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# Selective enrichment of sulfides, thiols and methylthiophosphates from water samples on metal-loaded cation-exchange materials for gas chromatographic analysis

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## Abstract

The suitability of using metal-loaded sorbents for solid-phase extraction to enrich organic sulfur compounds from water samples was studied. To test the retention behavior of a number of sulfides, thiols and methylthiophosphates, a cation-exchanger was loaded with various metal ions. The elution behavior of sulfur compounds was investigated with different solvents. A combination of  $\text{Pb}^{2+}$ -modified cation-exchanger as sorbent and  $\text{CS}_2$  (1%, v/v) in toluene proved to be the most suitable approach for the given problem. Using GC with a pulsed flame photometric detector yielded detection limits of between 0.6 and 2.9  $\mu\text{g}/\text{l}$ . The results showed good reproducibility with relative standard deviations of 2–11%. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Organic sulfur compounds (OSCs) are ingredients of numerous products used in the manufacture of fuels, chemical wood pulp, detergents and dyestuffs. Industry and domestic households emit these substances into the environment in the form of, for example, sulfides, thiophenes, thiazoles, thiols and sulfonic acids. Agriculture contributes to the pollution of soil and water through the broad application of sulfur-containing pesticides. Various of these compounds are well known to be toxic and muta-

genic [1,2] and therefore need to be studied and monitored.

Yet despite several papers dealing with their separation, the identification and determination of OSCs (especially in highly contaminated matrices) are still problematic. Increasing importance is being attached to selectivity in the choice of analytical procedures in order to enhance the sensitivity in more complex matrices.

Solid-phase extraction (SPE), one of the most common extraction techniques, has been used to enrich OSCs on several sorbents. Despite good extraction rates on bonded silicates [3,4] and polymers [3–10], extraction on these materials is limited in terms of selectivity to polarity and molecular size. By comparison, enrichment on metal-loaded sorbents

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is based on the formation of coordinated bonds between sorbents and OSC [11].

Metal-loaded sorbents have mainly been used for the extraction of OSCs in organic solvents. Detailed determinations have been performed to extract thiophenes, sulfides, mercaptanes and polycyclic aromatic sulfur hydrocarbons from fuel, as well as to separate these substances from polycyclic aromatic hydrocarbons [12–15].

Metal-loaded sorbents have also been utilized in ligand exchange chromatography. However, this technique was only partly successful for separating compounds like mercaptanes and disulfides, since retention in the chromatographic system was not sufficiently different for the satisfactory separation of these substances [16,17]. Moreover, poor recovery was partly explained by excessively strong bonds [11,17]. OSCs were enriched from water samples, albeit at a substantially lower level [18].

Due to their selectivity, we preferred metal-loaded sorbents to other ones. Modified sorbents were used to develop an extraction procedure for OSCs contained in water samples as described in this paper. Several metal ions and eluents were tested. The most suitable method was tested with respect to sensitivity and reproducibility as well as the influence of the different matrices investigated. The procedure was applied to determine OSCs in highly contaminated groundwater. The results are compared with those obtained using solid-phase microextraction (SPME).

## 2. Experimental

### 2.1. Reagents

To prepare eluents and calibration standards, the following substances were used: dimethyltrisulfide (Promochem); di-*n*-butylsulfide, *n*-heptylmercaptan, dimethylsulfide, dimethyldisulfide (Supelco); *O,O,O*-trimethylthiophosphate, *O,O,S*-trimethyldithiophosphate (Bayer); methanol, acetone, toluene, acetonitrile, CS<sub>2</sub>, chloroform, dichloromethane, CuSO<sub>4</sub>, AgNO<sub>3</sub>, SnCl<sub>2</sub>, Pb(NO<sub>3</sub>)<sub>2</sub> (Merck); thiophenol, diphenylsulfide, diethylamine and thioanisole (Sigma–Aldrich).

### 2.2. SPE

OASIS-MCX cartridges (30 mg, Waters) were used as cation-exchanger material. Cartridges were conditioned with 1 ml methanol and 1 ml distilled water, loaded with a large excess of aqueous metal salt solution (1 ml of a 0.1%, m/v, solution) and flushed with 2 ml distilled water. The tested compounds were then applied in aqueous solution. These mixtures were prepared by spiking distilled water with a methanolic solution of the organic sulfur compounds. The concentration of methanol in each aqueous solution was 0.05% (v/v). To eliminate the water from cartridges, they were dried by air suction for 20 min. The elution of analytes was carried out by 4.5 ml eluent without pressure. Eluates were collected and filled up to 5 ml with the eluent before injection (1 μl) for gas chromatographic separation.

### 2.3. SPME

Solid-phase microextraction was performed using a 65-μm divinylbenzene–polydimethyl siloxane (DVB–PDMS) fibre (Supelco). Calibration for the sulfur compounds analyzed was performed for 40 min extraction time and a stirring speed of 1000 rpm at room temperature. Extraction took place from distilled water, spiked with a methanolic solution of the OSCs and saturated with Na<sub>2</sub>SO<sub>4</sub>.

### 2.4. Instruments

For analytical investigations, capillary gas chromatography combined with mass-selective (MS) as well as pulsed flame photometric detection (PFPD) were used.

The mass-selective detector (MSD5973 HP) was fitted with a GC6890 system. To separate the analytes, an HP5-MS column (30 m×250 μm, 0.25 μm, Hewlett-Packard, HP) was used. The following conditions were applied for separation: injection 2 min splitless, 250 °C; oven temperature program: 50 °C–2 min–10 °C/min–280 °C–5 min; flow-rate 1.1 ml/min, helium.

For flame photometric detection we used a PFPD5380 (OI-Analytical) with a detection temperature of 225 °C. A GC6890 (HP) system was utilized as follows: injection 2 min splitless, 250 °C; column:

DB5-MS 60 m×250 μm, 0.25 μm, J&W; oven temperature program: 50 °C–2 min–10 °C/min–280 °C–5 min; flow-rate: 1.3 ml/min, helium.

### 3. Results

#### 3.1. Selection of sorbents

The object of the investigations was to find cations which are able to form stable bonds with both the sorbents and the organic sulfur compounds under the given experimental conditions. Benefiting from the experience of other authors [19–23], Sn<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Ag<sup>+</sup> were tested.

The retention of OSC at the modified cation-exchanger was directly measured by comparing concentrations in the extracted aqueous solution (50 μg of each OSC in 10 ml) before and after passing through the cartridges by using SPME.

Good results were obtained for all the cations tested. Modified cartridges retarded more than 99.6% of the amount for all OSCs applied. However, investigations of capacity in order to study the breakthrough profiles were not performed. To avoid overloading the cartridges, the solution to be extracted was spiked with less than 50 μg per OSC in the following tests.

#### 3.2. Elution

Because of the unknown bond strength between loaded cation-exchanger and OSCs, solvents of different polarity were tested for the desorption of OSCs. Different eluents which could be directly injected in GC (without any further preparation) such as toluene, acetonitrile, chloroform and dichloromethane were used. In these studies 5 μg of each OSC was extracted from 10 ml aqueous solution. Eluates were analyzed with GC–PFPD. Calibration was performed for each solvent separately. To quantify the recovery rates, OSCs were directly injected in the corresponding solvent at concentrations of 1 μg/ml.

Cartridges loaded with Sn<sup>2+</sup> ions seemed to form the weakest bonds between the coatings inspected and the OSCs. The recoveries of the compounds tested were between 31 and 118%.

Stronger interactions were observed upon the

application of Pb<sup>2+</sup>, Ag<sup>+</sup> and Cu<sup>2+</sup>. This resulted in lower recovery rates, the lowest being exhibited by mercaptanes. In addition, not all the sulfur compounds tested were eluted from cation-exchanger thus modified.

Therefore the goal of further investigations was to increase the elution strength of the solvents. Additives in the eluents were used, which interact more strongly with the metallic compounds fixed to the exchanger than OSCs in order to displace them. The additives were selected with regard to the nucleophilic behavior of heteroatoms and their relatively small molecule size for minimizing steric inhibitions during complex formation [15,18,24,25]. Judging from theoretical considerations, diethylamine (DEA), dimethyldisulfide (DMDS), dimethylsulfide (DMS) and CS<sub>2</sub> appeared suitable. Therefore solutions of these compounds in toluene (1%, v/v) were applied as eluents. Each of the OSCs tested could be identified in the eluate when the Sn<sup>2+</sup>- and Pb<sup>2+</sup>-modified sorbents and all the solvent mixtures were applied. Because of the stronger bonds, not all the OSCs were eluted from Ag<sup>+</sup> and Cu<sup>2+</sup> coatings.

The best results of the 32 combinations tested for modification and eluents were obtained by using Pb<sup>2+</sup> and 1% (v/v) CS<sub>2</sub> in toluene (Table 1). Since this combination exhibited good recoveries for all the OSCs, it was used for the following investigations.

#### 3.3. Calibration

Using Pb<sup>2+</sup>-modified OASIS-MCX cartridges and 1% (v/v) CS<sub>2</sub> in toluene as eluent, calibrations were performed based on seven calibration levels between 1 and 50 μg/l of aqueous solution. The eluates obtained were analyzed by using GC–PFPD. Detection limits ( $x_{\text{LOD}}$ ) were calculated according to the German standard DIN 32 645 [26] from calibration data by:

$$x_{\text{LOD}} = t_{f,\alpha} s_{x_0} \sqrt{\frac{1}{m} + \frac{1}{n} + \frac{\bar{x}^2}{Q_x}}$$

where  $\alpha$  is the level of statistical significance,  $f$  the degrees of freedom for the based linear regression,  $s_{x_0}$  the standard deviation of the method,  $n$  the number of calibration levels,  $m$  the number of

Table 1  
Recovery rates of most useable modification/eluent combinations

Modification/ eluent	Recovery rates (%) ( $n = 3$ )								Average (%)
	TP	TMTTP	DMTriS	nHeptM	DButS	TA	TMDTP	DPhenS	
Pb <sup>2+</sup> /CS <sub>2</sub>	58	89	79	47	89	106	107	100	84
Pb <sup>2+</sup> /DMDS	53	84	81	46	81	99	101	89	79
Sn <sup>2+</sup> /DMS	52	79	82	56	73	101	102	86	79
Cu <sup>+</sup> /CS <sub>2</sub>	0	89	88	0	106	115	109	116	78
Pb <sup>2+</sup> /ACN	0	120	108	0	61	110	115	106	78
Cu <sup>2+</sup> /DMS	0	82	85	12	95	105	105	124	76
Sn <sup>2+</sup> /DEA	46	86	79	42	58	96	103	91	75
Pb <sup>2+</sup> /DMS	38	82	80	35	77	98	102	75	73
Sn <sup>2+</sup> /CS <sub>2</sub>	42	75	74	43	67	97	102	78	72

TMTTP = *O,O,O*-Trimethylthiophosphate; TMDTP = *O,O,S*-trimethylthiophosphate; DbutS = di-*n*-butylsulfide; TP = thiophenol; DMTriS = dimethyltrisulfide; nHeptM = *n*-heptylmercaptan; DphenS = diphenylsulfide; TA = thioanisole.

replications, and  $Q_x$  the sum of quadratic deviations defined by:

$$Q_x = \sum_i (x_i - \bar{x})^2.$$

Under the given conditions, the detection limits were determined between 0.6 and 2.9  $\mu\text{g/l}$  (Table 2). The value of extracted aqueous solution was 100 ml, so further improvement of detection limits based on the enrichment of larger volumes and the concentration of eluates can be expected.

Relatively small effective ranges were calculated because only undiluted eluates were used for calibration to avoid dilution faults. Hence the calibration range was limited by the linear detector range, which amounts to about one and a half orders of magnitude in the case of maximum sensitivity. Further limitations arose from the different response of compounds. The results were well reproducible with

relative standard deviations of 2–11% calculated for a concentration level of 10  $\mu\text{g/l}$  per OSC.

### 3.4. Analysis of groundwater

The method was applied for the analysis of groundwater samples taken from the highly polluted region of Bitterfeld (Saxony-Anhalt, Germany). As shown in an SPME–GC–MS chromatogram (Fig. 1), this water contains several partly highly toxic sulfur compounds as well as aliphatic and aromatic halogenated hydrocarbons. Concentrations of halogenated hydrocarbons were quantified up to the mg/l range [27].

The identification of particular compounds is difficult and also influenced by the strong differences in the concentration of traces and matrix compounds. Qualitative comparison of chromatograms obtained by SPME and the SPE method developed (Fig. 1)

Table 2  
Calibration parameters for modification/eluent combination (Pb<sup>2+</sup> and 1%, v/v, CS<sub>2</sub> in toluene)

OSC	Detection limit ( $\mu\text{g/l}$ )	Correlation coefficients	Relative standard deviations ( $n = 6$ ) (%)	Range of measurement ( $\mu\text{g/l}$ )
Thiophenol	2.0	0.9996	11	6.0–32
<i>O,O,O</i> -Trimethyl-thiophosphate	0.8	0.9994	2	2.4–12
Dimethyltrisulfide	0.7	0.9993	4	2.1–10
<i>n</i> -Heptylmercaptan	1.5	0.9992	9	4.5–30
Di- <i>n</i> -butylsulfide	0.9	0.9993	3	2.7–20
Thioanisole	0.8	0.9994	3	2.4–20
<i>O,O,S</i> -Trimethyl-dithiophosphate	0.6	0.9991	3	1.8–13
Diphenylsulfide	2.9	0.9994	5	5.7–46

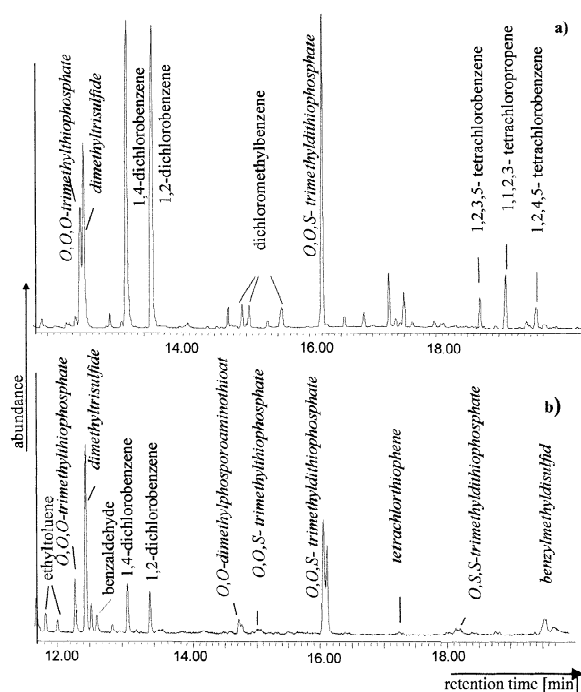


Fig. 1. GC–MS chromatograms of a groundwater (Bitterfeld, Saxony-Anhalt, Germany). For analysis conditions see Sections 2.2–2.4. (a) SPME, 65  $\mu\text{m}$  DVB–PDMS, sample diluted with distilled water (1:100), extraction time 40 min. (b) SPE, cation-exchanger modified with  $\text{Pb}^{2+}$ , eluent: 1% (v/v)  $\text{CS}_2$  in toluene, sample undiluted.

shows a reduced enrichment of chlorinated compounds in the case of the latter. The reduced preconcentration of chlorinated compounds resulted in the identification of further OSCs such as tetrachlorothiophene, *O,S,S*-trimethylthiophosphate and *O,O,S*-trimethylthiophosphate—compounds which could not be identified with SPME owing to superimposition. Benzaldehyde and the ethyltoluenes stemmed from the effluent eluate.

Dimethyltrisulfide, *O,O,O*-trimethylthiophosphate

and *O,O,S*-trimethylthiophosphate were quantified in a groundwater sample. For enrichment, 0.5 ml of samples were used. The results obtained are in the same order of magnitude as those achieved with SPME (Table 3). The reasons for the differences observed were not determined in detail. Because both methods are based on adsorption, differences were reduced to concurrence reactions of several substances in the highly contaminated sample. The adsorption mechanisms are different and variably influenced by matrix effects. In order to minimize such difficulties, both techniques should calibrate in a matrix similar to the determined sample. In our case calibration was performed from distilled water in both cases. The resulting differences may also have been intensified by extraction from variable dilution.

#### 4. Conclusions

The enrichment of organic sulfur compounds with modified cation-exchange materials was tested while varying metal ions and eluents. The highest recoveries were obtained by using  $\text{Pb}^{2+}$  ions and a 1% (v/v) solution of  $\text{CS}_2$  in toluene as eluent.

Detection limits between 0.6 and 2.9  $\mu\text{g}/\text{l}$  were achieved. Compared with SPME, the method developed shows partial differences of quantification for a groundwater. The reasons were reduced to matrix effects, whose minimization could be achieved by more adapted calibration conditions, e.g. standard addition.

The further improvement of recoveries is conceivable by using stronger eluents. This would promote the exertion of copper (II) and silver (I) ions. Positive influences with respect to selectivity were expected owing to their pronounced bonds with organic sulfur compounds.

Table 3

Quantification of organic sulfur compounds in a groundwater by SPE ( $\text{Pb}^{2+}$  and 1%, v/v,  $\text{CS}_2$  in toluene)–GC–PFPD and SPME (DVB–PDMS)–GC–MS

	SPE–GC–PFPD (mg/l)	SPME(DVB–PDMS)–GC–MS (mg/l)
<i>O,O,S</i> -Trimethylthiophosphate	3.5 ( $\pm 0.38$ mg/l)	3.48 ( $\pm 0.07$ mg/l)
<i>O,O,O</i> -Trimethylthiophosphate	5.9 ( $\pm 0.66$ mg/l)	10.85 ( $\pm 0.03$ mg/l)
Dimethyltrisulfide	3.1 ( $\pm 0.05$ mg/l)	1.2 ( $\pm 0.06$ mg/l)

In the form described, the method developed already represents a simple and efficient technique for selective enrichment. It facilitates the identification of OSCs in highly contaminated samples and provides an effective supplement for established enrichment methods.

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