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ORIGINAL PAPER

Dispersive liquid-liquid microextraction for the preconcentration and determination of some organic sulfur compounds in aqueous samples

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Abstract In this study, dispersive liquid-liquid microextraction was developed for preconcentration of some organic sulfur compounds in aqueous samples. In this extraction method, 1.0 cm^3 acetonitrile (as dispersive solvent) containing 12.0 mm^3 chlorobenzene (as extraction solvent) was rapidly injected into the water sample containing analytes, and a cloudy solution was formed. The cloudy state resulted from the formation of fine droplets of chlorobenzene, which have been dispersed in bulk aqueous sample. After centrifugation (2 min at 5,000 rpm), these droplets were sedimented in the bottom of the conical test tube (5 ± 0.2 mm^3). Then 2.0 mm^3 of sedimented phase containing preconcentrated analytes was injected into the gas chromatograph with flame ionization detector. The parameters affecting the extraction efficiency have been evaluated and optimized. Under the optimum conditions, the limits of detection and preconcentration factors were obtained in the range of 0.1–0.9 μg dm^{-3} and 564–768, respectively. The calibration graphs were linear in the range of 1–200 μg dm^{-3}. The relative standard deviations at 100 μg dm^{-3} concentration levels of analytes were found to be less than 10%. Finally, the accuracy of the proposed method was evaluated by extraction and determination of organic sulfur compounds from different water samples such as river, tap, and sea waters, and satisfactory results were obtained.

Keywords Dispersive liquid-liquid microextraction · Organic sulfur compounds · Gas chromatography · Preconcentration

Introduction

Organic sulfur compounds (OSCs) may occur in different aquatic environments as a consequence of industrial processes such as biogas production, sewage treatment, production of dye stuffs and detergents, or natural reduction processes in the presence of high amounts of organic matter and sulfate [1–4]. Also, some OSCs are generated as minor by-products of industrial processes, such as the manufacture of plastics and tires. Volatile OSCs have also been identified as the predominant odorants from bioindustry emissions [5]. Because of their very low odor threshold and extremely unpleasant odor, they contribute to pollution even when very small amounts are emitted [6, 7]. The International Labor Organization of the United Nations reports that some sulfur compounds can cause health problems, including damage to the human respiratory system, even at low concentrations, and that exposure to high levels of OSCs can be extremely harmful, causing unconsciousness and death [3, 4, 6]. According to the above considerations, determination of organic sulfur compounds in aqueous environmental samples is necessary and provides useful information about the source of input and quality of water.

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Up to now, various instrumental methods have been developed to identify the OSCs in samples, including gas chromatography (GC) [8, 9], ion chromatography [10], and liquid chromatography (LC) [11]. On the other hands, mass spectrometry [2], the sulfur chemiluminescence detector (SCD) [12], pulsed flame photometric detector (PFPD) [13], atomic emission detector (AED) [14], and flame photometric detector (FPD) [15–19] are the most commonly used detectors for GC. Also, sensitive spectrophotometric methods have been developed for determination of trace organic sulfur compounds in aqueous samples [20]. Since the sulfur compounds are found at trace levels in the environment and due to the complexity of environmental matrixes, a preconcentration step must be included in the analytical procedure to detect low concentrations of these compounds. Liquid-liquid extraction [21], solid phase microextraction (SPME) [22–24], and purge and trap [25] are conventional sample preconcentration methods for these compounds. Also, headspace sorptive extraction [26] was developed as a preconcentration step for OSCs prior to GC. Some of these methods are time consuming or require large amounts of toxic solvents.

A new mode of liquid-phase microextraction, namely dispersive liquid-liquid microextraction (DLLME), has been developed [27]. In DLLME an appropriate mixture of the extraction solvent and dispersive solvent is rapidly injected into the aqueous sample to produce high turbulence. This turbulent regimen gives rise to the formation of small droplets, which are dispersed throughout the aqueous sample. After the formation of a cloudy solution, the interfacial area between the extracting solvent and the aqueous sample becomes very large, so the equilibrium state is achieved quickly and, therefore, the extraction time is very short. After centrifugation of the cloudy solution, the fine droplets settle at the bottom of the conical test tube, and determination of analytes in the sedimented phase can be performed by instrumental techniques [27, 28]. Up to now, DLLME has been used successfully for the determination of various organic and inorganic analytes, which are included in a review by Yamini et al. [28].

Table 1 Name and abbreviations of selected OSCs

Compound	Formula	Abbreviation	Bp or Mp (°C)
Methyl phenyl sulfide	C_7H_8S	MPS	188 (Bp)
4-Methylthiophenol	C_7H_8S	4MTP	195 (Bp)
2-Naphthalenethiol	$C_{10}H_8S$	2NT	286 (Bp)
Diphenyl sulfide	$C_{12}H_{10}S$	DPS	NA[a]
Benzyl phenyl sulfide	$C_{13}H_{12}S$	BPS	197 (Bp)
Thiaanthrene	$C_{12}H_8S_2$	TH	366 (Bp)
Dibenzyl sulfide	$C_{14}H_{14}S$	DBS	44–47 (Mp)

[a] Not available

The object of this study was to investigate the applicability of DLLME for preconcentration and determination of OSCs in aqueous samples prior to gas chromatography-flame ionization detection (GC-FID). The names and abbreviations of selected OSCs are summarized in Table 1.

The effects of various experimental parameters on the extraction of OSCs from water samples were investigated and optimized. The results indicated that DLLME is an efficient extraction procedure for determination of OSCs in aqueous samples.

Results and discussion

Optimization of extraction parameters

Various parameters affecting the DLLME efficiency, including the type and volume of extraction and dispersive solvents, were studied and optimized by the univariate optimization approach to estimate the importance of each factor in the extraction efficiency. In all of the optimization steps, the sample solutions containing 100 μg dm^{-3} of each OSC were extracted using the recommended method. For obtaining optimum conditions, the sum of peak areas of compounds was used.

Type of extraction solvent

The selection of an appropriate extraction solvent is a major parameter for the DLLME process. The extraction solvent has to meet the following requirements: (1) to extract analytes well; (2) to be separated from analyte peaks in the chromatogram; (3) to have larger density than water to sediment at the bottom of the extraction tube; and (4) to form a cloudy solution containing tiny droplets in the presence of dispersive solvent when injected to aqueous solution. Due to high density of halogenated hydrocarbons, chlorobenzene (density 1.11 g cm^{-3}), carbon tetrachloride (1.59 g cm^{-3}), chloroform (1.48 g cm^{-3}), and tetrachloroethylene (1.62 g cm^{-3}) were selected as extraction phases and compared for extraction of OSCs from water. A series of sample solutions were studied by using 1.0 cm^3 of acetonitrile containing different volumes of extraction solvent to achieve about 5.0 mm^3 volume of sedimented phase. To obtain the required volume of sedimented phase, considering the solubility of extracting solvent in aqueous phase in the presence of dispersive solvent, 12, 13, 45, and 8 mm^3 of chlorobenzene, carbon tetrachloride, chloroform, and tetrachloroethylene were used, respectively. The results showed that the extraction recovery was increased with the order of $C_6H_5Cl > CCl_4 \approx C_2Cl_4 > CHCl_3$. Therefore, chlorobenzene was selected as the extraction solvent for further experiments.

Type of dispersive solvent

The selection of dispersive solvent is limited to solvents that are miscible with both organic (extraction solvent) and aqueous (sample solution) phases. Thereby acetone (AC), acetonitrile (ACN), and methanol (MeOH), which have this ability, were selected for this purpose [29]. A series of sample solutions was studied by using 1.0 cm^3 of each dispersive solvent containing 12.0 mm^3 chlorobenzene (as extraction solvent). According to the results, the extraction efficiency was increased as MeOH > ACN > AC. However, for further studies acetonitrile was selected as the dispersive solvent because of its better chromatographic behavior.

Effect of extraction solvent volume

A successful extraction should maximize the extraction efficiency and minimize the phase ratio to improve the preconcentration factor. It is clear that by increasing the volume of the extraction solvent, the volume of sedimented phase increases. To examine the effect of extraction solvent volume on the extraction efficiency, 1.0 cm^3 volumes of acetonitrile containing different volumes of chlorobenzene, in the range of 12–27 mm^3, were used in the DLLME procedure. According to the results, the peak area of the analytes was highest using 12 mm^3 of chlorobenzene. Increasing the volume of extraction solvent resulted in a decrease in the magnitude of the peak area of the analytes, probably because of the increase in the sedimented volume and the consequent further decrease in the preconcentration factor. So in the following studies, 12 mm^3 of chlorobenzene was chosen as the optimum volume for the extraction solvent in order to achieve the highest possible extraction efficiency and preconcentration factor.

Effect of dispersive solvent volume

Variation of the volume of acetonitrile (as dispersive solvent) causes changes in the volume of the sedimented phase. To achieve a constant volume of the sedimented phase, the volume of dispersive and extraction solvents were changed simultaneously. Therefore, different volumes of acetonitrile in the range of 0.50–2.0 cm^3 containing proper amounts of chlorobenzene were investigated. According to Fig. 1, the extraction of OSCs increases with the increase of dispersive solvent volume up to 1.0 cm^3. At low volumes of acetonitrile, the cloudy state is not formed well and therefore the recovery is low. At higher volumes, the extraction efficiency is reduced, probably because of the increase in the solubility of OSCs in water. Therefore, 1.0 cm^3 volume of acetonitrile has been chosen as the optimum volume for further experiments.

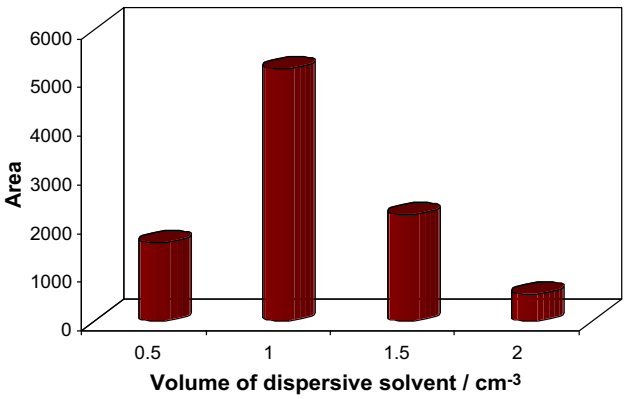

Fig. 1 Effect of dispersive solvent volume on the extraction efficiency of OSCs

Analytical performance of the method

Calibration curves were obtained using 5 cm^3 of the standard solutions and exhibited good linearity in a wide range of concentrations. For this purpose, each standard sample was extracted by the recommended DLLME procedure at optimum conditions, and the calibration curves were obtained by plotting the peak area of each OSC against its initial concentration in the aqueous phase. The figures of merit of the proposed method are summarized in Table 2.

The limits of detection (LODs), calculated as the concentration equivalent to three times of the blank standard deviation divided by the slope of the calibration curve, were in the range of 0.1–0.9 μg dm^{-3}. The preconcentration factor (PF) was calculated as $PF = C_{sed}/C_0$, where C_{sed} and C_0 are the concentration of analyte in sedimented phase and initial concentration of analyte in aqueous sample, respectively. Calculation of C_{sed} was done by direct injection of OSCs calibration standards into the GC-FID. Also, the extraction recovery (*ER*%) was obtained by the following equation:

$$ER\% = \frac{C_{sed} \times V_{sed}}{C_0 \times V_{aq}} \times 100 = PF \times \frac{V_{sed}}{V_{aq}} \times 100 \quad (1)$$

where V_{sed} and V_{aq} are the volumes of the sedimented phase and aqueous sample, respectively.

Under the optimum conditions, the preconcentration factors and recovery values were obtained in the range of 564–768 and 56.4–76.8%, respectively. The relative standard deviations (RSDs%) at 100 μg dm^{-3} concentration levels of OSCs were found to be less than 10%.

Analysis of real samples

The accuracy of the proposed method for the extraction and determination of target analytes was evaluated by calculating the recovery of OSCs from sea, river, and tap water

Table 2 Figures of merit for the DLLME of OSCs

Analyte	Linearity		LOD (μg dm^{-3})	Precision (RSD%, $n = 5$)	PF[a]	ER (%)
	LDR (μg dm^{-3})	R^2				
4MTP	2.0–200	0.9995	0.8	3.6	702	70.2
MPS	2.0–200	0.9976	0.5	7.1	628	62.8
2NT	2.0–200	0.9993	0.9	10.8	564	56.4
DPS	1.0–200	0.9964	0.7	9.7	752	75.2
BPS	1.0–200	0.9883	0.5	2.0	768	76.8
TH	1.0–200	0.9976	0.1	2.3	760	76.0
DBS	1.0–200	0.9904	0.4	1.3	735	73.5

[a] Preconcentration factors were calculated based on the extraction from solution containing 100 μg dm^{-3} of each OSCs

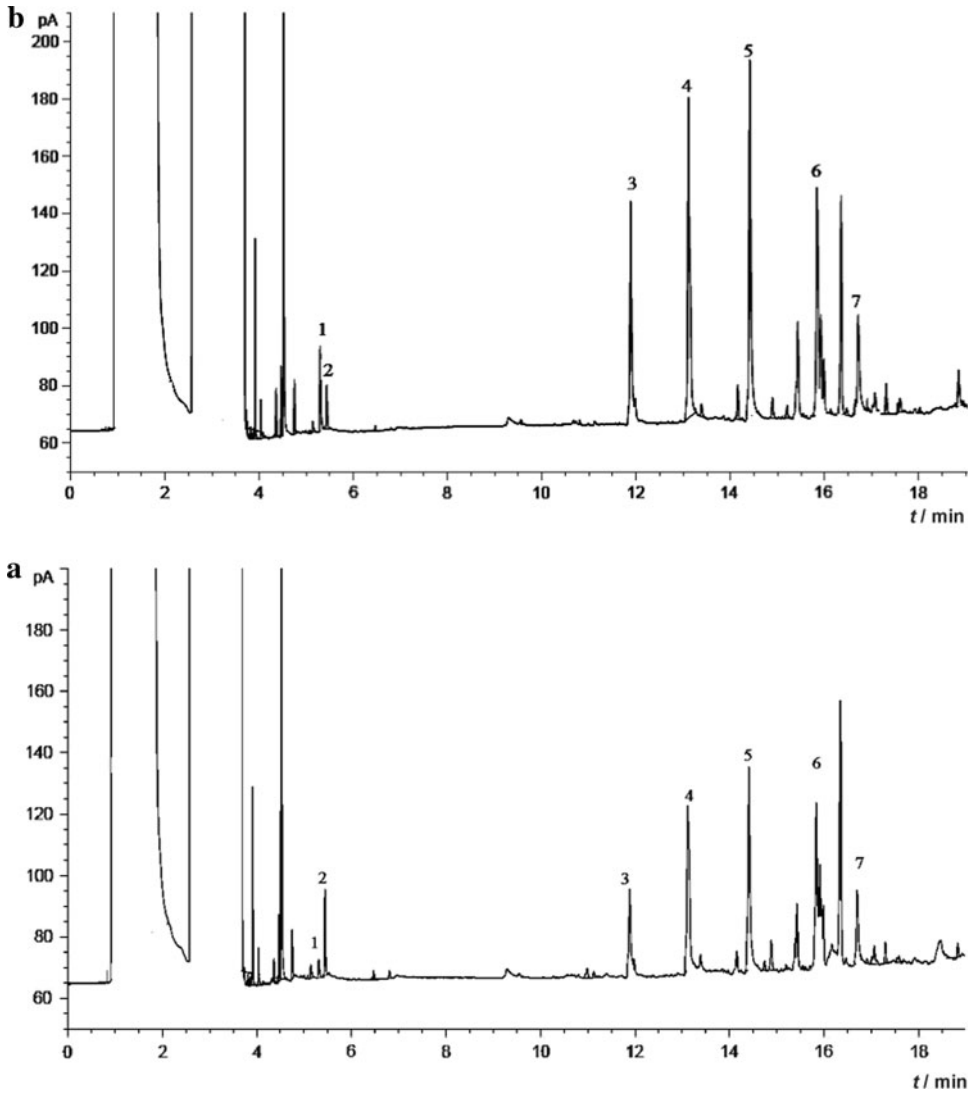

Fig. 2 Chromatograms of DLLME of OSCs after extraction from **a** 5 μg dm^{-3} standard solution, **b** of 20 μg dm^{-3} spiked tap water solution. *1* 4MT, *2* MPS, *3* 2NT, *4* DPS, *5* BPS, *6* TH, *7* DBS

samples. For studying the matrix effect, the samples were spiked with 20 μg dm^{-3} of the analytes, and the relative recovery was calculated as:

$$\mathrm{RE}\% = \frac{C_{\mathrm{Found}} - C_{\mathrm{Initial}}}{C_{\mathrm{Added}}} \times 100 \quad (2)$$

Figure 2 shows chromatograms for the extraction of analytes from standard solution (5 μg dm^{-3}) and 20 μg dm^{-3} spiked tap water solution at optimum conditions via the proposed DLLME method.

The results of three replicate extractions from the real samples are summarized in Table 3.

One can see that there is good agreement between the obtained results and the known values, indicating the successful applicability of this method for simultaneous determination of target analytes in aqueous samples.

Table 3 Analysis of real samples

Sample	MPS	DPS	BPS	TH	DBS
Sea water					
Initial concentration[a]	–	1.5	0.7	–	0.5
Found[b]	17.9	18.5	17.8	18.6	19.1
Relative recovery (%)	89.5	85	85.5	93	93
RSD%	7.6	3.0	11.3	12.0	1.8
Tap water					
Initial concentration	–	2.2	4.7	–	–
Found[b]	18.7	23.1	21.6	19.8	19.5
Relative recovery (%)	93.5	104.5	84.5	99	97.5
RSD%	3.8	8.2	12.4	6.8	6.7
River water					
Initial concentration	–	1.1	2.8	–	4.3
Found[b]	18.6	19.8	18.1	20.1	19.8
Relative recovery (%)	93	93.5	76.5	100.5	77.5
RSD%	9.6	9.8	5.1	3.8	8.1

[a] All concentrations are in μg dm^{-3}

[b] 20.0 μg dm^{-3} of each OSC was added

Conclusion

This study describes the application of DLLME as a preconcentration method prior to GC-FID for determination of trace amounts of organic sulfur compounds in aqueous samples. Compared to the conventional methods such as LLE, in DLLME consumption of sample and toxic organic solvents is minimum. In comparison with other microextraction techniques such as SPME, single drop microextraction (SDME), and hollow fiber-liquid phase microextraction (HF-LPME), DLLME is advantageous in terms of ease of operation, sensitivity, and preconcentration factor. Simplicity of operation, low cost, high recovery, and high preconcentration factor are some advantages of DLLME. Also, the proposed method has high sensitivity and a short extraction time that may be used successfully for determination of trace amounts of OSCs in environmental samples.

Experimental

Chemicals

The organic sulfur compounds with high purity were obtained from Acros (Belgium), Fluka (Switzerland), Merck (Germany), and Sigma-Aldrich (USA) companies. The other reagents used in the studies were of analytical reagent grade. Doubly distilled water was used throughout this work. A stock standard solution of each OSC (1,000 mg dm^{-3}) was prepared in methanol and stored in darkness at −10 °C. A fresh 10-mg dm^{-3} standard solution containing the OSCs was prepared in methanol every week and stored at 4 °C. The working standard solutions were prepared in doubly distilled water, stored at 4 °C in a fridge, and brought to ambient temperature prior to use.

Instrumentation

Separation and quantification of OSCs were carried out using an Agilent 7890 gas chromatograph, equipped with a FID detector and a DB-5 fused-silica capillary column (30 m × 0.32 mm i.d. × 0.25 μm film thickness). The injection was performed at splitless mode, and helium gas with high purity was used as carrier gas at the constant flow rate of 1.5 cm^3 min^{-1}. Nitrogen gas with a flow rate of 30 cm^3 min^{-1} was used as make-up gas for the FID. The injector and detector temperatures were 260 and 270 °C, respectively. The column temperature program was as follows: 50 °C for 1 min, increased to 100 °C at 15 °C min^{-1}, and then held for 1 min. Finally, the temperature increased to 270 °C at 10 °C min^{-1} and then was held at 270 °C for 2 min. The analytical signal was taken as the peak area of the organic sulfur compounds.

Extraction procedure

Briefly, the proposed dispersive liquid-liquid microextraction consisted of the following steps:

1. 5 cm^3 of sample solution containing OSCs was added to the conical 10 cm^3 vials.

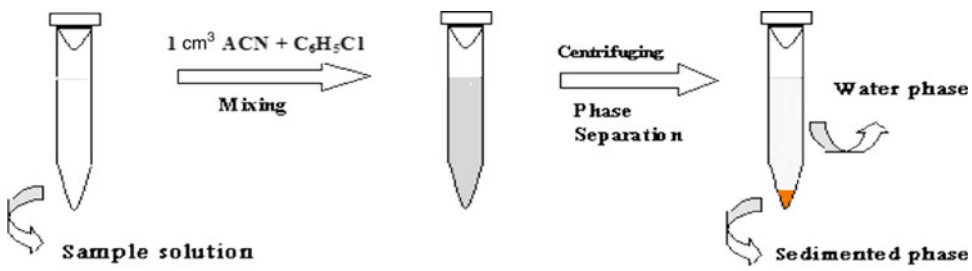

Fig. 3 A schematic diagram of the proposed dispersive liquid-liquid microextraction procedure

2. By a syringe, 1 cm^3 of acetonitrile (as dispersive solvent) containing 12 mm^3 chlorobenzene (as extraction solvent) was rapidly injected to the sample vial to produce a cloudy solution. The cloudy state resulted from the formation of fine droplets of chlorobenzene, which have been dispersed in bulk aqueous sample.
3. Separation of the phases was accelerated via centrifugation. After centrifugation, the droplets were sedimented at the bottom of the conical test tube (5 $\pm$ 0.2 mm^3).
4. 2 mm^3 of sedimented phase was injected into the GC-FID to separate and determine the OSCs.

A schematic diagram of the procedure is shown in Fig. 3.

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