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Determination of phenols in lake and ground water samples by stir bar sorptive extraction–thermal desorption–gas chromatography–mass spectrometry

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Abstract

A simple and inexpensive method for sorptive extraction of phenols from water samples is presented. A polydimethyl siloxane (PDMS) stir bar (Twister) is used as an extraction medium for derivatized phenols, which is thermally desorbed and analyzed by gas chromatography–mass spectrometry (GC–MS). Its performance was illustrated and evaluated for the enrichment of $\mu g\,l^{-1}$ to $ng\,l^{-1}$ of phenol and selected chlorophenols in water samples. The method showed good linearity, recoveries and blank levels, as well as advantages such as sensitivity, simplicity, low cost and high feasibility, being successfully applied for the analysis of phenolic compounds in natural water samples.

Keywords: Phenols and chlorophenols; Stir bar sorptive extraction; Derivatization; Gas chromatography; Thermal desorption

1. Introduction

A major task of commercial analytical laboratories is the determination of environmentally relevant pollutants such as polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and phenols/chlorophenols. The environmental aspects of phenolic compounds became increasingly important in recent years and both the US Environmental Protection Agency (EPA) and the European Union (EU) have included phenols on their priority pollutants list. Conventional analytical methods for these compounds are often extensive since they require numerous analytical steps in order to obtain significant results. The first and also one of the most important requirements is to find a suitable sample preparation technique that allows the separation of the substances of interest from the sample matrix. The analysis of phenols in water is normed by EPA method 625 [1]. A main disadvantage of this time-consuming and cost-intensive method is the large sample volume required for the extraction and the use of large volumes of toxic organic solvents. Therefore, current developments in the field of sample preparation aim for fast and low-cost treatment of environmental samples. Solid-phase microextraction (SPME) conforms to the sample preparation requirements. The use of non-polar or polar fiber coatings in SPME offers a wide range of applications for this technique. SPME with a polyacrylate fiber coating was used successfully for the effective extraction of phenols from water [2–4] and soil samples [5,6]. A disadvantage of SPME is the fiber fragility, especially in fully-automated systems.

Another technique—open tubular capillary columns (or open-tubular trap-liquid desorption) the sample is flushed through the coating of a short piece of a capillary GC column. As in any dynamic sorptive extraction, the breakthrough for each analyte has to be determined to guarantee that the capacity of a definite mass of sorbent has not been exceeded. This technique was recently used in the determination of phenols, with detection limits (LODs) below 6 μg/l [7].

A more recent technique, known as stir bar sorptive extraction (SBSE), was suggested 4 years ago [8] as a novel, simple and solventless procedure, allowing the enrichment of volatile and semivolatile micropollutants in aqueous samples. It consists of a magnetic rod incorporated into a glass jacket which is coated with a 0.5 mm layer of polydimethyl-

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siloxane (PDMS). It allows sorptive interaction between the coating and the compounds to be extracted. This stir bar is placed in the water sample and extraction is achieved by stirring the sample. Since SBSE allows the use of a larger volume of coating material compared to SPME, it has the advantage of higher sensitivity especially for compounds with log $K_{O/W}$ larger than 3 [8], showing good blank levels and no deterioration even after 100 extractions [9]. Interestingly, components with different polarities showed similar recoveries in SBSE with PDMS coatings [10]. SBSE combined with thermodesorption gas chromatography–mass spectrometry (GC–MS) or HPLC was already successfully applied for fast quality control of beverages [11,12] and the determination of mid- to nonpolar environmental pollutants such as pesticides [13], PAHs [14] and organochlorinated compounds [15]. The determination of volatile phenols in wines was recently published by Diez et al. [16], using SBSE without derivatization. The LODs for the studied phenols were between 6 μg/l (4-ethylphenol) and 373 μg/l (4-vinylphenol), indicating a low extraction efficiency for the method. By using a PDMS coated stir bar for the extraction of phenols, low recoveries for compounds with small log $K_{O/W}$ values (between 1 and 2) as well as for highly polar phenols is conjecturable. The conversion of phenols to their acetates [17] overcomes this problem by lowering the polarity of the analytes thus enhancing the importance of SBSE as a simple, practical and cost-effective extraction method.

2. Theoretical

Baltussen et al. [8] estimated the recovery of an analyte from the sample by the following equation:

$$\frac{m_S}{m_0} = \frac{K_{O/W}/\beta}{1 + (K_{O/W}/\beta)} \quad (1)$$

where m_S is the mass of the analyte in the PDMS phase, m_0 the total amount of the analyte in the water sample, $K_{O/W}$ the octanol/water partition coefficient and $\beta = V_W/V_S$ the phase ratio between the volume of the water sample V_W and the volume of the PDMS phase of the stir bar V_S. The octanol/water partition coefficients of the compounds investigated are listed in Table 1 and range between log $K_{O/W}$ = 1.46 (phenol) and 5.12 (pentachlorophenol) [18]. With V_S = 25 μl, V_W = 10 ml, β = 400 the recoveries can be estimated providing that equilibrium is reached. Using the octanol/water partition coefficients of the underivatized phenols the m_S/m_0 values should be between 0.067 for phenol and 0.996 for pentachlorophenol, meaning that recoveries between 6.7 and 99.6% can be expected considering that the equilibrium has been reached. Therefore, derivatization could be used to enhance recoveries of the phenols with lower log $K_{O/W}$ values.

Table 1
Octanol/water partition coefficients ($K_{O/W}$) and *m/z* of the analytes [18]

Compound	log $K_{O/W}$	*m/z*
Phenol	1.46	94, 136
2-Chlorophenol	2.15	128, 139
2,4-Dimethylphenol	2.30	107, 122
2,4-Dichlorophenol	3.06	162, 164
4-Chloro-3-methylphenol	3.10	107, 142
2,4,6-Trichlorophenol	3.69	196, 198
Pentachlorophenol	5.12	266, 268
1H-inden-1-ol, 2-bromo-2,3-dihydro	–	133

3. Experimental

3.1. Chemicals

An EPA phenols calibration standard (50 mg l^{-1} each in methanol) was obtained from Supelco (Bellefonte, USA). The standard solution was diluted to a concentration of 10 mg l^{-1} in methanol and used to spike 10 ml water samples at the μg l^{-1} to ng l^{-1} level. Methanol and dichloromethane were obtained in LiChrosolv quality from Merck (Darmstadt, Germany). HPLC-purity water was obtained from J.T. Baker (Deventer, Netherland). Acetic anhydride, sodium chloride and potassium carbonate were of analytical reagent grade and obtained from Fluka (Buchs, Switzerland). Bromo-indenol (1H-inden-1-ol, 2-bromo-2,3-dihydro) at a concentration of 5 μg ml^{-1} was used as an internal standard.

3.2. Stir bars: pre-treatment, extraction and desorption

The commercial stir bar Twister for sorptive extraction was obtained from Gerstel (Gerstel GmbH, Mülheim an der Ruhr, Germany). It consists of a 10 mm length glass-encapsulated magnetic stir bar, externally coated with 22 μg of PDMS. This layer is 0.5 mm thick, which corresponds to a volume of 25 μl of PDMS. Prior to first use and after each analysis, the stir bar was placed into a vial containing 1 ml of a 1:1 dichloromethane/methanol mixture for 15 min. This procedure was repeated once more with fresh solvent mixture followed by a drying step using a lint-free tissue. The Twister was then conditioned overnight at 250 °C with a nitrogen stream of 30 ml min^{-1}.

For phenols extraction, the twister was inserted in a septum-capped 10 ml flask (Supelco) containing 10 ml of a water sample. Water samples were prepared using 10 ml of HPLC-grade water (J.T. Baker) spiked with 5 μl of the phenols standard solution (10 mg l^{-1}), so that the absolute content of phenols in water was 50 ng, 0.25–0.75 g of K_2CO_3, 0.25–0.75 ml of acetic anhydride, and eventually 3.3 g of NaCl to enhance the extraction efficiency were added to the spiked water samples. The extraction was immediately started by introducing the stir bar into the flask and submitting it to a stirring speed of 1000 rpm (Variomag Multipoint 6/15, H + P Labortechnik, Oberschleissheim, München, Germany) for an extraction time ranging from 5 to 180 min. After that, the Twister was removed from the aqueous solution with tweezers, dried with a lint-free tissue

and inserted into the appropriated Gerstel thermal desorption glass tube (187 mm length × 4 mm i.d.), already spiked with 1 μl of a 5 μg ml^{-1} solution of the internal standard Bromo-Indenol. This tube was inserted in the thermal desorption unit (a rack with capacity for 20 tubes available from Gerstel for automated analysis by thermodesorption GC–MS). Prior to use, the Gerstel glass tubes (used as a recipient for the samplers in the thermodesorption rack) were also treated with acetone under sonication for 15 min, followed by a drying step in an oven heated at 250 °C in a nitrogen stream.

3.3. Instrumental

The analysis was performed on an Agilent 6890 GC system equipped with a 5973 mass selective detector (Agilent Technologies, Palo Alto, CA, USA) coupled to a Gerstel TDS A thermodesorption system. The cold injection system CIS 4 (Gerstel, Mülheim an der Ruhr, Germany)—using liquid nitrogen as a coolant—consisted of an empty liner used for cryofocussing of the analytes prior to splitless introduction into the capillary column.

The conditions for the thermodesorption system were as follows: desorption temperature 250 °C; desorption time 5 min; helium flow rate 150 ml min^{-1} (solvent vent mode). The transfer line situated between the thermodesorption device and the cold injection system was set at 250 °C.

The method utilized for the cold injection system was as follows: during thermal desorption the temperature was set at −100 °C; followed by heating at a rate of 10 °C s^{-1} to 250 °C (hold for 2 min.); the injector was used in splitless mode for 1.5 min.

A HP-5 capillary column (30 m length, 250 μm i.d. and 0.25 μm film thickness) was used with a GC oven temperature program starting from 50 °C (held for 2 min) to 200 °C at a rate of 10 °C min^{-1}, followed by heating to 300 °C at 25 °C min^{-1}. Helium was used as carrier gas with an average linear velocity of 40 cm s^{-1}. The detection method (5973 Network MSD Detector, Agilent) was programmed for single ion monitoring (SIM) considering two characteristic ions for each compound (Table 1).

3.4. Samples

Three natural water samples of the mining lake Schwelvollert at the lignite district Vollert-Süd (Zeitz, Germany) and two groundwater samples from gage bore holes nearby the lake were extracted and analyzed using the Twister. The lake samples were collected at three different depths (0.2, 15 and 24 m from the surface level) and the groundwater samples were extracted at 5 and 6 m depth from the mining surface. Two aliquots of each sample were diluted 50 times and then a 10 ml volume of the diluted sample was added to the extraction vial, treated with K_2CO_3 until pH 11 and derivatized with acetic anhydride. To increase the extraction efficiency 3.3 g of NaCl were added to the samples. The vial was closed immediately and extraction with the Twister was performed for 45 min. Thermodesorption and GC–MS analysis were carried out with the optimized parameters, the compounds were identified and quantified.

4. Results and discussion

4.1. Optimization of phenol derivatization and extraction

Water samples with seven EPA-phenols were analyzed. According to Eq. (1) a higher sample volume V_W could cause lower recoveries of the phenols investigated due to an increase in the phase ratio β. Therefore, a sample volume of 10 ml was chosen. To enhance the $\log K_{O/W}$ values of the analytes the phenols were derivatized into their acetates by adding potassium carbonate and acetic acid anhydride to the water samples [17]. To optimize the derivatization step three different concentration levels of these reagents were tested: (A) 0.5 g K_2CO_3 and 250 μl $C_4H_6O_3$, (B) 1.0 g and 500 μl and (C) 1.5 g and 750 μl, respectively. Significant differences in signal intensity were observed for the different concentration ratios of the derivatization agents. The lower the concentration level the higher becomes the signal intensity of the analyte. Therefore the lowest concentration level A (0.5 g K_2CO_3 and 250 μl acetic acid anhydride) was chosen for derivatization of the phenols. Using the lowest concentration (level A) reduces another disadvantage of the acidic derivatization medium. After desorption of the substances from the twisters, the chromatograms showed a high concentration of siloxane peaks which may overlap with the peaks of interest. The highly acidic extraction medium (pH 2, after addition of acetic anhydride) may corrode the PDMS coating of the stir bar resulting in the observed siloxane peaks and a decreased reproducibility by repeated use of the stir bar, as also found by Thurow et al. [19].

Additionally, the influence of salting-out on the extraction efficiency of the phenol acetates was investigated. Saturation of the water samples with NaCl (3.3 g NaCl per 10 ml water sample) increased the signal intensity up to 30% compared with no addition of salt. The behaviour described in the literature about the salting-out effect regarding phenol acetates is controversial and inconclusive—either a positive [20] or a negative effect [7] has been observed by some authors, including a different effect—positive or negative for some compounds—when under different pH value and salt concentration [16]. Taking this into consideration, a deeper future study will be important to draw a conclusion—for example with variation of pH and salt concentration at several levels.

4.2. Optimization of instrumental conditions

The influence of TDS helium flow rate, TDS temperature (maximum temperature of the thermodesorption ramp program), desorption time and CIS temperature (maximum

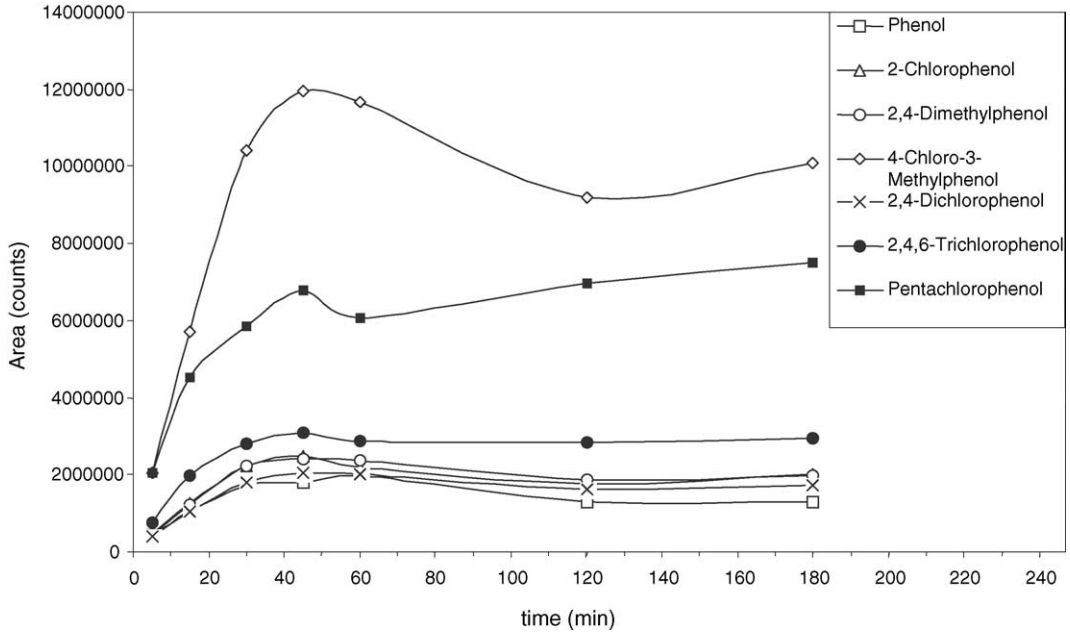

Fig. 1. Extraction time profiles for the phenolic compounds.

temperature of the heating step in the cold injection system) were studied for the derivatized phenols. It was found that the desorption conditions (desorption temperature and desorption time) significantly influence the extraction yield for the studied compounds.

The helium flow rate was set at 100, 150 and 200 ml min^{-1}. It was observed that the variation of the gas flow rate influences the desorption process and therefore the signal intensity. The highest signal was obtained at 150 ml min^{-1}, so this flow rate was maintained for all subsequent experiments.

The TDS temperature varied between 230 and 280 °C and the CIS temperature between 250 and 300 °C. Best results for signal intensity of all phenols analyzed were obtained at a TDS temperature of 250 °C and the optimum CIS temperature was also 250 °C.

Desorption times of 3, 5 and 7 min were tested. Signal intensities for the investigated phenols showed no significant differences. TDS desorption time was set at a mid value of 5 min.

4.3. Extraction time profiles

After optimization of the instrumental conditions the extraction time profiles were investigated. The exposure time of the twister in the aqueous sample and the intensity of the mixing process (stirring speed) significantly influence the signal intensity of the compounds analyzed. Since a very intensive stirring is known to shorten the extraction time, the maximum stirring speed allowed by the sample flask geometry (1000 rpm) was chosen. The extraction time profiles were determined by enriching the twisters in a sample volume of 10 ml at a phenol concentration of 10 μg l^{-1} each at extraction times of 5, 15, 30, 45, 60, 120 and 180 min. The curves obtained for the phenol acetates are shown in Fig. 1.

Between 50 and 60 min extraction time, the saturation of the PDMS coating is reached for some compounds. To minimize the analysis time, an extraction time of 45 min was chosen. The optimized experimental and instrumental conditions are summarized in Table 2.

To ensure that no exhaustive extraction takes place, the same spiked sample (10 μg l^{-1} of each compound) was extracted three times successively, each time with a clean stir bar, each of the stir bars being exposed to the solution for 45 min. The three twisters corresponding to the three runs were then placed in the thermodesorption tube (previously spiked with the internal standard), thermodesorbed and analyzed.

The total amount of the extracted phenol acetates was calculated using literature $K_{O/W}$ values for acetates [7] and the respective peak area for a particular run. From the amount extracted in the particular runs and the total amount of acetates initially in water, the area ratios for each acetate were

Table 2
Optimized experimental and instrumental parameters

Parameter	Value
Derivatization	0.5 g K_2CO_3, 250 μl acetic anhydride
Stirring speed (rpm)	1000
Extraction time (min)	45
Desorption temperature (°C)	250
Desorption time (min)	5
Helium gas flow (ml min^{-1})	150
CIS temperature (°C)	250

Table 3
Area ratios[a] and extraction efficiency for the phenols extracted with twisters: consecutive extractions of the same water sample (10 μg l^{-1} of each phenol initially)

Compound	1st extraction	2nd extraction	3rd extraction	Extraction efficiency[b]
Phenol	0.25	0.20	0.14	0.60
2-Chlorophenol	0.42	0.17	0.09	0.68
2,4-Dimethylphenol	0.50	0.15	0.07	0.71
4-Chloro-3-methylphenol	0.52	0.14	0.07	0.74
2,4-Dichlorophenol	0.53	0.14	0.07	0.74
2,4,6-Trichlorophenol	0.52	0.15	0.10	0.77
Pentachlorophenol	0.56	0.14	0.13	0.82

[a] Area ratio calculated as the quotient between the area in each SBSE extraction and the area corresponding to the initial acetate amount in the sample (calculated from theoretical distribution coefficients [7]).
[b] Apparent extraction efficiency in terms of area ratios, calculated as the quotient between the total area corresponding to the three SBSE extractions and the area from the total amount of acetate initially present in the sample.

calculated, as well as the apparent extraction efficiency (ratio between acetate extracted with SBSE in three runs and the total amount of acetate initially in water). The results are shown in Table 3, where two observations are important. First, the yields experimentally found for the phenol acetates are below the theoretically expected values [7]. Second, for the more substituted compounds, the total amount of phenol acetates extracted after three runs are far below the theoretical amount expected for phenols (for example, experimentally 82% for pentachlorophenyl acetate against 99% for pentachlorophenol theoretically), consequently affecting the correlation between the apparent $K_{O/W}$ found here for acetates and the $K_{O/W}$ theoretically expected for phenols.

The derivatization makes the phenolic compounds less polar by replacing the hydroxyl group with an acetate group and therefore forming a compound with more affinity toward the PDMS coating [21]. In SBSE, the extraction yield shall increase with the increase of the substance's hydrophobicity. The non-observance of this effect, especially for the more substituted phenols, lead to the hypothesis that another parameter might be affecting the efficiency of the derivatization and, consequently, apparently reducing the extraction yields. A closer look in the literature pointed out the effect of the pH value as a possible cause for this behavior.

The esterification of phenols was shown to depend on the acidity of the medium. Phenol derivatisation with acetic anhydride in the presence of potassium carbonate can be performed in aqueous samples in a few minutes with high yield [20]. At pH above 11 (which is the case of the present work), the phenolic compounds studied here (with pK_a values from 4.09 to 10.63) are present in the water sample as phenolates and, in the presence of acetic anhydride, the acetylation is promoted. However, once formed, the phenyl acetates can undergo hydrolysis if the pH is high. This affects the extraction yields: in former studies, the extraction of phenyl acetates showed better results at pH 6 than at pH 9 [7]. However, an important improvement in the extraction was observed for the more substituted phenols 2,4,6-trichlorophenol and 2,3,4,6-tetrachlorophenol when the pH was adjusted to 3 after completion of the derivatisation [22].

A comparison of the obtained distribution coefficients for phenol acetates (from experimental extraction efficiencies) showed a good correlation with the theoretical $K_{O/W}$ for phenols up to 2,4-dichlorophenol. This might give the impression that the extraction was inefficient for the more substituted phenols. The pH, being above 7, has much probably favored the less substituted phenol acetates to undergo hydrolysis preferentially than the most substituted phenol acetates because of steric effects. A better correlation including these compounds might have been obtained with the adjustment of pH to 3 [7].

The goal in the SBSE procedure proposed here was to avoid laborious work and reduce the total sample preparation time by performing the derivatization and extraction of phenols in one step (as the Twister consists of a stir bar and an extraction material, it stirs, it promotes the derivatization and it extracts at the same time). The changing of pH to 3 would represent a drawback in the proposed procedure, since one more step would be needed before the extraction with SBSE. However, by choosing this procedure a compromise was reached since, even with low extraction yields, it was possible to obtain good reproducibility and detection limits within a faster analytical procedure.

4.4. Calibration

Fig. 2 shows a chromatogram obtained from an extraction with twister of a pure water sample after spiking and derivatization of phenols. Calibration was performed by extracting pure water samples spiked at concentrations ranging from 1 to 15 μg l^{-1} for each phenolic compound.

The linear range was investigated by exposing the twisters for 45 min to this batch of 10 ml water samples containing the compounds of interest at the considered concentrations. The parameters for the calibration curves are shown in Table 4. All investigated phenols showed a good linearity in the investigated range (r^2 = 0.9955–0.9996).

The detection limits were calculated from the sample signals with a concentration of 1 μg l^{-1}. A signal-to-noise ratio of 3 was considered to obtain the detection limits, which are also listed in Table 4. Compared to the literature (for exam-

Table 4
Calibration parameters, reproducibility (RSD) and detection limits (LOD)

Compound	R^2	RSD (%)	LOD (μg l^{-1})
Phenol	0.9955	13	0.3
2-Chlorophenol	0.9987	13	0.2
2,4-Dimethylphenol	0.9994	27	0.3
2,4-Dichlorophenol	0.9990	6	0.1
4-Chloro-3-methylphenol	0.9996	11	0.2
2,4,6-Trichlorophenol	0.9992	7	0.1
Pentachlorophenol	0.9779	21	0.4

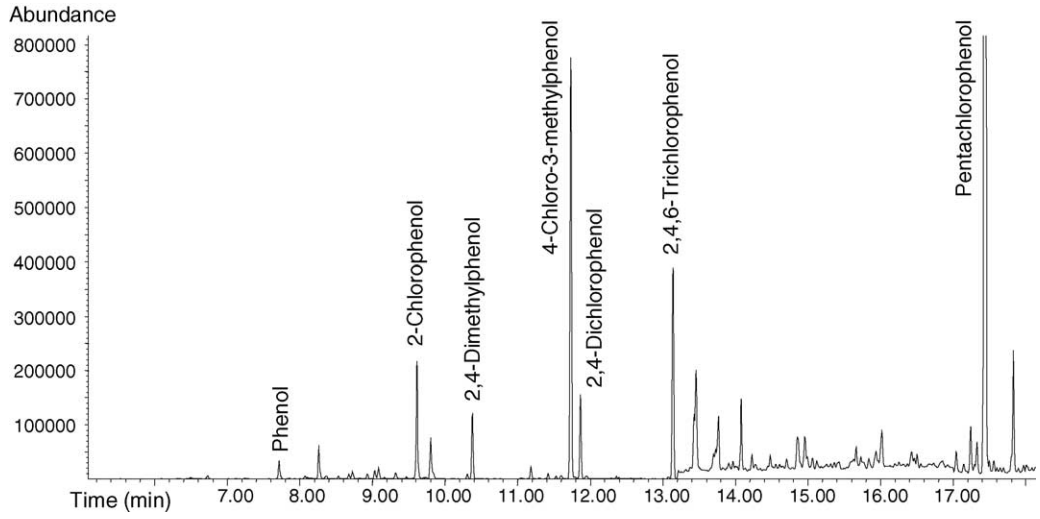

Fig. 2. Chromatogram of the derivatized phenols (pure water sample spiked with phenols, conditions as given in Table 2).

ple, LODs from 3.9 to 7.5 μg/l [16]) the present study was carried out using a shorter extraction time (45 min) than the equilibrium time and represented a compromise condition, in which lower LODs in the 0.1–0.4 μg/l range were achieved.

To study the reproducibility and carry-over effect for each compound, the twisters were enriched for 45 min in 10 ml water samples spiked with phenols to give a concentration of 10 $\mu g\,l^{-1}$ each, followed by thermodesorption GC–MS. The relative standard deviation (RSD) for the studied compounds ranged from 5.8 to 27.3%.

After the first desorption step a following second and third thermal desorption were carried out with the same stir bar. Carry-over was calculated considering the phenol acetates percentage remaining in the twisters. Carry-over levels were found to be 0.15–4.25% of the peak area at 10 $\mu g\,l^{-1}$ concentration of each phenol.

4.5. Real sample analysis

Five aliquots of 10 ml groundwater and lake water from different depths were extracted using twisters and their phenols content analyzed. Samples A and B were taken from gage bore holes at (A) 6 m and (B) 5 m depth from the mining surface. Samples C (0.2 m), D (15 m) and E (24 m) were taken from the lake Schwelvollert. Phenols content in samples A and B should be lower than in the water sample taken from Schwelvollert due to the filtering effect of the soil. Additionally, phenols concentration in the surface water of the lake (sample C, 0.2 m) should be significantly lower than those of the water samples from 15 m (D) and 24 m (E) depth caused by volatilization of the phenols, while the concentration of the deeper layers (samples D and E) remains nearly constant or shows a slight decrease. Fig. 3 shows a chromatogram of a

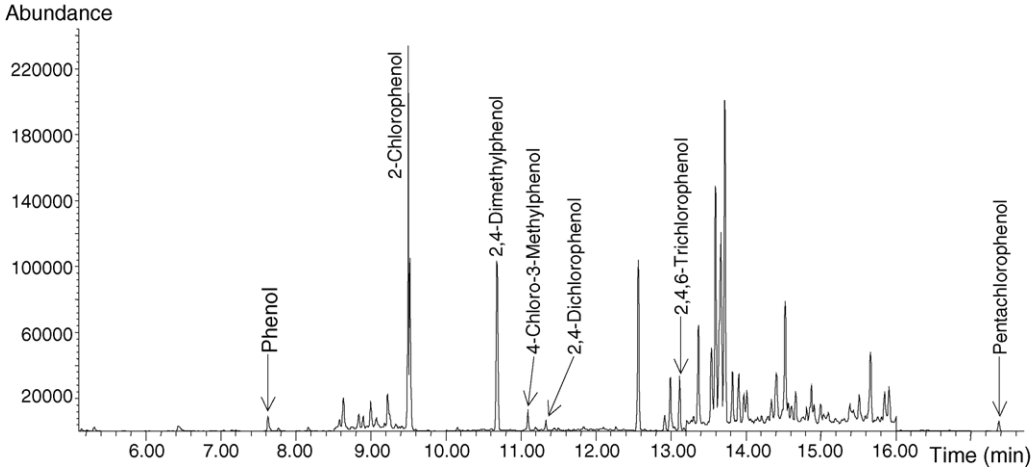

Fig. 3. Chromatogram of sample D (lake water, 15 m depth) (conditions as given in Table 2 and Section 3).

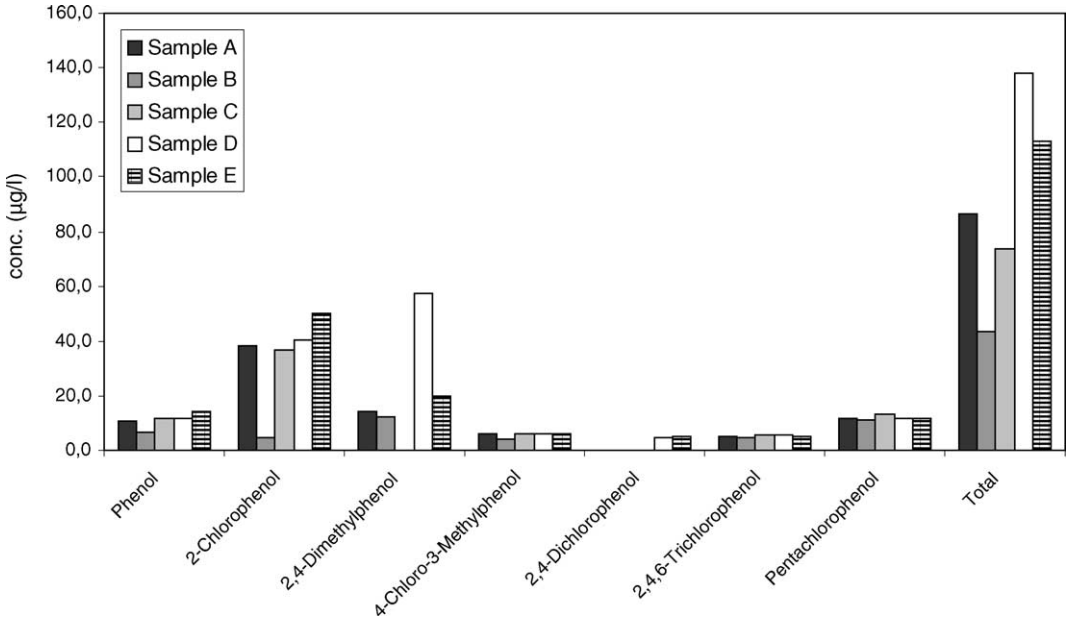

Fig. 4. Phenols content of the lake water and groundwater samples.

real sample extracted with the stir bar (sample D: lake water from a depth of 15 m).

The total amount of analyzed phenols ranged from 43 to 138 $\mu g\,l^{-1}$ for the appropriate samples. The results of the SBSE–TD–GC–MS method for the samples are listed in Fig. 4, showing good agreement with the considerations mentioned above. Interestingly, 2,4-dichlorophenol could not be detected in the ground water samples.

5. Conclusion

A TD–SBSE–GC–MS method for the determination of chlorophenols in water samples was developed. Influences of several parameters for the SBSE (extraction time and efficiency) and for the thermodesorption system (helium flow rate, TDS temperature and desorption time, CIS temperature) were investigated and optimized. Calibration was carried out and showed good linearity over the investigated concentration range with correlation coefficients above $R^2 = 0.97$ for all the analyzed phenols. Detection limits in the range from 0.1 $\mu g\,l^{-1}$ (2,4-dichlorophenol) to 0.4 $\mu g\,l^{-1}$ (pentachlorophenol) were obtained corresponding to about 10 times lower limits than those required by EPA method 625.

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