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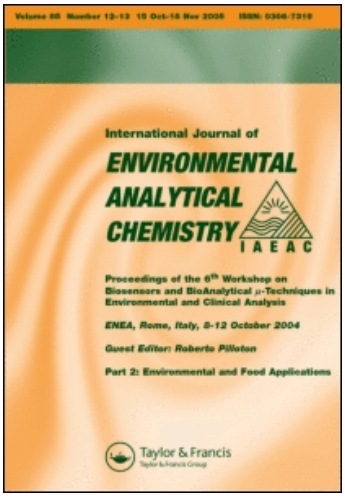


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# HEADSPACE SINGLE-DROP MICROEXTRACTION WITH GAS CHROMATOGRAPHY FOR DETERMINATION OF VOLATILE HALOCARBONS IN WATER SAMPLES

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A simple, rapid and inexpensive procedure for extraction and analysis of volatile halocarbons in water samples was presented using the headspace single-drop microextraction (HS-SDME) technique and gas chromatography with microcell electron capture detector (GC-μECD). Operation parameters, such as extraction solvent, headspace volume, organic drop volume, salt concentration, temperature and sampling time, were studied and optimized. Extraction of 10 volatile halocarbon compounds was achieved using the optimized method. Calibration curves of 10 target compounds yielded good linearity in the respective range of concentration ($R^2 \geq 0.9968$, chlorodibromomethane in the concentration range of 0.05 – 50 μg/L). The limits of detection were found between 0.002 (tetrachloroethene) and 0.374 μg/L (1,1,2-trichloroethane), and relative standard deviations (RSD%) ranged between 4.3 (chloroform) and 9.7% (1,1,2,2-tetrachloroethane). Spiked recoveries of tap water and ground water agreed well with the known values between 118.97 (20.0 μg/L of 1,1,2-trichloroethane) and 82.61% (10.0 μg/L of tetrachloroethene), demonstrating that the HS-SDME combined GC-μECD was a useful and reliable technique for the rapid determination of volatile halocarbon compounds in water samples.

*Keywords:* Headspace single-drop microextraction; Volatile halocarbons

## INTRODUCTION

Chloroform, dichlorobromomethane, chlorodibromomethane and bromoform are the major groups of volatile halocarbon by-products in drinking water [1,2]. Carbon tetrachloride in drinking water mainly comes from the impurity of the disinfectants. 1,1,1-Trichloroethane, trichloroethene and tetrachloroethene are related to the pollution of water from industrial discharge and might be present in the extraction water at water treatment plants [3,4]. Since adverse effects of these volatile halocarbons with regard to carcinogenicity and/or mutagenicity have been reported [5–7], volatile

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chlorinated compounds, especially low-molecular-weight halocarbons in drinking water, have been listed as the priority pollutants of environment in many countries and organizations.

Since the concentrations of these compounds are normally low (μg/L or less) in drinking water, extraction or concentration pretreatment is necessary before final determination by GC/ECD or GC/MS. The general pretreatment methods for those volatile organic compounds include liquid–liquid extraction (LLE), the static headspace sampling technique and the purge-and-trap technique (dynamic headspace sampling technique). Recently, solid-phase microextraction (SPME) has also been used to determine these compounds in environmental water samples [6–8]. However, some disadvantages in LLE mainly relate to the losses of volatile analytes during the course of multiple extractions except for the operation time and solvent consumption. Static headspace sampling requires very careful calibration, the purge-and-trap technique requires expensive experimental equipment, and the fiber of SPME is expensive and fragile, and has a limited durability.

Single-drop microextraction (SDME) is a type of liquid–liquid extraction in which the analyte is partitioned between the aqueous phase and a very small volume of organic solvent. In 1997, Jeannot and Cantwell [9], and He and Lee [10] independently introduced this method in which analytes were extracted by suspending one or several milliliters of organic solvent from the needle tip of a microsyringe in an aqueous solution, and then a drop of the organic solvent was withdrawn into the microsyringe and injected directly into the gas chromatograph. In recent years, SDME has been described in several papers [11–20]. The advantages of this method are that it requires only a small amount of toxic organic solvent and simple experimental equipment, and sampling, extraction, concentration and sample introduction are integrated into a single step. However, in this method, the two major disadvantages are that it can only be used for liquid samples, and the matrix will have an important effect as a result of organic drop immersion in the aqueous phase. These drawbacks can be eliminated if headspace single-drop microextraction (HS-SDME) is adopted. In HS-SDME, a microdrop of high-boiling-point solvent is extruded from the needle of a microsyringe, then suspended in the headspace of solution. Since only the volatile compounds or semivolatile compounds volatilizing to the headspace will be extracted to the microdrop, interference from the complex matrix will decrease greatly. The technique was first reported in 2000 [21]. In 2001, Tankeviciute *et al.* [22] used HS-SDME to analyze low-molecular-weight alcohols in beer. Apart from quantification of alcohol [22,23], HS-SDME has also been used successfully in the determination of benzene congeners [24–27], PAHs [28], etc.

In 2002, Buszewski *et al.* [11] reported the analysis of trihalomethanes in water using the single-drop extraction *vs.* SPME. The experiment results highlight the usefulness of single-drop extraction for the analysis of trihalomethanes present in tap water at ppb levels and the comparability with SPME in precision and analysis time. However, in the extraction process, the authors did not position the microdrop in the headspace but suspended the organic drop in the tip of a syringe directly immersed in the aqueous phase. To our knowledge, there have been no reports on the analysis of volatile halocarbons using HS-SDME.

In the present work, HS-SDME is studied for the quantitative analysis of volatile halocarbons in water samples to minimize any interferences from the sample matrix. Ten volatile halocarbons are selected as our target compounds, which

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include: (1) chloroform, (2) 1,1,1-trichloroethane, (3) carbon tetrachloride, (4) bromodichloromethane, (5) trichloroethene, (6) 1,1,2-trichloroethane, (7) tetrachloroethene, (8) dibromochloromethane, (9) bromoform and (10) 1,1,2,2-tetrachloroethane. All the compounds selected have been included in the 'priority pollutants' listings implemented by the US Environmental Protection Agency (USEPA) and are also listed – with three exceptions, (4), (8), (9) – by the China National Environmental Monitoring Center as China's priority pollutants in water. The results indicated that HS-SDME is an effective extraction technique with which to analyze the volatile halocarbons in water samples. It was also demonstrated that HS-SDME is extraordinarily fast, simple, convenient and inexpensive.

## EXPERIMENTAL

### Apparatus

The magnetic stirring apparatus used was Model IKA®RH-KT/C (Germany, made in Guangzhou). A 10-μL Hamilton gas-tight microsyringe (Hamilton, Model 1701) with a beveled needle tip (length: 5.1 cm, i.d.: 0.013 cm, bevel 22°) was used in the HS-SDME [25]. Chromatographic analysis was carried out on an Agilent 6890 gas chromatograph equipped with a microcell electron capture detector (GC-μECD). The column used was a HP-5 fused capillary column (30 m × 0.53 mm, 0.88 μm film thickness). The injector and detector temperature were 250 and 300°C, respectively. The oven temperature was held initially at 35°C for 2 min, programmed to 60°C at a rate of 5°C/min, and increased to 220°C at 10°C/min. The split mode was utilized, and the split ratio was 25 : 1. Nitrogen gas was used as a carrier gas and make-up gas.

Przyjazny and Kokosa [25] found that the internal standard method can improve the precisions of analytes among 2.7–5.9%, but satisfactory precision can also be obtained in the range of 6.9–9.6% by the external standard method when this technique is used to analyze benzene, toluene, ethylbenzene and xylenes. In our study, the target compounds were quantified using an external standard method and identified by the GC retention time of the standard solution, and the results were confirmed by GC/MS. GC/MS was performed on an Aglient 6890 GC equipped with a 5973 mass-selective detector (MSD). An HP-5ms column with dimensions of 30 m × 0.25 mm (0.25 μm film thickness) was used. The GC operation parameters were similar to those in the GC/ECD determination described above, except that helium was used as carrier gas. The ion source and quadrupole temperatures were 250 and 150°C, respectively. MS was operated in the selected ion monitoring (SIM) mode with electron-impact ionization at an electron energy of 70 eV. Two characteristic ions of each analyte were selected. Identification was based on the retention time and the ion intensity ratio of sample peaks within 10% of the mean values obtained from the corresponding standards.

### Reagents

(1) Chloroform, (2) 1,1,1-trichloroethane, (3) carbon tetrachloride, (4) trichloroethene, (5) dichlorobromomethane, (6) 1,1,2-trichloroethane, (7) chlorodibromomethane, (8) tetrachloroethene, (9) bromoform and (10) 1,1,2,2-tetrachloroethane as standard

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materials were obtained from Aldrich (Milwaukee, WI). The above-mentioned numerical orders of compounds represent the eluting peak sequences in GC. 1-Octanol, ethylene glycol and hexadecane were chromatography reagent grade and were obtained from Beijing Chemical Plant (Beijing, China). Sodium chloride (from the Beijing Shuanghuan Chemical Plant) was of analytical reagent grade and heated at 600°C for 4 h before use. The water used for preparing the standard solution and the blank sample was purified by Milli-Q water purification system (Millipore, Bedford, MA).

The individual stock solution was prepared in methanol at a concentration of 1.00 mg/mL. Appropriate portions of the stock solutions of the target compounds were combined and diluted with methanol to prepare a second stock solution. These solutions were stored in amber glass bottles at 4°C.

### Extraction Procedure

The 40-mL water solution was transferred to a 65-mL clear silanized glass vial and sealed tight. One microliter of 1-octanol was drawn into the microsyringe. The microsyringe was then fixed in such a way that the extraction needle tip protruded to a depth of 1 cm down into the vial cap. The microsyringe plunger was then completely depressed to release a 1.0-μL drop on the needle tip. The stirring velocity was controlled at about 1000 rpm. Temperature was controlled by a water bath at 25°C. After extraction for 10 min, the plunger was withdrawn, and the microdrop was drawn into the microsyringe. The content in the microsyringe was then injected into the GC injector for determination.

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## RESULTS AND DISCUSSION

### Optimization of HS-SDME

For HS-SDME, several parameters affecting the extraction performance, such as the extraction solvent, organic drop volume, salt concentration, temperature and sampling time, were tested, and these are discussed in detail in the following sections. The spiked concentrations of compounds in the water sample were 4.0, 2.0, 0.5, 4.0, 2.0, 20.0, 2.0, 2.0, 5.0 and 5.0 μg/L, in terms of the eluting peak sequences (listed earlier). For simplicity, three compounds (1), (5) and (10) were selected as representatives to show the effect of different extraction conditions in optimizing the extraction conditions.

#### *Solvent Extraction*

It is very important to select an appropriate extraction solvent for the HS-SDME method. Three basic requirements must be met: a high boiling point and a low volatility, and a good extraction efficiency for the target compounds should be high so as not to interfere with the analysis of the target compounds in the chromatography. In accordance with the above requirements, ethylene glycol, 1-octanol and hexadecane were selected as extraction solvents and tested for their suitability. Each solvent was evaluated using an enrichment factor in the extraction of a 40-mL water sample with a 5-min extraction time at 25°C in the stirred solution with a 1.0-μL organic drop. Each enrichment factor was calculated as the ratio of analyte concentration in both

TABLE I Enrichment factors for different extraction solvents

| *Compounds* | *1-Octanol* | *Ethylene glycol* | *Hexadecane* |
|---|---|---|---|
| Chloroform | 53 | 40 | 27 |
| 1,1,1-Trichloroethane | 133 | 119 | 120 |
| Carbon tetrachloride | 209 | 186 | 203 |
| Trichloroethene | 174 | 164 | 168 |
| Dichlorobromomethane | 80 | 58 | 37 |
| 1,1,2-Trichloroethane | 50 | 47 | 30 |
| Chlorodibromomethane | 172 | 105 | 67 |
| Tetrachloroethene | 645 | 583 | 798 |
| Bromoform | 218 | 201 | 136 |
| 1,1,2,2-Tetrachloroethane | 212 | 205 | 102 |

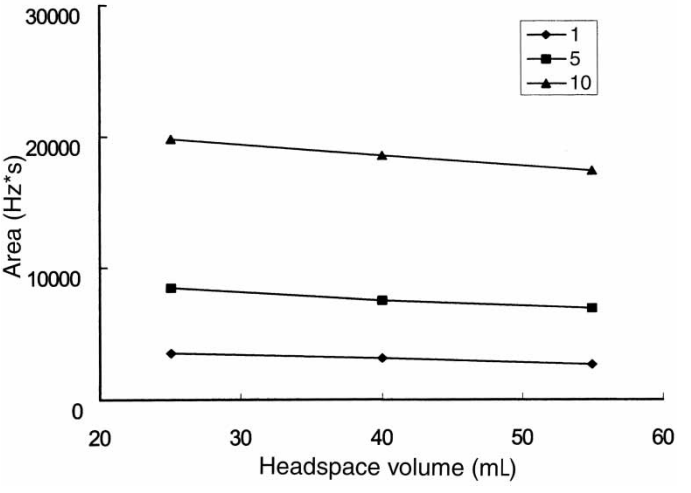


FIGURE 1 Comparison of GC response signals using different headspace volumes. The spiked water sample (40 mL) was extracted using 1.0 μL of a drop of 1-octanol at 25°C for 5 min under constant rotation speed. (1) Chloroform, (5) dichlorobromomethane and (10) 1,1,2,2-tetrachloroethane.

the aqueous solution and the solvent drop (Table I). Of the three solvents examined, nonpolar hexadecane has the best chromatographic behavior, but both 1-octanol and ethylene glycol had relatively better enrichment factors than hexadecane except for tetrachloroethene. The main reason was that 1-octanol and ethylene glycol had a stronger affinity for target compounds. The perfect extraction solvent should be based not only on the extraction efficiency but also, selectively, on the incidence of drop loss and rate of drop dissolution [29]. Since 1-octanol has a relatively higher boiling point and lower vapor pressure, it was selected as the extraction solvent for the following study.

### *Headspace Volume*

Headspace volume is an important factor that affects the analytical precision, repeatability and accuracy. In our study, headspace volumes of 25, 40 and 55 mL were tested in a 65-mL vial with 5 min of extraction at 25°C in the stirred solution with 1.0 μL of 1-octanol. As shown in Fig. 1, the lower the ratio of the gas phase to

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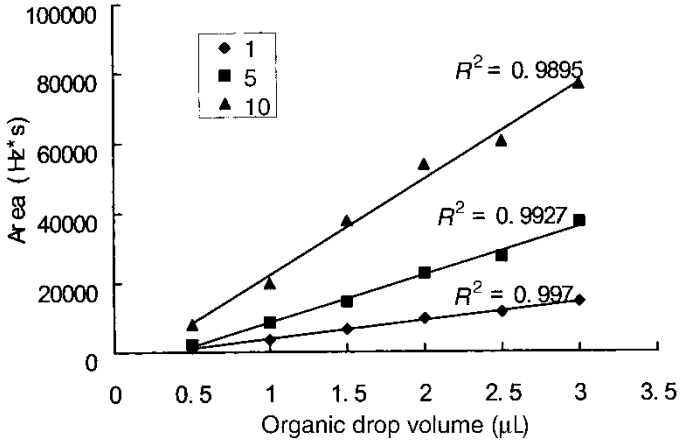


FIGURE 2 Comparison of GC response signals with different organic drop volume. The spiked water sample (40 mL) was extracted using a drop of 1-octanol at 25°C for 5 min under a constant rotation speed. (1) Chloroform, (5) dichlorobromomethane and (10) 1,1,2,2-tetrachloroethane.

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liquid phase, the larger the area of the target chromatographic peak. Although the sensitivity of the determination is better with a smaller headspace, it is difficult to manipulate the experiment if the headspace is too small. A liquid phase : gas phase ratio of about 1 : 2 is suitable, and so the 25-mL headspace volume or 40-mL liquid volume was appropriate in our study.

### *Organic Drop Volume*

A comparison of extraction results with 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 μL of 1-octanol is shown in Fig. 2. It can be seen that the target peak areas improved with increasing organic drop volume. Moreover, there appeared to be a good linear relationship between the peak area and drop volume, with correlation coefficients ($R^2$) in the range of 0.9606–0.9817 (except for chlorodibromomethane, which was 0.9079). Przyjazny [25] reported that the relationship between the amount of analyte extracted and the microdrop volume was approximately linear when keeping the certain conditions constant (vial size, sample, headspace volume and so on), and a similar result was reported by Hou and Lee [13]. Although a larger organic drop volume may enhance the extraction efficiency, a very large organic drop volume would not be suitable, because its manipulation would be more elaborate and less reliable. Also, large injection volumes can result in a large and extensive solvent peak in the GC chromatogram, which may interfere with the determination of target compounds [25]. On this basis, 1.0 μL was used to study the performance of HS-SDME, because this enabled a good enrichment to target compounds and easy manipulation.

### *Salt Concentration*

In SDME, the presence of salt generally decreases the extraction efficiency of analytes, such as chlorobenzenes [27], nitroaromatic explosives [19], PAHs [11], etc. However, in HS-SDME, the presence of salt increases the extraction efficiency [28]. In our present study, the effect of sodium chloride with concentrations of 0, 0.10, 0.20 and

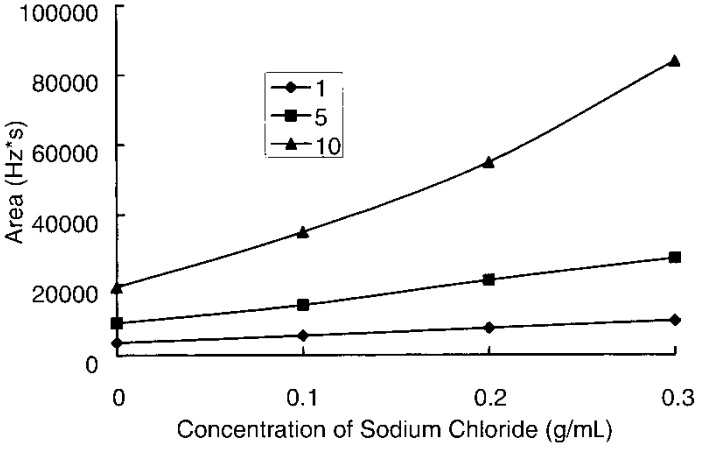


FIGURE 3 Comparison of GC response signals at different salt concentrations. The spiked water sample (40 mL) was extracted using 1.0 μL of a drop of 1-octanol at 25°C for 5 min at a constant rotation speed. (1) Chloroform, (5) dichlorobromomethane and (10) 1,1,2,2-tetrachloroethane.

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0.30 g/mL was investigated. The results, based on triplicate analyses, showed that the peak areas of analytes in the GC chromatogram were improved with increasing sodium chloride concentration, and those of the compounds with a larger molecular weight appeared to have been enhanced even more. For example, the GC response signals of 1,1,2,2-tetrachloroethane in 0.10, 0.20 and 0.30 g/mL salt were about 1.8, 2.8 and 4.3 times higher than without salt; that of chloroform in 0.10, 0.20 and 0.30 g/mL salt was about 1.5, 2.0 and 2.6 times higher than without salt (Fig. 3). The results from our study indicate that the presence of salt in the solution can increase the extraction efficiency for this group of compounds, and the appropriate concentration of sodium chloride is 0.30 g/mL.

### *Temperature*

Temperature is a very important factor for extraction efficiency in the SDME method. The effect is even more complex in HS-SDME due to the partition of analytes among the liquid phase, the gas phase and the extraction phase. Temperature was found to have a different effect on the different analytes. For example, for benzene, toluene, ethylbenzene and xylene, the higher the temperature, the lower the extraction efficiency was [25], but the reverse was true for alcohols [22] and PAHs [28]. In this study, the effect of sampling temperature was studied by exposing 1.0 μL of 1-octanol in the headspace for 5 min in the 40-mL stirred solution containing 0.30 g/mL sodium chloride at 25, 35 and 50°C, respectively. The result is shown in Fig. 4A and B. In this range of temperatures, for lower-molecular-weight compounds such as chloroform and trichloroethene, higher temperatures reduced the extraction efficiency (Fig. 4A), but for higher-molecular-weight compounds such as bromoform and 1,1,2,2-tetrachloroethane, the extraction efficiency reached a maximum at 35°C (Fig. 4B).

Temperature has a significant effect on both the kinetics and thermodynamics of the sorption process. At the higher temperature, the vapor pressure of the analytes and the concentration in the headspace increase, improving the extraction efficiency, but the adsorbtion of analytes in the microdrop is exothermic, and the partition coefficients

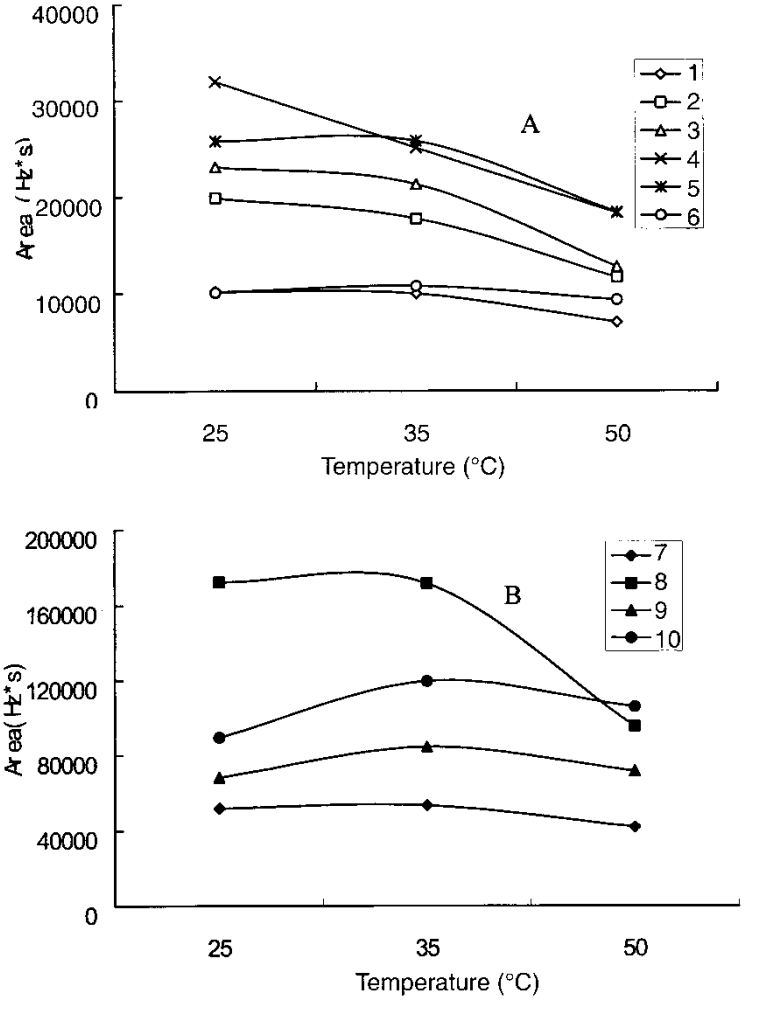


FIGURE 4 Comparison of GC response signals at different temperatures. The spiked water sample (40 mL) was extracted using 1.0 μL of a drop of 1-octanol for 5 min under a constant rotation speed. (1) Chloroform, (2) 1,1,1-trichloroethane, (3) carbon tetrachloride, (4) trichloroethene, (5) dichlorobromomethane, (6) 1,1,2-trichloroethane, (7) chlorodibromomethane, (8) tetrachloroethene, (9) bromoform, (10) 1,1,2,2-tetrachloroethane.

to the extraction phase decrease, thus reducing the extraction efficiency. The phenomena from Fig. 4 can be explained as the interactional results of the kinetics and the thermodynamics. In Fig. 4A, the compounds with a lower molecular mass could volatize to the headspace and transfer to the microdrop rapidly, with the result that removal from the microdrop would be faster than the absorbtion from the headspace at the higher temperature. In Fig. 4B, the extraction efficiency at 35°C was higher than at 25°C. This may be because the analytes can volatize more to the headspace at the higher temperature, and the adsorbility of analytes from the headspace exceeds the removal of analytes from the microdrop. With further increases in temperature, the degree of analyte removal from the microdrop is high, thus decreasing the efficiency.

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In this experiment, for most analyzed compounds, the maximum extraction efficiency was reached at 25°C. Therefore, 25°C was selected as the appropriate temperature for the analysis of the target compounds in our experiments.

### *Sampling Time*

In HS-SDME, exhaustive extraction does not occur as mentioned above. The amount of analytes transferred to the organic drop reaches its maximum when equilibrium among the three immiscible phases is established. Normally, the time to reach equilibrium is selected as the sampling time to increase the extraction efficiency (if it is not too long). In this experiment, sampling times of 3, 5, 10, 15 and 20 min were used together with the optimized operation parameters described above. The result, as shown in Fig. 5, indicates that there are a maximum number of GC signals at 10 min, and the GC signals are not improved over a longer period of time. Therefore, equilibrium was established in 10 min for these target compounds, and 10 min was selected as the extraction time in our experiment.

Finally, the optimized conditions are as follows: analytes extracted for 10 min and 0.30 g/mL sodium chloride in 40 mL of stirred solution with 1.0 μL of 1-octanol.

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## Evaluation of Method Performance

### *Main Method Parameters and Spiked Recoveries*

The determination linearity for these analytes with HS-SDME method was tested using spiked water samples under the optimized conditions described above. The spiked water samples were prepared by diluting the secondary stock solution with water. Calibration curves were made at six different concentration levels, and all target compounds yielded a good linearity ($R^2 \geq 0.9968$, chlorodibromomethane in the concentration range of 0.05–50 μg/L). From this, the signal-to-noise ratio was found to be equal to 3, and the detection limits of the target compounds were found to be 0.002 (tetrachloroethene) to 0.374 μg/L (1,1,2-chloroethane). The Relative Standard Deviations (RSD)% ranged from 4.3 (4.0 μg/L of chloroform) to 9.7% (5.0 μg/L of 1,1,2,2-tetrachloroethane) in the spiked working solution from seven repeating experiments when the external standard method was used for quantitative analysis. These results are listed in Table II. Previous studies on THMs in water samples have shown that the limits of detection (LODs) and RSD% using SPME-GC-MS [4] were 1.0–2.8 and 0.9–19%, and those using SPME-GC-ECD were 0.01–0.005 μg/L [5]. In the purge-and-trap technique, the LODs and RSD% were 0.02–0.07 μg/L and 2.46–5.23% [30,31]. In the static headspace technique, the LODs and RSD% were 0.1–0.2 μg/L and 5.1–13.5% [32]. Compared with these techniques, the HS-SDME method in our study can yield similar results to those from the SPME and purge-and-trap technique, and LODs lower than those from the static headspace technique.

For real environmental sample determination, the tap water and ground water from the Haidian district of Beijing were analyzed for volatile halocarbons. Five compounds including chloroform, carbon tetrachloride, dichlorobromomethane, chlorodibromomethane and bromoform were detected from the tap water and were identified by GC-MS in the following quantities: 7.74, 0.03, 4.41, 0.95 and 0.63 μg/L, respectively (Fig. 6). No target compounds were found in the ground-water sample. The higher

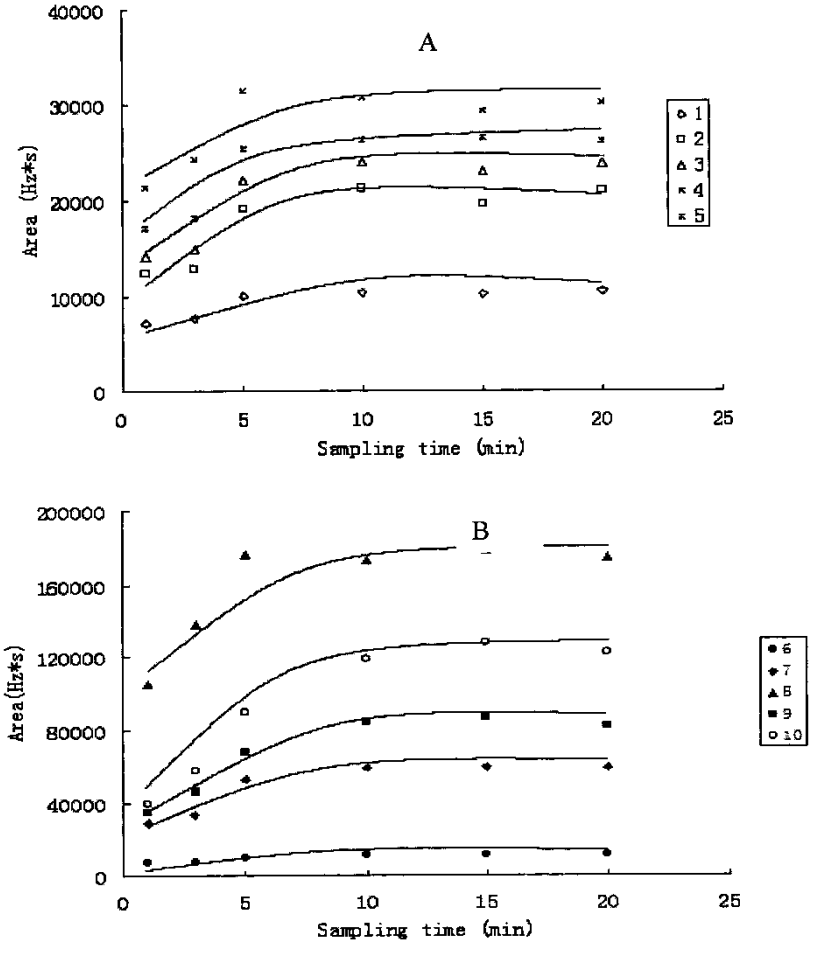


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FIGURE 5 Comparison of GC response signals with different sampling time. The spiked water sample (40 mL) was extracted using 1.0 μL of a drop of 1-octanol at 25°C under a constant rotation speed. (1) Chloroform, (2) 1,1,1-trichloroethane, (3) carbon tetrachloride, (4) trichloroethene, (5) dichlorobromomethane, (6) 1,1,2-trichloroethane, (7) chlorodibromomethane, (8) tetrachloroethene, (9) bromoform, (10) 1,1,2,2-tetrachloroethane.

TABLE II Main method parameters: linear range, correlation coefficient, relative standard deviation (RSD%) and detection limits[a]

| *Compound* | *Linear range* (μg/L) | $R^2$ | *RSD* (%) ($n=7$) | *LOD* (μg/L) |
|---|---|---|---|---|
| Chloroform | 0.1–100 | 0.9994 | 4.3 (4.0) | 0.035 |
| 1,1,1-Trichloroethane | 0.05–50 | 0.9998 | 5.1 (2.0) | 0.021 |
| Carbon tetrachloride | 0.0125–12.5 | 0.998 | 6.2 (0.5) | 0.004 |
| Trichloroethene | 0.1–100 | 0.9998 | 5.3 (4.0) | 0.025 |
| Dichlorobromomethane | 0.05–50 | 0.9968 | 4.7 (2.0) | 0.015 |
| 1,1,2-Trichloroethane | 0.5–500 | 0.9994 | 6.3 (20.0) | 0.374 |
| Chlorodibromomethane | 0.05–50 | 0.9999 | 9.6 (2.0) | 0.011 |
| Tetrachloroethene | 0.05–50 | 0.9997 | 6.5 (2.0) | 0.002 |
| Bromoform | 0.25–250 | 0.9992 | 7.7 (5.0) | 0.043 |
| 1,1,2,2-Tetrachloroethane | 0.25–250 | 0.9992 | 9.7 (5.0) | 0.028 |

[a]Data in parentheses represent the concentration of compounds in the spiked water sample (μg/L).

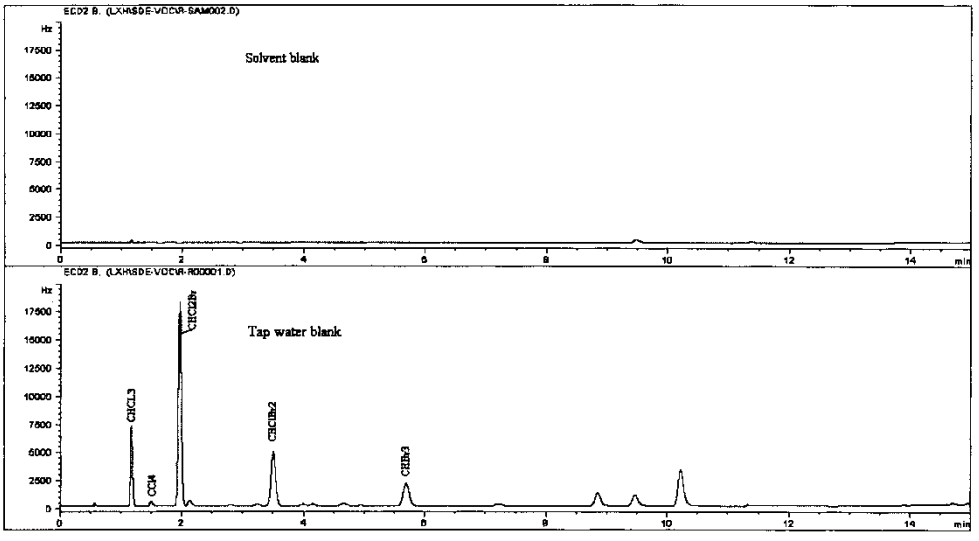


FIGURE 6 Chromatogram of a tap-water blank with headspace single-drop microextraction and solvent blank.

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level of bromoform in the tap water might be because the water treatment plant draws water from surface water (reservoir), there may be more bromide ions present in the source water, or the chlorine used as a disinfectant may have become contaminated by bromine. At the same time, the experiment was carried out in the autumn, and higher levels of bromoform may be present then. To evaluate the matrix effect, the two level concentrations of compounds were spiked to two media. The amount of analytes extracted by HS-SDME accorded well with known values spiked to the medium. The spiked recoveries and RSD% were in the range of 118.90–82.61 and 2.4–15.5%, respectively. The good linearity and satisfactory recoveries showed that HS-SDME was feasible in the analysis of volatile chlorinated compounds in water samples. The results are detailed in Table III.

## CONCLUSIONS

In this study, a novel mode HS-SDME method has been developed to determine volatile halocarbons in water samples on the basis of SDME. The extraction solvent, headspace volume, organic drop volume, salt, temperature and sampling time have been investigated, and the optimal operation parameters are as follows: a 40-mL water sample extracted with a 1.0-μL 1-octanol drop at 25°C for 10 min with 0.3 g/mL in the stirred solution. In the optimized condition, the linear calibration curves, the precision, accuracy and spiked recoveries obtained show that the HS-SDME method is a useful and reliable technique to determine volatile halocarbon compounds in water samples. Compared with the other preconcentration method for volatile halocarbons, the advantages of this method are that it is simple, rapid and inexpensive, and it requires only small volumes of organic solvents and samples. Compared with the SDME, HS-SDME can be used for both liquid and solid samples. Since HS-SDME can be used to extract analytes in the headspace, the analytes are not disturbed

TABLE III Amounts of volatile halocarbons detected originally and spiked recoveries in tap water and ground water[a]

| *Compound* | *Tap water* | | | *Ground water* | | |
|---|---|---|---|---|---|---|
| | *Detected* (μg/L) | *Recovery* | | *Detected* (μg/L) | *Recovery* | |
| | | *1*[b] | *2*[c] | | *1*[b] | *2*[c] |
| Chloroform | 7.74 | 101.62 (8.1) | 102.47 (4.9) | n.d.[d] | 112.46 (5.6) | 90.43 (6.9) |
| 1,1,1-Trichloroethane | | 114.46 (2.4) | 108.50 (5.5) | n.d. | 116.61 (9.4) | 108.95 (6.8) |
| Carbon tetrachloride | 0.03 | 93.69 (7.9) | 113.09 (11.5) | n.d. | 90.21 (10.4) | 109.32 (5.8) |
| Trichloroethene | | 108.10 (9.6) | 103.4 (7.2) | n.d. | 93.15 (4.9) | 87.5 (18.5) |
| Dichlorobromomethane | 4.41 | 103.99 (5.1) | 102.90 (9.3) | n.d. | 103.04 (3.3) | 92.50 (15.5) |
| 1,1,2-Trichloroethane | | 118.97 (10.2) | 104.44 (7.3) | n.d. | 117.66 (6.6) | 90.98 (6.2) |
| Chlorodibromomethane | 0.95 | 99.94 (3.6) | 99.36 (9.0) | n.d. | 90.41 (3.7) | 112.06 (5.4) |
| Tetrachloroethene | | 98.54 (7.6) | 82.61 (8.5) | n.d. | 94.87 (14.3) | 84.16 (6.1) |
| Bromoform | 0.63 | 96.21 (3.2) | 114.28 (9.3) | n.d. | 102.68 (4.3) | 114.37 (4.9) |
| 1,1,2,2-Tetrachloroethane | | 110.42 (7.5) | 90.5 (11.1) | n.d. | 112.65 (3.5) | 91.71 (5.0) |

[a]Data in parentheses represent the RSD% in the spiked water sample (μg/L).
[b]Recovery 1: the spiked concentration level of the compounds in the table is 4.0, 2.0, 0.5, 4.0, 2.0, 20.0, 2.0, 2.0, 5.0 and 5.0 μg/L from the top down, respectively.
[c]Recovery 2: the spiked concentration level of the compounds in the table is 20.0, 10.0, 5.0, 20.0, 10.0, 100.0, 10.0, 10.0, 25.0 and 25.0 μg/L from the top down, respectively.
[d]n.d.: not detected.

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by a 'dirty' matrix, and so the technique can be used to analyze samples containing a complex matrix. In addition, HS-SDME requires a shorter extraction time than SDME because the analytes in the headspace can be extracted more rapidly than they would be in the liquid phase. The cost-effectiveness of the technique makes it more suitable for fast screen determination of these compounds in environmental investigations in which a large number of samples need to be analyzed in a relative short period. The concentrations of target analytes detected in tap water in this work are all below the respective regulation limits of the USEPA Priority Pollutant in Water listing and China PP listing.

Overall, HS-SDME is an attractive technique for the preconcentration of volatile and semivolatile compounds. In addition to environmental applications, the use of HS-SDME can be extended to pharmaceutical, forensic and food analysis [29].

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