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Single drop microextraction and gas chromatographic determination of volatile halogenated hydrocarbons

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A simple, rapid and inexpensive procedure for extraction of volatile halogenated hydrocarbons by headspace single drop microextraction is presented. Decane was selected as the extracting solvent. The operation parameters such as organic drop volume, sample stirring rate, extraction time, salt concentration were optimized. Quality parameters of the method were determined. The repeatability of the method was 5.0–6.5%. Calibration graphs were linear up to 50 μg l^{-1} ($R^2 \geq 0.995$) and detection limits ranged from 0.42 to 1.78 μg l^{-1}. For all the target compounds, the limits of detection were much lower than the maximum contaminant level permitted in drinking water. The proposed technique was applied for volatile halogenated hydrocarbon determination in groundwater.

Key words: headspace single drop microextraction, gas chromatography, volatile halogenated hydrocarbons, water

INTRODUCTION

Volatile halogenated hydrocarbons (VHHs) are anthropogenic compounds. Volatile chlorinated hydrocarbons such as chloroform, 1,1,1-trichloroethane, tetrachloromethane, 1,1,2-trichloroethylene, tetrachloroethylene are widely used in industrial and commercial processes [1]. During their use they are often released into the environment. Moreover, water is often disinfected with chlorine. Trichloromethanes (chloroform, bromodichloromethane, dibromochloromethane, bromoform) are products of disinfection when chlorine reacts with organic matter and bromides present in water [1, 2]. Because of their high volatility, VHHs are easily transported in the atmosphere and thus are present not only close to their sources but also spread all over the environment, including all aqueous matrices.

VHHs are stratospheric ozone depleting gases and greenhouse gases [3] and so influence the global climate change. These compounds are suspected to be carcinogenic. For these reasons, VHHs are widely monitored. According to Lithuanian Legislation [4], the maximum contaminant level (MCL) permitted in drinking water for a single volatile halogenated compound should not exceed 5–37.5 μg l^{-1}; the total VHHs have been set at 150 μg l^{-1} and will be reduced to 100 μg l^{-1} on 31 December 2008. Since the concentrations of VHHs in water are normally low, a preconcentration step is necessary.

Different extraction techniques, including liquid–liquid extraction [5], solid-phase extraction [5], solid-phase microextraction [3, 6, 7], in-tube extraction [8, 9], purge and trap extraction [1, 2], solvent microextraction [10, 11] have been reported for this purpose. Solvent microextraction techniques can be divided into two main groups: liquid phase microextraction using immiscible liquid films, and single drop microextraction (SDME). The latter was suggested in 1996 [12, 13] and is based on the distribution of the analytes between the aqueous solution and a microdrop of organic solvent at the tip of a microsyringe needle. The extraction technique requires very small volumes of organic solvents, is fast, can be performed with the simplest devices, a conventional microsyringe, and those are significant advantages over the most commonly used liquid–liquid extraction technique.

SDME initially was accomplished by immersing a solvent drop directly into the aqueous solution (direct SDME). Headspace SDME (HS-SDME) was suggested in 2001 [14]. This extraction mode is especially useful in the case of volatile analytes which readily pass from the aqueous phase into the headspace, meanwhile less volatile compounds remain in the water and do not interfere with the analysis. Headspace SDME was successfully applied for the determination of alcohols [15, 16], esters [17], volatile aromatic hydrocarbons [18], chlorinated hydrocarbons [10], chlorobenzenes [19], short-chain fatty acids [20], aldehydes [21].

In this study, we have applied the HS-SDME technique for preconcentration of VHHs in water samples. Extraction conditions such as extraction solvent type, solvent drop size, sample stirring rate, extraction time and ionic strength of a sample were studied and optimized. The method has been applied for real water sample analysis.

EXPERIMENTAL

Reagents and solutions

Chloroform (≥99.8%), bromoform (≥99%), bromodichloromethane (≥98%), dibromochloromethane (≥98%), trichloroethene (≥99.5%), tetrachloroethene (≥99%), chlorobenzene (≥99%), bromobenzene (≥99%), carbon tetrachloride (≥99%), hexane (≥97%), octane (≥98%), decane (≥99%) and acetone

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(≥99.9%) were purchased from Sigma-Aldrich. NaCl (analytical grade) was purchased from Reachim (Ukraine). All the reagents were used without further purification.

A standard stock solution of chloroform, bromoform, bromodichloromethane, dibromochloromethane, trichloroethene and tetrachloroethene at a concentration of 0.5 mg l^{-1} was prepared in acetone. The stock solution was stored refrigerated at +4 °C. Working standard solutions were prepared daily by diluting the stock standard solution with distilled water to desirable concentrations.

The extraction organic phase was decane containing a fixed concentration of chlorobenzene as the internal standard.

INSTRUMENTATION

Single-drop microextraction was performed in a 4-ml vial closed with a PTFE coated septum placed in the cap. For the extraction, 2 ml of aqueous solution was used. Single-drop microextraction was performed with a commercially available 10 µl microsyringe (Hamilton Microliter 700 series syringe). During the extraction, the syringe was fixed above the extraction vial so that the needle passed the septum and the needle tip appeared about 1 cm above the surface of the solution. Then a drop of the extracting solvent was suspended from the needle tip. The extraction being finished, the drop was retracted back into the needle and injected directly into the gas chromatograph.

Gas chromatography was carried out in a Shimadzu GC-2010 (Japan) gas chromatograph equipped with an electron capture detector and an EC-5 fused silica capillary column (30 m × 0.53 mm, 1 µm film thickness). Injector and detector temperatures were 200 °C and 250 °C, respectively. The oven temperature was programmed: it was initially set at 35 °C for 5 min, then gradually ramped to 45 °C (1 °C min^{-1}), 100 °C (7 °C min^{-1}) and held for 1 min. The following gas flow rates were used: carrier (nitrogen) 4 ml min^{-1}, make-up gas (nitrogen) 26 ml min^{-1}.

RESULTS AND DISCUSSION

Extraction solvent

Selection of a proper extraction reagent is one of the main conditions that ensure a high extraction efficiency. An extraction solvent for SDME has to meet two main requirements: to extract analytes well and to be separated from the analyte peaks in the chromatogram. According to [22], hexane is suggested for the traditional liquid–liquid extraction of VHHs. Hexane and other aliphatic hydrocarbons are not detected by the electron capture detector, so the peaks of those solvents would not interfere with the analyte peaks. So we examined the possibility to apply hexane or other solvent of the same class to HS-SDME as well.

Preliminary trials were accomplished exposing a 2-µl solvent drop in the headspace of aqueous solution containing 10 µg l^{-1} of VHHs. Three solvents – hexane, octane and decane – were examined. Hexane was too volatile for HS-SDME: after a 5-min of exposure to the headspace, the hexane drop completely evaporated. The evaporation of octane was slower, however, even in this case after 30 min of exposure the volume of the drop diminished to 0.5 µl. Decane was the best from all the solvents tested, because its drop after 30 min was 1.5 µl. In order to correct for variable injection volumes, an internal standard chlorobenzene was added into the extraction solvent. An analytical signal was taken as the peak area ratio of analyte to chlorobenzene.

Drop volume

SDME is not an exhaustive extraction technique, so the amount of the analytes extracted increases with the organic drop volume. 0.5–5 µl decane drop volumes were examined. With increasing the drop volume to 3 µl, the amount of extracted analytes increased. However, a 3 µl drop was difficult to handle, it tended to fall down before the extraction was finished. 4–5 µl drops were even less stable and detached from the microsyringe needle tip in a few minutes. In order to obtain a good extraction efficiency and repeatability, a decane drop volume of 2 µl was chosen for HS-SDME of VHHs.

Stirring rate and sampling time

The extraction rate depends on the aqueous phase mass transfer, the diffusion of analyte molecules from the aqueous phase to the gaseous phase, headspace mass transfer and the analyte diffusion into the extracting drop. Stirring of the solution should mainly influence the aqueous phase mass transfer, so the equilibrium between the aqueous and vapor phases can be achieved more rapidly by stirring the aqueous sample.

In our experiments, samples were continuously agitated on a magnetic stirrer for 15 min at different stirring rates. The peak areas of the analytes increased with the stirring rate up to 150 rpm. At higher stirring rates, formation of a spatter which damaged the drop was noted. For the further work, the 150 rpm stirring rate was chosen.

For the optimum extraction efficiency and repeatability, an equilibrium among the extracting liquid, the headspace and the sample should be reached. The extraction time necessary to reach the equilibrium was examined by exposing the solvent drop to the headspace for up to 35 min. As one can see in Fig. 1, relative peak areas of the analytes did not change any more after 20 min of exposure. So, for the further work, an exposure time of 20 min was chosen.

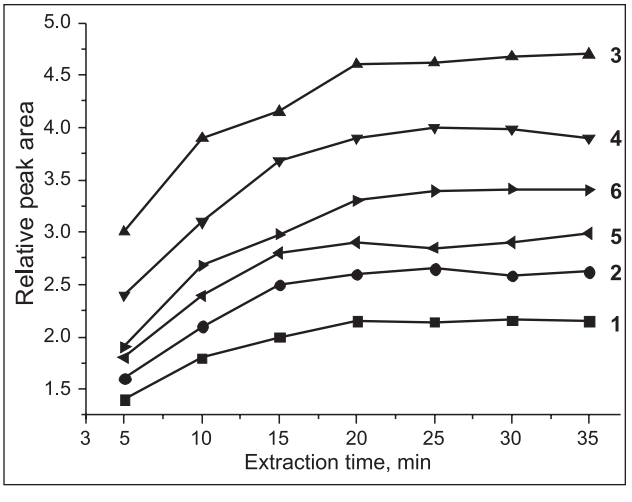

Fig. 1. Effect of HS-SDME time on the peak area of (1) chloroform, (2) trichloroethene, (3) tetrachloroethene, (4) bromoform, (5) dibromochloromethane and (6) bromodichloromethane. The concentrations of the analytes are 10 µg l^{-1}, toluene drop volume 2 µl, stirring rate 150 rpm

Ionic strength of solution

Addition of salt exerts a contradictory effect on the efficiency of HS-SDME: in some cases it improves the extraction of analytes [14, 15]; on the other hand, it has been shown [17, 23] that SDME efficiency decreases with an increase in salt concentration.

The ionic strength of solution was modified by adding NaCl which is commonly used for this purpose. Up to 0.4 g ml^{-1} of NaCl was added. The plot of the relative peak areas vs. the amount of NaCl added is shown in Fig. 2. It is evident that the addition of NaCl increases the extraction efficiency and promotes the transport of VHHs to the headspace and hence to the extraction drop. The explanation should be that water molecules form hydration spheres around the salt ions. These hydration spheres reduce the concentration of water available to dissolve the analyte molecules, and thus this drives additional analytes into the extraction phase [24]. However, at NaCl quantities above 0.4 g ml^{-1}, the extraction efficiency did not change any more. The reason may be the saturation of the sample with NaCl. So, for the further work, saturated salt conditions with the NaCl concentration of 0.4 g ml^{-1} were chosen.

Quality parameters

The optimum extraction conditions were the following: 0.8 g of NaCl was added to the extraction vial containing 2 ml of VHH solution. Sampling was carried out into a 2 µl decane drop for 20 min at a 150 rpm stirring rate. A chromatogram of the standard solution of esters, obtained after HS-SDME in optimized extraction conditions, is presented in Fig. 3.

The linear ranges, correlation coefficients, repeatabilities (as RSDs) and limits of detection (LOD) of HS-SDME for all the analytes obtained in optimized extraction conditions are presented in Table.

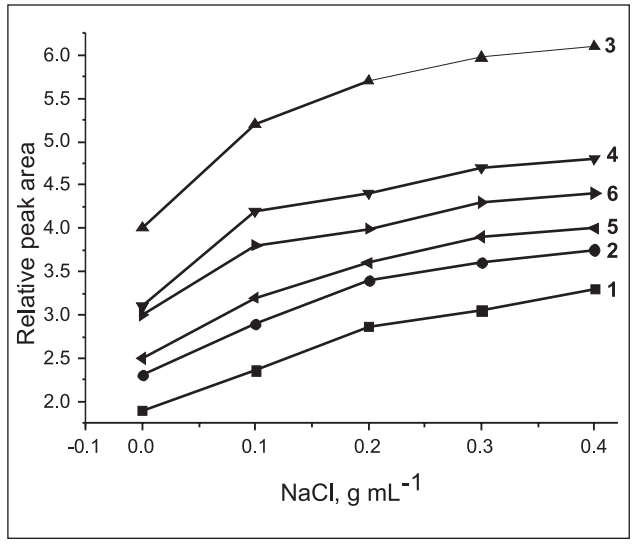

Fig. 2. Effect of NaCl content on the peak area of (1) chloroform, (2) trichloroethene, (3) tetrachloroethene, (4) bromoform, (5) dibromochloromethane and (6) bromodichloromethane. The concentrations of the analytes are 10 µg l^{-1}, toluene drop volume 2 µl, stirring rate 150 rpm, extraction time 20 min

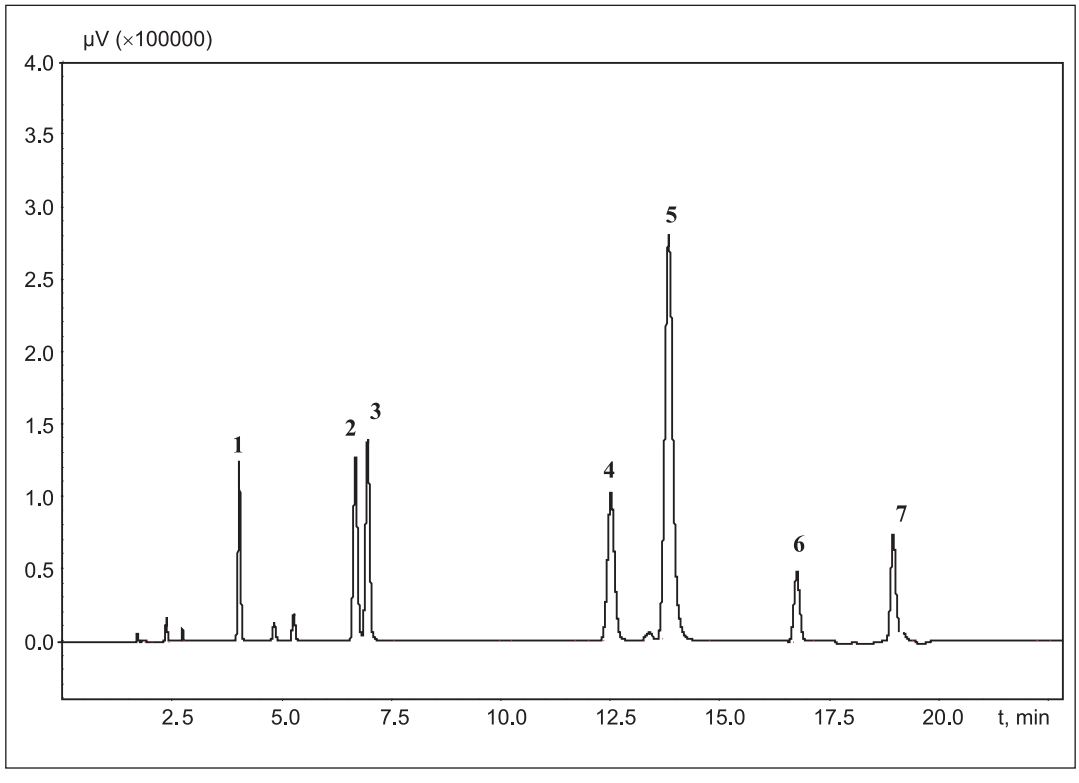

Fig. 3. Chromatogram of standard solutions of (1) chloroform, (2) trichloroethene, (3) bromodichloromethane, (4) dibromochloromethane, (5) tetrachloroethene, (6) chlorobenzene and (7) bromoform, obtained after HS-SDME in optimum conditions. The concentrations of the analytes are 10 mg l^{-1}. For GC conditions, see the Experimental section of the paper

Table. **Analytical characteristics of HS-SDME for volatile halogenated hydrocarbons**

Compound	Linear range (μg l^{-1})	R^2	RSD (%) (n = 6 at 10 μg l^{-1})	LOD (μg l^{-1})	MCL (μg l^{-1}) [4]
Chloroform	2–50	0.996	5.3	1.78	37.5
Trichloroethene	2–50	0.999	5.4	1.55	5
Tetrachloroethene	2–50	0.995	5.5	1.58	5
Bromoform	2–50	0.998	5.0	1.43	37.5
Dibromochloromethane	2–50	0.996	6.5	0.72	37.5
Bromodichloromethane	2–50	0.998	6.1	0.42	37.5

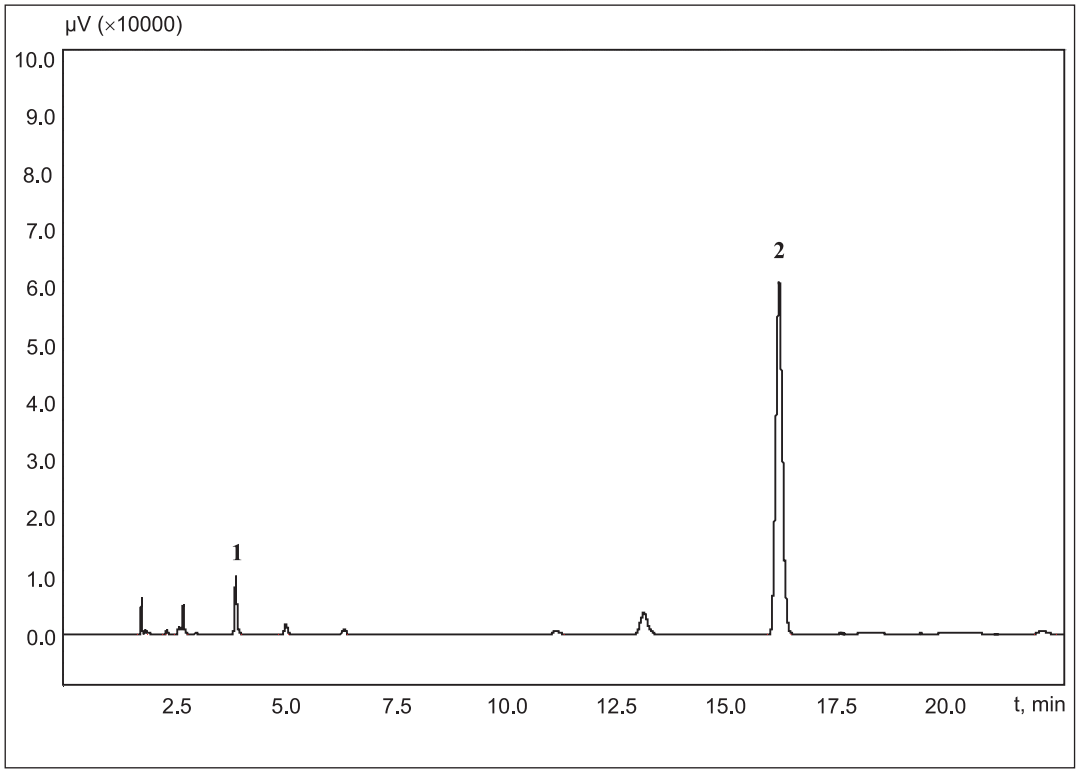

Fig. 4. Chromatogram of groundwater from Šiaulėnai watering-place obtained after HS-SDME in optimum conditions: (1) chloroform, (2) chlorobenzene. For GC conditions, see the Experimental section of the paper

The repeatabilities were calculated among six concurrent measurements of the standard solution containing 10 μg l^{-1} of each analyte. According to Lithuanian Legislation [4], the RSD values should not exceed 25%. As RSDs of the suggested method were less than 7%, the method met the repeatability requirements. The limits of detection were defined as a three fold baseline noise. It is evident (Table) that for all the target compounds the LOD were much lower than the maximum level permitted in drinking water [4]. It means that the method can be applied for drinking water quality control.

Application

The proposed HS-SDME method was applied for determination of volatile halogenated hydrocarbons in groundwater (Šiaulėnai watering-place). The extraction conditions were as presented above. As one can see in Fig. 4, the peak of only one analyte – chloroform – is evidenced in the chromatogram. The repeatability of the results was 5.8% (n = 5), the concentration of chloroform was 4.9 μg l^{-1} and was lower than the maximum level permitted in drinking water.

CONCLUSIONS

The paper describes the use of headspace single-drop microextraction for the sampling and preconcentration of volatile halogenated hydrocarbons. The extraction technique is compatible with gas chromatographic analysis. The proposed method reduces to 2 μl the volume of the solvent necessary for extraction and shows a good repeatability. Its detection limits are lower than the maximum contaminant level permitted in drinking water by Lithuanian Legislation. Due to its simplicity, rapidity and low cost, the method is a promising technique for VHH analysis in drinking and natural water.

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LAKIŲ HALOGENINTŲ ANGLIAVANDENILIŲ MIKROEKSTRAKCIJA TIRPIKLIO LAŠU IR DUJŲ CHROMATOGRAFINIS NUSTATYMAS

S a n t r a u k a

Siūloma paprasta, greita ir pigi lakių halogenintų angliavandenilių mikroekstrakcija tirpiklio lašu iš viršerdvės. Ekstrakcijai naudojamas dekano lašas. Optimizuotos ekstrakcijos sąlygos (ekstrahuojančio tirpiklio tūris, ekstrakcijos trukmė, tirpalo maišymo greitis bei joninė jėga).

Nustatytos siūlomo metodo analizinės charakteristikos. Rezultatų pasikartojamumas yra 5,0–6,5%, kalibracinė kreivė tiesinė iki 50 μg l^{-1} analičių koncentracijos, aptikimo ribos yra 0,42–1,78 μg l^{-1}. Visų analičių aptikimo ribos mažesnės, nei geriamajam vandeniui leistinos ribos. Pasiūlytas metodas pritaikytas lakiems halogenintiems angliavandeniliams gruntiniame vandenyje nustatyti.