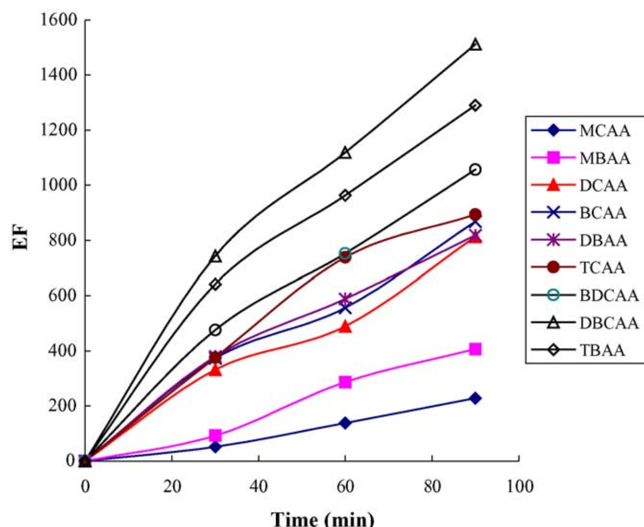

Fig. 4. Enrichment factor as a function of extraction time. A 8.5 cm of X20 membrane was used; the donor was 20 mL of water containing 40–400 μg/L HAAs; the acceptor was 10 μL of 0.03 M NaOH; and the extraction was at stirring setting 5.

rity was tested, this explanation was confirmed. The higher purity ether showed less interference, and the base line noise was also lower. The purer DHE was used in the rest of the study.

Fig. 5 is an overlay of chromatograms of SLMME of spiked water sample containing μg/L–sub-μg level HAAs, direct injection of a standard solution without SLMME, and SLMME of a blank (reagent water). It should be pointed out that even using the purer DHE there was still an unknown peak that coeluted with DCAA. This interfering peak was from an impurity in the DHE, not from the blank, because it was not present when DHE from the other source was used. This peak existed in all blanks, standards, and samples that underwent SLMME, with consistent peak areas. Given this consistency, blank subtraction was a viable approach in quantitative measurement. There was also a small peak coeluting with BDCAA. However, it was at such a trace level that its peak area was even much smaller than that of 0.4 μg/L BDCAA. Its impact on analytical results is negligible considering HAAs are present in tap water usually at μg/L levels.

The following SLMME conditions were used for the spiked samples and the blank in Fig. 5. The donor was 236 mL of water mixed with 14 mL of concentrated sulfuric acid. The acceptor was 30 μL of 0.05 M Tris buffer solution at pH 10. The membrane was 10.8 cm PP Q 3/2, with DHE containing 5% TOPO as the membrane liquid. The extraction time was 60 min and the stirring was at setting 9. Enrichment factors in the range of 300–3000 were obtained, demonstrating the effectiveness of SLMME. Table 2 lists the method detection limits (MDLs), EFs, EEs, linear dynamic ranges, precisions, and method accuracies obtained under the same conditions as those for Fig. 5. The EFs were proportional to the EEs, and this is in agreement with Eq. (5). The MDLs were lower than or comparable to those by EPA method 552.2 for most of the nine HAAs. The MDL of MCAA was higher than that by the EPA method. There are two main reasons for this. One is that at 210 nm the detector response to MCAA is the lowest among all HAAs. The other is that EF of MCAA is also the lowest, partly due to its highest hydrophilicity. Its octanol–water partition coefficient is considerably lower than the other HAAs (see Table 1).

The developed SLMME–LC method was tested with real world samples. Tap water from Newark, NJ, USA was analyzed. Fig. 6 shows such a chromatogram obtained under the same conditions as those for Fig. 5. External calibration was used for quantification. The blanks, standards, and samples were processed under the same SLMME conditions and procedures. Blank subtraction was performed for the determination of DCAA. Although there were some other unknown peaks in the chromatogram, their levels were low and did not interfere with the quantification of other HAAs. Five HAAs, MCAA, DCAA, TCAA, DBCAA and TBAA, were identified, and their concentrations were determined to be 14.5, 4.43, 0.41, 12.8, and 0.42 μg/L, respectively.

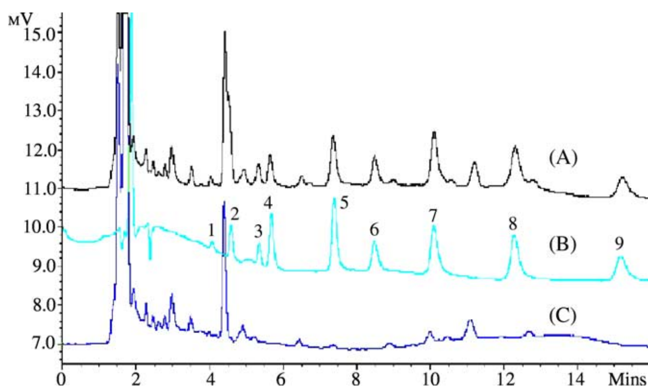

Fig. 5. Overlay of chromatograms of: (A) SLMME of spiked water sample containing 8.4 μg/L MCAA, 2.4 μg/L DCAA, 4.4 μg/L MBAA, and the other six HAAs at 0.4 μg/L each; (B) direct injection of a standard solution containing nine HAAs at 1 mg/L each; and (C) SLMME of a blank (reagent water). The numbered peaks in the chromatograms are: 1 = MCAA, 2 = DCAA, 3 = MBAA, 4 = BCAA, 5 = DBAA, 6 = TCAA, 7 = BDCAA, 8 = CDBAA, and 9 = TBAA.

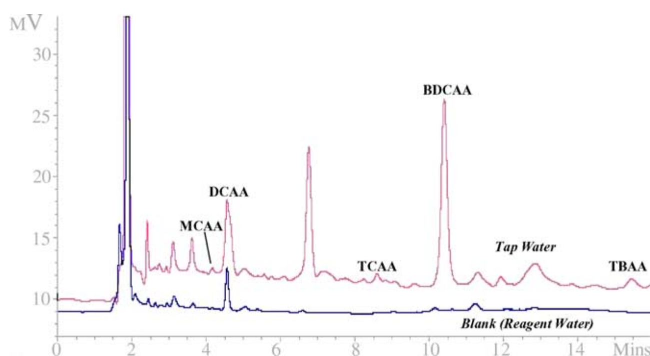

Fig. 6. Overlay of chromatograms of a blank and a tap water sample from Newark, NJ, USA. Both were obtained by SLMME–HPLC–UV under the same conditions as in Fig. 5.

Table 2
Analytical performance of SLMME–HPLC–UV

	MDL by EPA Method 552.2 [12] (μg/L)	MDL (μg/L)[a]	EF	EE (%)	Linear dynamic range (μg/L)	Linear regression coefficient	R.S.D. (%)[b]	Accuracy (%)[b]
MCAA	0.273	2.69	324	3.89	8.4–20	1.000	10.8	94.5
DCAA	0.204	0.25	1413	17.0	2.4–40	0.997	5.0	66.1
MBAA	0.242	0.23	366	4.39	4.4–40	0.997	2.1	78.8
BCAA	0.251	0.04	1153	13.8	0.4–20	1.000	4.3	81.8
DBAA	0.066	0.06	1260	15.1	0.4–20	1.000	5.0	94.3
TCAA	0.079	0.05	2411	28.9	0.4–40	0.999	4.6	80.0
BDCAA	0.091	0.02	1910	22.9	0.4–20	1.000	1.5	100.8
DBCAA	0.468	0.02	1250	15.0	0.4–20	1.000	2.0	86.5
TBAA	0.82	0.03	3298	39.6	0.4–20	1.000	3.7	73.9

[a] The method detection limit (MDL) was obtained following a standard EPA procedure [32].
[b] The relative standard deviation (R.S.D.) based on seven replications was obtained at concentrations of 8.4, 4.4, and 2.4 μg/L for MCAA, MBAA, and DCAA, respectively, and 0.4 μg/L for the rest of the HAAs. Method accuracies were obtained using spiked water samples at the above concentrations.

This demonstrates excellent selectivity and sensitivity as the SLMME–HPLC–UV technique was applied to drinking water, the most common sample for HAA analysis.

4. Conclusions

Supported liquid membrane microextraction followed by HPLC–UV analysis was developed as a technique for the determination of nine HAAs in water. It was simple, sensitive, relatively fast, and did not require any derivatization. Enrichment factors in the range of 300–3000 were obtained in a 60-min extraction. The extract was directly analyzed by HPLC with 15 min of run time. This method showed excellent precision, and the detection limits were lower than or comparable to those by the standard EPA methods.

The SLMME device is inexpensive, easy to make, and uses only a few microliters of organic extractant per sample. A large number of samples can be extracted simultaneously to increase the sample throughput. It is possible to use a new membrane for each extraction, so that the extraction is free of memory effects, and the membrane life is not a concern. SLMME can also be used with IC and CE methods.

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