Headspace liquid-phase microextraction of trihalomethanes in drinking water and their gas chromatographic determination

Ru-song Zhao, Wen-jian Lao, Xiao-bai Xu*

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, PR China

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Abstract

In the present work, a novel method for the determination of trihalomethanes (THMs) such as chloroform, dichlorobromomethane, chlorodibromomethane and bromoform in drinking water has been described. It is based on coupling headspace liquid-phase microextraction (HS-LPME) with gas chromatography-electron capture detector (GC-ECD). A microdrop of organic solvent at the tip of a commercial microsyringe was used to extract analytes from aqueous samples. Three organic solvents—xylene, ethylene glycol and 1-octanol—were compared and 1-octanol was the most sensitive solvent for the analytes. Extraction conditions such as headspace volume, extraction time, stirring rate, content of NaCl and extraction temperature were found to have significant influence on extraction efficiency. The optimized conditions were 15 ml headspace volume in a 40 ml vial, 10 min extraction time and 800 rpm stirring rate at 20 °C with 0.3 g ml⁻¹ NaCl. The linear range was 1–100 µg l⁻¹ for THMs. The limits of detection (LODs) ranged from 0.15 µg l⁻¹ (for dichlorobromomethane and chlorodibromomethane) to 0.4 µg l⁻¹ (for chloroform); and relative standard deviations (RSD) for most of THMs at the 10 µg l⁻¹ level were below 10%. Real samples collected from tap water and well water were successfully analyzed using the proposed method. The recovery of spiked water samples was from 101 to 112%.

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1. Introduction

Chlorine is applied to drinking water in order to deactivate microorganisms and/or to ensure the residual concentrations in drinking water distribution systems, thus protecting water from microorganisms regrowth [1]. As a result of disinfection of natural water, THMs are produced by available chlorine reacting with organic matrices [2,3]. Naturally occurring bromide ions in the water form the brominated THMs [2]. The frequently formed THMs are chloroform (CHCl₃), dichlorobromomethane (CHCl₂Br), chlorodibromomethane (CHClBr₂) and bromoform (CHBr₃). They are all considered to be possible carcinogens (Table 1) and, therefore, human exposure to such compounds should be minimized [4,5]. Basing on the health risks by these compounds, different countries have set limits for THMs in drinking water. In 1979, the United States EPA initiated a regulatory standard of 100 µg l⁻¹ for THMs, under the “Safe

Drinking Water Act”. Currently, this standard has been reduced to 80 µg l⁻¹. The Swedish regulation of total THMs is divided into two parts: first the guide level of 20 µg l⁻¹ and a limit value of 50 µg l⁻¹ [2]. Hence, for fast monitoring of THMs in drinking water and accomplishing risk assessment, sensitive, rapid and simple analytical methods are necessary.

In view of the analysis of THMs and other volatile organic compounds in water, the conventional liquid–liquid extraction (LLE) often needs large amount of toxic solvent and time-consuming procedures [6]. The purge and trap method is, however, more time-consuming [7,8]. Headspace method is suitable for the analysis of samples with high contents of volatiles [2]. Solid-phase microextraction (SPME) has been developed for pretreatment of THMs [4]. Recently, liquid-phase microextraction (LPME) or solvent microextraction was developed as a solvent-minimized pretreatment technique, which is fast, simple and inexpensive. This novel technique eliminates the disadvantages of conventional extraction methods, such as time-consuming operation and using specialized apparatus. Since very little solvent is used, there is minimal exposure to toxic organic solvent for the

* Corresponding author. Fax: +86-10-6292-3563.

E-mail address: xuxb@public.bta.net.cn (X.-b. Xu).

Table 1

Cancer group, molecular weights and weight responses of ^{63}Ni ECD of THMs

Compound	Cancer group (EPA) ^a	MW	Counts ($\text{g} \times 10^{-16}$) ^b
CHCl_3	B2	119.38	2.1
CHCl_2Br	B2	163.83	16.3
CHClBr_2	C	208.29	12.9
CHBr_3	B2	252.75	4.33

^a Group B2: probable human carcinogen (sufficient data from animal studies); and group C: possible human carcinogen.

^b Data from [6].

operator. At the same time, LPME combines extraction, concentration and sample introduction in one step.

LPME technique has been discussed in several papers [9–12]. It is based on the distribution effect of the analytes between a microdrop of organic solvent at the tip of a microsyringe needle and aqueous sample solution. The organic solvent drop is first exposed to the sample solution and target analytes are extracted from the sample matrix into the drop. After the equilibrium is reached, the drop with concentrated analytes is then transferred to the injection port of a gas chromatography for analysis. Similar to SPME, there are two modes of LPME sampling: direct LPME and headspace LPME (HS-LPME). The direct extraction mode has been successfully used for the determination of polycyclic aromatic hydrocarbons (PAHs) [13], organochlorine pollutants [14–16], nitroaromatic explosive [12,17], triazine herbicides [18], cocaine and cocaine metabolites [19] so far. Although the headspace extraction mode was first reported in 2000 [20], recently Theis et al. [21] described detailed kinetic studies of headspace mode. To date, only a few studies have been reported on the application of HS-LPME [22,23]. To our knowledge, there is no report on the determination of THMs in water samples using the headspace mode. This paper proposes a simple and sensitive method for extraction and determination of THMs in drinking water by HS-LPME combined with a capillary gas chromatography-electron capture detector (GC-ECD). Factors affecting the performance of HS-LPME have been studied and optimized.

2. Experimental

2.1. Reagents

Standard solutions of 100 mg l^{-1} THMs in methanol were purchased from ChemService Inc. (West Chester, PA, USA), including CHCl_3 , CHCl_2Br , CHClBr_2 and CHBr_3 , respectively. Their molecular weights and weight response factors of ^{63}Ni ECD are shown in Table 1. HPLC-grade methanol was purchased from Tianjin Siyou Technical Company. Xylene (Beijing Yili Jingxi chemical company, China), ethylene glycol (Beijing Chemical Reagent Factory, China), 1-octanol (Chinese medical company, China) and sodium chloride

(Beijing chemical reagent factory, China) were of analytical grade. 1-Octanol were further purified by vacuum distillation for 45 min to remove residual volatile contaminants, and stored at 4°C . A fixed concentration of hexachloroethane (ChemService Inc.) internal standard ($200 \mu\text{g l}^{-1}$) was prepared in the extraction solvent, 1-octanol. Working solutions of THMs were diluted using double distilled water, which was boiled for 1 h in a large beaker to remove THMs. All solutions were stored at 4°C in dark.

Water samples were collected in glass jars (250 ml) with screw caps and teflon inserts. Glass jars were carefully and completely filled. Samples were stabilized by the addition of 25 mg ascorbic acid (Beijing chemical reagent factory, China) per 20 ml water samples. The samples were analyzed directly or stored at 4°C within 48 h.

2.2. Apparatus

An Agilent 6890 gas chromatograph equipped with ^{63}Ni electron-capture detection system was used for all analyses (Hewlett-Packard, Palo Alto, CA, USA). The analytical column was HP-5 ($30 \text{ m} \times 0.32 \text{ mm} \times 1.0 \mu\text{m}$) (Hewlett-Packard). The gas chromatography (GC) conditions were as follows: injector temperature: 280°C ; detector temperature: 300°C ; initial oven temperature: 50°C for 5 min, increased to 275°C at a rate of $25^\circ\text{C min}^{-1}$, then maintained at 275°C for 3 min. The total time for one GC run was 17 min. The inlet was operated in split mode with a split ratio of 10:1 and nitrogen of high purity was served as carrier gas at a flow-rate of 1.0 ml min^{-1} .

2.3. HS-LPME procedure

A vial with a stir bar was placed on a magnetic stirrer and maintained at a desirable temperature by a water bath. HS-LPME was performed with a commercially available $10 \mu\text{l}$ GC microsyringe (Shanghai, China). Before each extraction, the syringe was rinsed for at least 20 times with solvent. During the extraction, the microsyringe was fixed above the extraction vials with a septum. After the needle passed through the septum, the needle tip must keep about 1 cm above the surface of THMs working solutions or sample solution. Then $1 \mu\text{l}$ extraction solvent containing $200 \mu\text{g l}^{-1}$ of I.S. was extruded out of the needle and kept suspending at the needle tip. When the extraction was finished, the drop was retracted into the needle and injected directly into the GC inlet.

3. Results and discussion

The HS-LPME theory indicates that analytes in headspace are transferred into the organic solvent extruded from the needle tip of a gas chromatography microsyringe; a dynamic equilibrium was finally established between the concentration of the analytes in headspace and that of analytes in the

organic solvent drop. The amount of the analyte n extracted by the microdrop at equilibrium is described by the following equation [23]:

$$n = \frac{K_{\text{odw}} V_d C_0 V_s}{K_{\text{odw}} V_d + K_{\text{hs}} V_h + V_s} \quad (1)$$

where K_{odw} and K_{hs} are the organic drop–water (sample) and the gas–water distribution constants, respectively; C_0 the initial concentration of the analyte in the matrix; and V_d , V_s and V_h the volumes of the drop, the sample, and the headspace, respectively. Eq. (1) after some manipulation becomes

$$\frac{1}{n} = \frac{1}{C_0} \left[\frac{1}{V_s} + \frac{1}{K_{\text{odw}} V_d} \left(\frac{K_{\text{hs}} V_h}{V_s} + 1 \right) \right] \quad (2)$$

In Eq. (2) relationships between n and other parameters such as K_{odw} , V_d , V_s and V_h are clearer. These parameters and their relationships are most important for the optimum of extraction conditions such as selection of solvent, organic solvent droplet size, sample volume, etc.

It is essential to select a proper organic solvent for the establishment of a HS-LPME method, which is dependent on the chemical nature of the target analytes. The extraction solvent must meet two requirements: to extract analytes well and to be separated from the analyte peak in the chromatogram [22]. Three solvents differing in polarity, 1-octanol, xylene and ethylene glycol were tested. Trials data indicated that 1-octanol gave best extraction efficiency. Moreover, 1-octanol has a very low vapor pressure (0.07 mm Hg at 25 °C), which results in minimal evaporation of the microdrop during the extraction time [21]. Therefore, 1-octanol was chosen as the extraction solvent in further work. From Eq. (2), it can be found that a larger organic drop gives an improved signal, however, its manipulation is more elaborate and less reliable [23]. Further, large injection volumes result in more extensive band broadening in capillary GC. Considering these factors, in the following investigations the drop volume was fixed at 1 μL . At the same time, in order to correct for variable injection volumes hexachloroethane was used as an internal standard (200 $\mu\text{g l}^{-1}$). The analytical signal was the relative peak area of the analyte to the internal standard [23].

3.1. Headspace volume

In order to optimize the procedure, the effects of the water sample and headspace volume were investigated. The experiment was performed using 40 ml vials and the volume of headspace was increased from 10 to 30 ml (water volume from 30 to 10 ml). THMs working solutions with 0.3 g ml^{-1} NaCl were analyzed in duplicate with 1 μL 1-octanol. The extraction time was 10 min at 20 °C and stirring rate was 800 rpm. The relative peak areas obtained for each analyte with different headspace volume are shown in Fig. 1.

As indicated by Eq. (2), for high-sensitivity HS-LPME the volume of gaseous phase (headspace) should be mini-

Fig. 1. Effect of headspace volume on the relative peak areas of THMs. 1-Octanol drop was exposed to aqueous solution with 0.3 g ml^{-1} NaCl content for 10 min at 20 °C at a stirring rate of 800 rpm.

mized. Summarily, in Fig. 1 the relative peak areas of the analytes decrease with increase of headspace volume. However, Fig. 1 shows that compared to the headspace volume of 15 ml, the relative peak area of the headspace volume of 10 ml remained basically constant for analytes. This is probably attributable to insufficient equilibration time, since in this case a significant portion of the analyte has to be transported to the microdrop from the liquid sample and not just from the headspace, and also mass transfer of the analytes into the bulk of the drop represents a slow step in the overall extraction process [21]. On the basis of the above considerations, 15 ml of headspace volume (water volume 25 ml) was selected since this quantity provided acceptable results for all analytes.

3.2. Extraction time

Like HS-SPME, HS-LPME is a process dependent on equilibrium [15]. The procedure requires a period of time for equilibrium. The extraction time profiles were examined by monitoring the variation of relative peak area with exposure time under the following conditions: 25 ml THMs working solution with addition of 0.3 g ml^{-1} NaCl content, stirring at 800 rpm, extraction temperature 20 °C. As can be seen in Fig. 2, relative peak areas of all analytes increased

Fig. 2. Effect of extraction time on the relative peak areas of (1) CHCl₂Br, (2) CHClBr₂, (3) CHBr₃ and (4) CHCl₃. 1-Octanol drop was exposed to the headspace of 15 ml of aqueous solution with the addition of 0.3 g ml^{-1} NaCl content at 20 °C at a stirring rate of 800 rpm.

Fig. 3. Effect of stirring rate on the relative peak areas of THMs. 1-Octanol drop was exposed to the headspace of 15 ml of aqueous solution with the addition of 0.3 g ml^{-1} NaCl content for 10 min at 20°C .

with extraction time up to 10 min. After 10 min, the amount of analytes extracted showed a much slower increase. The main reason is that as soon as the headspace concentration of the analyte falls below the equilibrium value with respect to the aqueous phase, analyte molecules begin to diffuse from the aqueous phase to the gaseous phase, which is a rate-determining step [23]. Since it is not practical to wait for equilibrium to occur, the extraction time should be just long enough for the extraction rate to slow down for improved precision [23]. Therefore, in all subsequent optimized experiments, 10 min extraction time was used.

3.3. Stirring rate

The next step was to optimize the stirring rate. Twenty-five ml working solutions were continuously agitated for 10 min at different stirring rates. It is clear that the relative peak areas of all analytes increase with increase of stirring rate in Fig. 3.

Based on the penetration theory of mass transfer of solute, the aqueous phase mass-transfer coefficient β_{aq} is given by

$$\beta_{\text{aq}} = 2 \left(\frac{D_{\text{aq}}}{\pi t_e} \right)^{1/2} \quad (3)$$

where D_{aq} is the diffusion coefficient in the aqueous phase, and t_e the exposure time of a small fluid volume element of one phase momentarily in contact with the other phase [11]. According to the theory, β_{aq} increases with increasing stirring rate because at a faster stirring rate the value of t_e is smaller [11]. As a result, agitation enhanced extraction efficiency. Our experiment results support this explanation.

Nevertheless, although higher stirring rates ($>800 \text{ rpm}$) resulted in greater extraction efficiency, it also gave rise to instability of organic drop. While at lower stirring rates, stir bar tends to be unsteady, even reversed. Therefore, a stirring rate of 800 rpm was used for subsequent experiments.

3.4. Extraction temperature

For volatile analytes, extraction temperature has a double impact on HS-LPME: at a higher temperature, diffusion

coefficients in both water and headspace are higher and the extraction time may be shorter; but the partition coefficients K_{oh} ($K_{\text{oh}} = K_{\text{odw}}/K_{\text{hs}}$) for the analyte between the organic solvent and gaseous phase [9,21] are lower. The effect of temperature was studied by exposing a 1-octanol drop for 10 min in the headspace of 25 ml THMs working solution, in triplicate, at 20 and 50°C . It was observed that, as expected, the amounts of THMs extracted at 20°C were 1.5–2.2 times as large as those extracted at 50°C . The main reason is that the process of analyte absorption in the microdrop is exothermic and the partition coefficient K_{oh} is temperature dependent [23]. If a low microdrop temperature is maintained during sampling, partition coefficient K_{oh} will increase. As a result, a greater mass transfer of analyte into the microdrop occurs and sensitivity should significantly increase. So, 20°C was used for subsequent experiments.

3.5. Salting-out effect

Salting-out effect has been used universally in SPME and LLE [18]. Addition of certain amount of salt can decrease the solubility of analytes in the aqueous sample and enhance their partitioning into the fiber coating for SPME or the organic phase for LLE. Salting-out effect was assessed by the addition of NaCl. Fig. 4 shows the effect of salt concentration on HS-LPME efficiency of THMs. With the agitation of the solution, the salt concentration from 0 to 0.2 g ml^{-1} had no obvious effect on the extraction of THMs. When NaCl concentration increased to 0.3 g ml^{-1} , extraction efficiency increased to reach a platform. So, further experiments were conducted at 0.3 g ml^{-1} NaCl.

3.6. Linear range, limit of detection and repeatability

Under the above optimum conditions, linear range, limit of detection and repeatability were obtained (Table 2). Linearity was observed over the range of $1\text{--}100 \mu\text{g l}^{-1}$ for four analytes. Coefficients of correlation (R^2) ranged from 0.998 to 0.9992 . The results agreed well with Eq. (2) that the amount of analyte n extracted by the microdrop is proportional to the initial concentration of the analyte C_0 . The limits of detection (LODs), based on a signal-to-noise ratio

Fig. 4. Effect of NaCl concentration on the relative peak areas of (1) CHCl_2Br , (2) CHClBr_2 , (3) CHBr_3 and (4) CHCl_3 . 1-Octanol drop was exposed to the headspace of 15 ml of aqueous solution for 10 min at 20°C at a stirring rate of 800 rpm .

Table 2

Linear range, correlation of coefficient (R^2), precisions and limits of detection (LODs) using HS-LPME-GC-ECD analysis

Compound	Linear range ($\mu\text{g l}^{-1}$)	R^2	RSD (%) ($n = 6$)	LOD ($\mu\text{g l}^{-1}$)	EPA method 624 [4] LOD ($\mu\text{g l}^{-1}$)	SPME [4] LOD ($\mu\text{g l}^{-1}$)
CHCl_3	1–100	0.9982	11.3	0.40	2.8	1.6
CHCl_2Br	1–100	0.9983	9.4	0.15	1.4	2.2
CHClBr_2	1–100	0.9992	8.2	0.15	1.0	3.1
CHBr_3	1–100	0.9980	8.7	0.20	1.2	4.7

Fig. 5. Chromatogram of a tap water sample by HS-LPME-GC-ECD. Peaks: (1) CHCl_3 , (2) CHCl_2Br , (3) CHClBr_2 , (4) CHBr_3 , (5) internal standard—hexachloroethane.

(S/N) of 3, ranged from 0.15 to $0.4 \mu\text{g l}^{-1}$. In comparison with previously reported SPME method [4] and EPA method 624 [4], we obtained the lowest LODs for all four targeted analytes. To assess the precision of the measurement, the repeatability of the method was determined by performing six times using aqueous standard solutions with $10 \mu\text{g l}^{-1}$ THMs. The RSD was found to be below 10% except that the repeatability of CHCl_3 was 11.3%.

3.7. Real water sample analysis

The proposed HS-LPME method was then applied to analyze the concentrations of THMs in tap water and well water samples. Well water came from deep-groundwater, which was relatively clean and can be drunk directly without pre-

treatment. Tap water was collected from a laboratory. The results for well water showed that it was free of THMs contamination. In tap water samples, CHCl_3 , CHCl_2Br , CHClBr_2 and CHBr_3 were detected and they were confirmed by comparing with a standard chromatogram. Fig. 5 shows the chromatogram obtained for tap water sample. However, the concentration of total THMs was below $20 \mu\text{g l}^{-1}$ and the concentration of each THM was below the guideline of the World Health Organization (WHO). THMs with $10 \mu\text{g l}^{-1}$ level were spiked into well water and tap water samples to assess matrix effects. The recoveries for CHCl_3 , CHCl_2Br , CHClBr_2 and CHBr_3 were from 101 to 112% in tap water and well water (the results are shown in Table 3). The results demonstrate that well water and tap water matrices have little effect on HS-LPME.

Table 3

Determination of THMs in well water and tap water

Compound	Well water		Tap water		WHO guidelines ^a ($\mu\text{g l}^{-1}$)
	Found ($\mu\text{g l}^{-1}$)	Recovery (%)	Found ($\mu\text{g l}^{-1}$)	Recovery (%)	
CHCl_3	n.d. ^b	108.8	10.3	101.0	200
CHCl_2Br	n.d.	109	4.58	105.3	60
CHClBr_2	n.d.	108.4	2.30	103.6	100
CHBr_3	n.d.	112	0.37	101.7	100

^a Data from [24].^b Not detected.

4. Conclusion

Headspace liquid-phase microextraction technique coupled to capillary column gas chromatography was successfully applied to determine THMs in drinking water. Among the organic solvents examined, 1-octanol was the most suitable solvent for the analytes. Extraction conditions such as headspace volume, extraction time, stirring rate, extraction temperature and salting-out effect are optimized and must be kept constant during the procedure of analysis. The optimized conditions were as follows: 15 ml headspace volume in a 40 ml vial, 10 min extraction time, 800 rpm stirring rate at 20 °C and 0.3 g ml⁻¹ NaCl added. In tap water samples, CHCl₃, CHCl₂Br, CHClBr₂ and CHBr₃ were detected and their concentrations were 10.3, 4.58, 2.30 and 0.37 µg l⁻¹, respectively. And the concentration of total THMs was below 20 µg l⁻¹. It can be concluded that LPME is a useful tool for the analysis of drinking water. More samples from Beijing city are analyzed using HS-LPME which will be reported later.

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