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Journal of Chromatography A, 835 (1999) 127–135

JOURNAL OF CHROMATOGRAPHY A

Determination of hydroxyaromatic compounds in water by solid-phase microextraction coupled to high-performance liquid chromatography

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Received 24 June 1998; received in revised form 16 October 1998; accepted 30 December 1998

Abstract

Solid-phase microextraction (SPME) coupled with high-performance liquid chromatography (HPLC) for the analysis of hydroxyaromatic compounds is described. Three kinds of fibers [50 μm carbowax–templated resin (CW–TPR), 60 μm polydimethylsiloxane–divinylbenzene (PDMS–DVB) and 85 μm polyacrylate (PA) fibers] were evaluated. CW–TPR and PDMS–DVB were selected for further study. The parameters of the desorption procedure (such as desorption mode, the composition of the solvent for desorption and the duration of fiber soaking) were studied and optimized. The effect of the structure and physical properties of analytes, carryover, duration of absorption, temperature of absorption, pH and ionic strength of samples were also investigated. The method was applied to environmental samples (lake water) using a simple calibration curve.

Keywords: Water analysis; Solid-phase microextraction; Hydroxyaromatic compounds

1. Introduction

The isolation and identification of hydroxyaromatic compounds is of great importance owing to their wide applicability in drugs, dyes, pesticides and foods. The impact of hydroxyaromatic compounds on the environment is subject to increasing attention. The US Environmental Protection Agency (EPA) lists 11 substituted phenols as ''priority pollutants'' [1]. Much research is devoted to these phenolic substances [2–7]. However, the separation and determination of other toxic hydroxyaromatic compounds [8] [e.g., 2,7-dihydroxynaphthalene (2,7-DHNA), 4,4′-dihydroxybiphenyl (4,4′-DHBP), 5-hydroxy-1,4-naphthoquinone (5-HNQ), 2-hydroxynaphthalene (2-HNA) and 1-hydroxynaphthalene (1-HNA)] has received little attention.

Hydroxyaromatic compounds are typically analyzed by liquid–liquid [2] or solid-phase extraction (SPE) [3] followed by determination with high-performance liquid chromatography (HPLC) or gas chromatography (GC) (derivatization may be required for GC-based analytical procedure) [4]. Liquid–liquid extraction is time-consuming and tedious, and requires large quantities of toxic and environmentally unfriendly solvents. Conventional off-line SPE requires less solvent, but the presence of

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0021-9673/99/$ – see front matter
PII: S0021-9673(99)00040-0

particulate matter in samples can cause plugging of the cartridges, and a large volume of sample is generally required for trace analysis. Sample volume does not play a role when analyzing surface water. Derivatization prolongs the analytical procedure, and is susceptible to contamination and loss of analytes. Most of the drawbacks can be reduced or even eliminated by using the on-line SPE [5–7,9]. Brouwer and Brinkman [5] determined phenolic compounds in surface water using on-line SPE–HPLC with diode array UV detection. With 50-ml samples, limits of detection (LODs) are at the low to sub-μg/l level. The mean RSD value is 3% (range 0.5–8.0%). Puig and Barceló [6] determined phenolic compounds in natural waters using on-line SPE–HPLC with UV detection. With 50–100 ml sample volumes, they found LODs below 0.1 μg/l for most phenols. The reproducibility varied from 3–7%. Puig and Barceló [7] also developed a high-sensitivity method for the determination of phenolic compounds in water. Using on-line SPE–HPLC and dual coulometric detection. LODs at part per trillion (ppt) levels (range 0.1–5.4 ng/l) were obtained using only 5 ml of water. The RSDs were 3–6% when working with river water. Slobodnik et al. [9] developed a fully automated on-line SPE–HPLC system.

Solid-phase microextraction (SPME), a relatively new extraction technique, was introduced by Pawliszyn and co-workers [10,11]. Recent trends in SPME were reviewed by Eisert and Pawliszyn [12]. The SPME technique integrates sampling, extraction, concentration and sample introduction into a single step [13]. Until recently, the extensive applications of SPME were based almost exclusively on separation and analysis by GC [14–16]. However, many classes of organic compounds widely used today (such as pharmaceutical products, drugs, peptides and proteins, some pesticides and polycyclic aromatic hydrocarbons) are semi- or non-volatile, and are best analyzed by HPLC. SPME coupled with HPLC was recently reported by Chen and Pawliszyn [17]. The extraction process used for SPME–HPLC is exactly the same as that described for GC analysis; only the desorption technique must be modified for HPLC analysis. The interface for SPME and HPLC has only recently become commercially available from Supelco. It is based on the initial design of Chen and Pawliszyn for coupling SPME with HPLC [17]. The SPME–HPLC interface enables the mobile phase to contact the SPME fiber, remove the adsorbed analytes, and deliver them to the column for separation. Analytes can be removed in a moving stream of mobile phase (dynamic desorption) or, when analytes are more strongly adsorbed onto the fiber, the fiber can be soaked in the mobile phase or another stronger solvent for a specific period of time before the material is injected onto the column (static desorption). Only a few applications of SPME–HPLC, such as the analysis of polyaromatic hydrocarbons [17], alkylphenol ethoxylate surfactants [18], proteins [19], pesticides [20–21] and corticosteriods [22], were found in the literature.

In this paper, we present the first application of SPME–HPLC to the analysis of hydroxyaromatic compounds. Three kinds of fiber [50 μm carbowax–templated resin (CW–TPR), 60 μm polydimethylsiloxane–divinylbenzene (PDMS–DVB) and 85 μm polyacrylate (PA)] were evaluated for the extraction of the hydroxyaromatic compounds. CW–TPR and PDMS–DVB were selected for further study. The effects of structure and physical properties of analytes, desorption mode, the composition of the solvent for desorption, the duration of fiber soaking, carryover, duration and temperature of absorption, pH and ionic strength (Na_2SO_4) of samples were also investigated. This method was applied to the analysis of environmental samples (lake water).

2. Experimental

2.1. Reagents

Analytical-reagent grade 2,7-DHNA, 4,4′-DHBP and 5-HNQ were purchased from Tokyo Chemical (Tokyo, Japan), 2-HNA and 1-HNA were obtained from Riedel-de Haen (Seelze, Germany). LC-grade sodium acetate was obtained from Fisher Scientific (Fair Lawn, NJ, USA) and acetonitrile was obtained from Tedia (Fairfield, OH, USA). Stock standard solutions were prepared by weighing the hydroxyaromatic compounds and dissolving them in methanol (Tedia). A working composite standard solution was prepared by combining an aliquot of each of the stock standard solutions and diluting the mixture

with water. Sodium sulfate (Merck, Germany) was used to prepare the sample solution. Deionized water was purified in a Milli-Q filtration system (Millipore, Bedford, MA, USA). Lake water from the National Tsing Hua University served as the environmental sample.

2.2. Apparatus and procedure

The SPME fiber assembly and SPME–HPLC interface were purchased from Supelco (Bellefonte, PA, USA). The SPME–HPLC interface consists of a six-port injection valve and a desorption chamber which replaces the injection loop in the HPLC system. After sample extraction, needle of the SPME device is inserted into the desorption chamber and the fiber is exposed under ambient pressure when the injection valve is in the load position. For static desorption, the fiber was soaked in the mobile phase (or other solvent) for 3 min, and then the valve was switched to the inject position and integration was begun. During the first 3 min, the analytes were delivered to the column at a lower flow-rate (0.1 ml/min) to minimize band broadening and peak tailing on the column. After 3 min the valve was returned to the load position and the mobile phase was introduced into the column without passing through the desorption chamber at an increased rate (1 ml/min). The fiber was held in the desorption chamber for 5 min, flushed twice with 500-μl volumes of mobile phase to minimize the possibility of analyte carry-over, and then the SPME fiber was removed. For dynamic desorption, the analytes were removed in a moving stream of mobile phase at a lower flow-rate (0.1 ml/min) during the first 3 min, and then the valve was returned to the load position and the flow-rate was increased to 1 ml/min. The microextraction fibers (from Supelco) were coated with CW–TPR (50 μm), PDMS–DVB (60 μm) or PA (85 μm). The fiber should be conditioned with the mobile phase, until a very stable baseline is obtained. Furthermore, the fibers show greater affinity to the analytes for the first several runs, and then results with reproducible extraction efficiency can be obtained. Therefore, the fiber should also be conditioned by repetitively adsorption and desorption of the analytes several times until a stable extraction efficiency is obtained.

Aliquots of 3 ml of standard solution or sample were extracted from 4-ml vials sealed with hole caps and PTFE septa. The concentrations of hydroxy-aromatic compounds spiked were 500 ng/ml (2,7-DHNA, 2-HNA and 1-HNA) and 100 ng/ml (4,4′-DHBP and 5-HNQ), unless otherwise specified. The sample solution is stirred with a stirring bar and controlled by a Digital/Magnetic Stirrer (Electrothermal HS 4000/5000, Essex, UK). The speed of rotation of the stirring bar was 550±10 rpm and the initial temperature of the sample solution used was 25±2°C, unless otherwise specified (the optimum extraction temperature was 20°C). After extraction for 20 min, the fiber is introduced to the desorption chamber of the SPME–HPLC interface.

The HPLC system, assembled from modular components (Waters, Milford, MA, USA), consisted of a Model 600E pump and a Model 486 UV detector. A Millennium workstation (Waters) was utilized to control the system and for acquisition and analysis of data. A 4 μm Nova-Pak Phenyl column (75 mm×3.9 mm, Waters) was used. The mobile phase was a mixture of acetonitrile–0.1 *M* acetate buffer (pH 4.7) (22:78) and UV detection was at 254 nm.

3. Results and discussion

3.1. Fiber evaluation

The relative extraction efficiencies of the hydroxy-aromatic compounds with various fiber coatings were compared under the same experimental conditions (absorption time 20 min, static mode, 25°C and no salt added) for all fibers, and not under the optimum conditions of each fibers. The most polar CW–TPR fiber provided higher extraction yields than the non-polar PA fiber for all compounds. The most polar CW–TPR fiber exhibited better extraction efficiency for the more polar analytes 2,7-DHNA and 4,4′-DHBP than the other fibers. For the other less polar analytes, the less polar PDMS–DVB fiber exhibited better or approximately equal extraction efficiency as compared to the CW–TPR fiber. CW–TPR and PDMS–DVB fibers were therefore used for further investigation.

3.2. Desorption mode and compositions of solvent for desorption

When CW–TPR fiber was used, the static mode using the mobile phase (mixture of acetonitrile and acetate buffer) gave only slightly better sensitivity than the dynamic mode. Most of the differences between the dynamic and static modes were insignificant (duplicated runs). The static mode with the mobile phase as desorption solvent was chosen for subsequent experiments using the CW–TPR fiber. When the PDMS–DVB fiber was used, somewhat better sensitivity was achieved in the dynamic mode than in the static mode. This indicates that the analytes desorb more rapidly from the PDMS–DVB fiber than from the CW–TPR fiber. The diffusion of the analyte in the desorption chamber (for the static mode) may decrease the peak areas of the analytes somewhat. Increasing the proportion of acetonitrile in the desorption solvent (a mixture of acetonitrile and acetate buffer) decreased the analyte desorption from the PDMS–DVB fiber. The mobile phase (acetonitrile–acetate buffer) is a better solvent to desorb the analytes from the PDMS–DVB fiber than the other solvent (mixture of acetonitrile and acetate buffer). The dynamic mode was used for further study with the PDMS–DVB fiber.

3.3. Desorption period

The effects of the desorption period (the period during which the fiber is flushed by the mobile phase) were studied. For the CW–TPR fiber, the peak area of the analytes increased with increasing desorption period (especially when the desorption period is increased from 1 to 2 min), which indicates that the desorption of analytes from the CW–TPR fiber is a slow process. Significant peak broadening and tailing appear for a desorption period of 5 min with either fiber. Therefore a desorption period of 3 min was chosen as the optimum.

3.4. Flow-rate during desorption

During the desorption period the analytes were delivered to column at a lower flow-rate (0.1 ml/min) to minimize band broadening and peak tailing on the column. Band broadening and peak tailing were observed if a higher flow-rate (0.2 ml/min) was used during the desorption period.

3.5. Soaking period

The effect of duration of the soaking of the CW–TPR fiber in the desorption solvent in the desorption chamber was studied. No significant variation in the recovery of the analytes was observed for the soaking periods from 1 to 5 min. This is to be expected as SPME is a partitioning process and the volume of solvent in the desorption chamber is small (200 μl). Therefore, increasing the soaking time cannot desorb more analytes from the fiber. A soaking period of 2 min was chosen for further study as it offered somewhat better sensitivity.

3.6. Carryover

For the runs using the CW–TPR fiber, no carryover of 2,7-DHNA, 4,4′-DHBP and 5-HNQ was found, and the carryover of the 2-HNA and 1-HNA was 6.5 and 6.3%, respectively. For the runs using the PDMS–DVB fiber, no carryover of 2,7-DHNA and 4,4′-DHBP was observed, and the carryover of 5-HNQ, 2-HNA and 1-HNA was 2.5, 4.4 and 2.6%, respectively. The concentrations of analytes spiked were 500 ng/ml (2,7-DHNA, 2-HNA and 1-HNA) and 100 ng/ml (4,4′-DHBP and 5-HNQ). All compounds have no carryover by the second desorptions. However, carryover in SPME is not of major big concern as in many other methods because SPME is an equilibration method. Carryover may become a problem only when the concentration of the analyte in the following sample is so low that the equilibrium concentration in the coating is lower than the concentration caused by carryover from previous analysis [16]. When samples of widely differing concentrations are analyzed in sequence, it is recommended that the fiber be conditioned by a second desorption step.

3.7. Absorption–time profile

The absorption–time profiles using the CW–TPR and PDMS–DVB fibers are shown in Figs. 1 and 2. The equilibration periods required are longer than 60 min except for 5-HNQ (equilibration period is 20

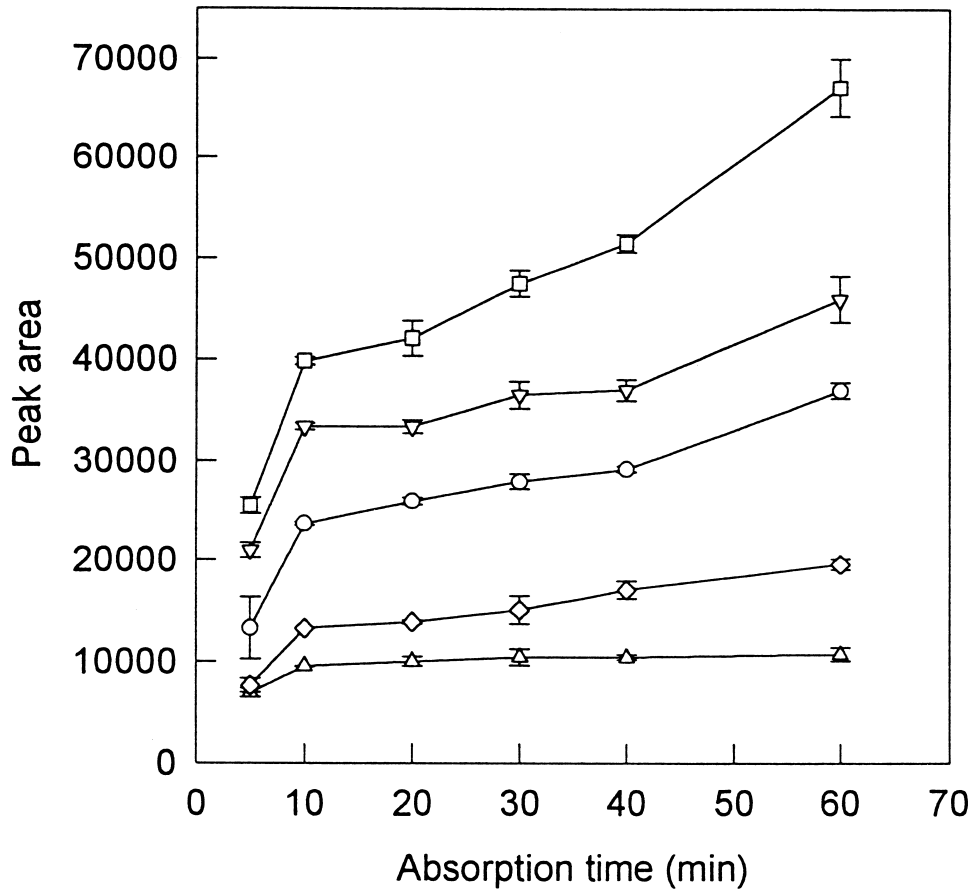

Fig. 1. Absorption–time profile for CW–TPR fiber. ○: 2,7-DHNA (500 ng/ml); □: 4.4′-DHBP (100 ng/ml); △: 5-HNQ (100 ng/ml); ▽: 2-HNA (500 ng/ml); ◊: 1-HNA (500 ng/ml). Desorption mode: static 2 min.

min with the CW–TPR fiber). Factors that influence the equilibration period were investigated by Pawliszyn and co-workers [14,15]. The equilibration rate is limited by the mass transfer rate of the analytes through a thin static aqueous layer at the fiber–solution interface. The equilibration period increased with increasing distribution constant of the analyte and with increasing thickness of the fiber coating. An extraction period of 20 min was chosen for subsequent experiments, since this time was approximately equivalent to the time required to run the HPLC chromatogram.

3.8. Effect of pH

It was found that the pH of the sample solution in the range pH 3–9 does not have a significant effect on the extraction efficiency of the hydroxyaromatic compounds using the CW–TPR or PDMS–DVB fiber. When the pH of the solutions was adjusted to 11, the absorption of analytes on the fibers decreased, due to the ionization of the weak acids in the basic solution.

3.9. Effect of extraction temperature

The absorption–temperature profile obtained using a CW–TPR fiber is shown in Fig. 3. Optimum extraction efficiency was achieved at 20°C. The lower absorption of the analytes at 10°C was due to the decreased rate of diffusion of the analytes. The decrease in absorption with increasing temperature

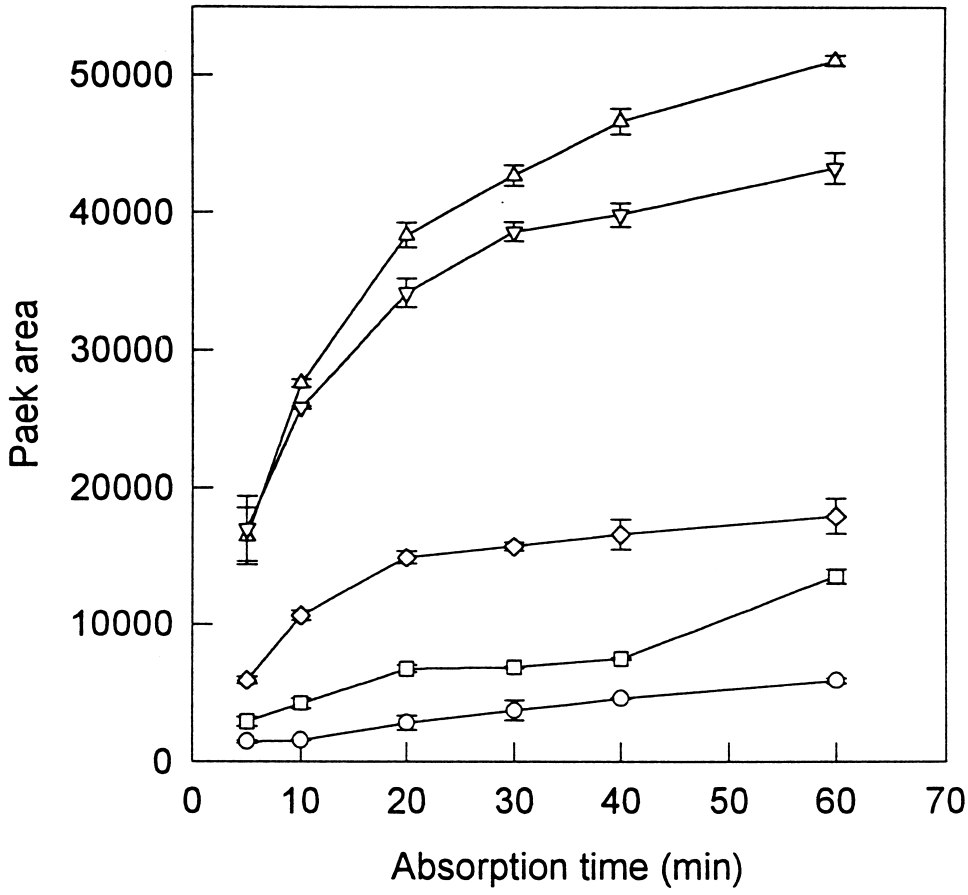

Fig. 2. Absorption–time profile for PDMS–DVB fiber. Desorption mode: dynamic. Concentration and notations as in Fig. 1.

above 20°C is due to the decrease of the distribution constant with increasing temperature. Because absorption is generally an exothermic process, the amount of analyte absorbed decreases with increasing temperature [15]. The amounts of analytes absorbed on the CW–TPR fiber decreased by 71–90% as the temperature increased from 20 to 60°C.

The absorption–temperature profile using a PDMS–DVB fiber is similar to that using a CW–TPR fiber.

3.10. Effect of ionic strength

The effect of ionic strength on the absorption of hydroxyaromatic compounds by a CW–TPR fiber and a PDMS–DVB fiber was studied by preparing standards with Na_2SO_4 concentration ranging from 0 to 20% (w/v). The increase in absorption of analytes, resulting from the ''salting out effect'' was highly significant except for 5-HNQ on the PDMS–DVB fiber. The effect of Na_2SO_4 on the absorption of 5-HNQ onto the fibers is probably due to three factors. The first is the salting out effect, which decreases the solubility of analytes and thus increases the absorption. Secondly, salt dissolved in the solution may change the physical properties of the static aqueous layer on the fiber, and reduce the rate of diffusion of the analyte through the static aqueous layer to the fiber. Thirdly, the zwitterion of the resonant forms of 5-HNQ molecule is more stable in the solutions with higher ionic strength, so that 5-HNQ becomes more soluble in water due to the increased contribution of zwitterion form to the resonance structure. These effects compensate each

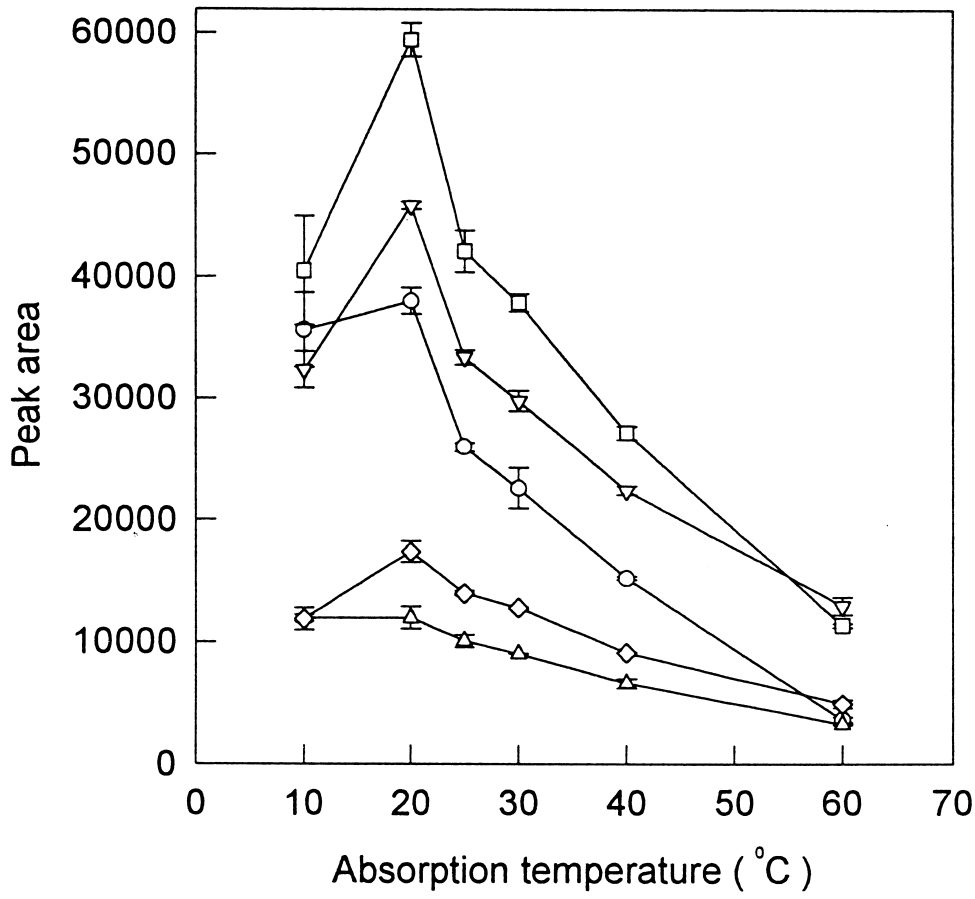

Fig. 3. Absorption–temperature profile for CW–TPR fiber. Concentration and notations as in Fig. 1.

other, so that the absorption of 5-HNQ on the PDMS–DVB fiber is hardly effected by the salt. The absorption of 5-HNQ on the CW–TPR fiber is significant increased from solutions with higher ionic strength, resulting from the ''salting out effect''.

3.11. Test on environmental samples

These hydroxyaromatic compounds were not found in the lake water sample. The slopes of the calibration curves of hydroxyaromatic compounds based on deionized water and lake water were compared using a CW–TPR or a PDMS–DVB fiber. The slopes of the calibration curves were almost independent of the matrix of the sample solution (difference in slopes is less than 3%). This indicated that the SPME–HPLC method based on a simple calibration curve could be used to analyze hydroxyaromatic compounds in natural waters. The linear range, R^2, limit of detection (LOD) and RSDs for the analysis of hydroxylaromatic compounds in lake water under optimum conditions (absorption temperature 20°C, 20% Na_2SO_4 added) are shown in Table 1. The linear range is good to three-orders of magnitude. LODs are calculated as three-times the standard deviation of seven replicate runs of lake water samples spiked with low concentrations (approximately 2.5-times the low limits of linear range) of the analytes. LODs are at the level of μg/l for both fibers. RSDs in the range 1–6% can be achieved. The chromatogram for the SPME analysis of hydroxyaromatic compounds using CW–TPR fiber is shown in Fig. 4. A similar chromatogram was obtained using the PDMS–DVB fiber. SPME–HPLC

Table 1
Linear range, R^2, limit of detection[a] (LOD) and relative standard deviation (RSD) for the analysis of hydroxyaromatic compounds in lake water under optimum conditions[b]

Compound	CW–TPR					PDMS–DVB				
	Linear range (mg/l)	R^2	LOD (μg/l)	RSD[c] (%)	RSD[d] (%)	Linear range (mg/l)	R^2	LOD (μg/l)	RSD[c] (%)	RSD[d] (%)
2,7-DHNA	0.01–10	0.9997	3.0	4	3	0.01–5	0.9986	4.2	4	2
4,4′-DHBP	0.002–2	0.9996	0.86	7	4	0.002–1	0.9987	0.99	5	1
5-HNQ	0.002–2	0.9995	0.66	10	6	0.002–1	0.9994	1.2	10	6
2-HNA	0.005–10	0.9999	3.2	4	3	0.01–5	0.9969	2.6	3	3
1-HNA	0.01–10	0.9999	2.5	5	2	0.01–10	0.9953	4.1	5	1

[a] LOD: Calculated as three-times the standard deviation of seven replicated runs of lake water samples spiked with low concentrations of the analytes.
[b] Absorption temperature 20°C, 20% Na_2SO_4.
[c] RSD: $n=7$, fortification level: 25 μg/l (2,7-DHNA; 2-HNA and 1-HNA), 5 μg/l (4,4′-DHBP and 5-HNQ).
[d] RSD: $n=4$, fortification level: 100 μg/l (2,7-DHNA; 2-HNA and 1-HNA), 20 μg/l (4,4′-DHBP and 5-HNQ).

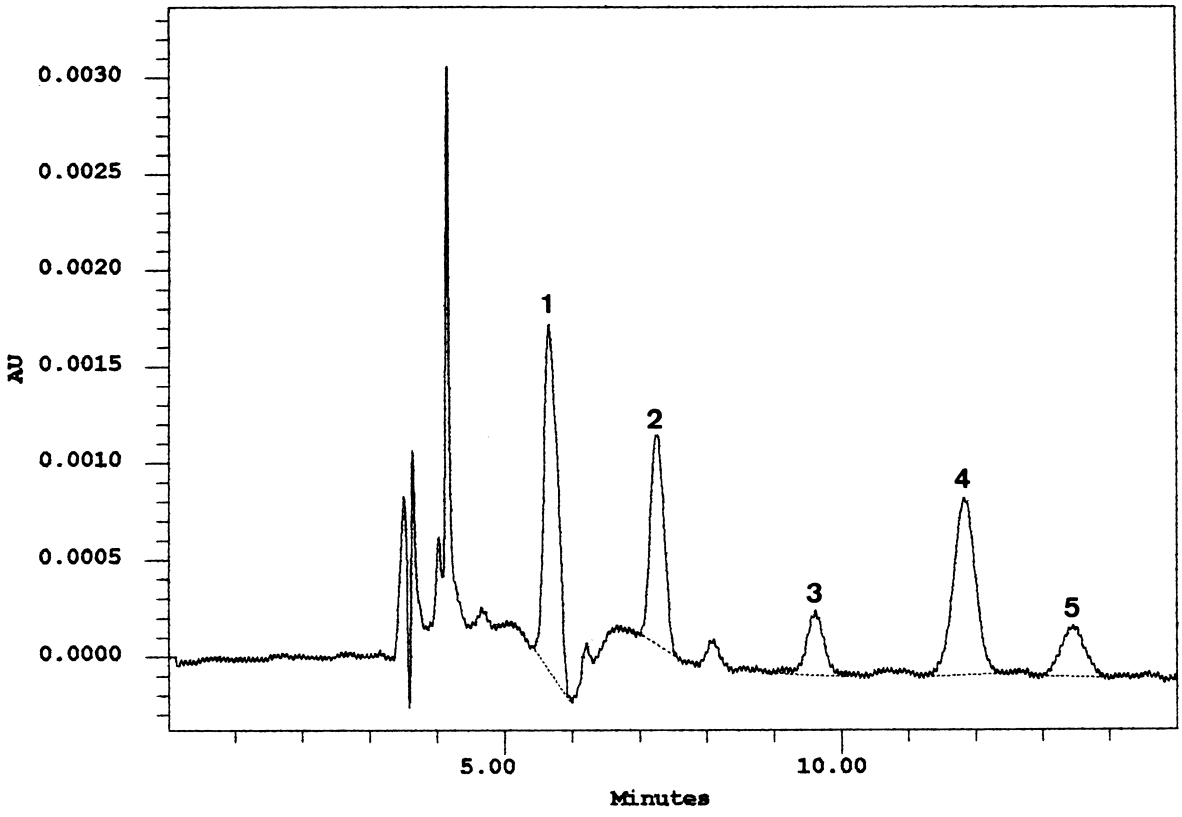

Fig. 4. Chromatogram for the SPME–HPLC analysis of the spiked lake water sample under optimum condition. Analytes spiked: 2,7-DHNA, 2-HNA and 1-HNA (250 ng/ml); DHBP and 5-HNQ (50 ng/ml). Sample volume 3 ml. Peaks: 1=2,7-DHNA; 2=DHBP; 3=5-HNQ; 4=2-HNA and 5=1-HNA.

Table 2
Percent recoveries[a] of hydroxyaromatic compounds

Compound	CW–TPR	PDMS–DVB
2,7-DHNA	3	1
4,4′-DHBP	5	2
5-HNQ	1	4
2-HNA	3	3
1-HNA	4	4

[a] Percent of analytes recovered from a 3-ml sample solution.

is an equilibrium technique, only 1–5% of the hydroxylaromatic compounds were adsorbed onto the fibers (see Table 2).

4. Conclusions

SPME–HPLC with UV detection was successfully applied to the analysis of hydroxyaromatic compounds in water. However, the proposed technique (with LODs at ug/l level) is not sensitive enough to detect these analytes in natural waters. Using detectors with better sensitivity (such as coulometric detection) should greatly improve the sensitivity and detectability. Developing new fibers with greater affinity for the analytes is also desirable. When SPME is coupled to HPLC, it retains the advantages of SPME (coupled to GC) as a fast, portable, requiring little or no solvent and inexpensive. SPME–HPLC is an equilibrium technique, but the procedure facilitates high-sensitivity analysis since the total amount of extracted material is transferred onto the HPLC column; which is different from liquid–liquid extraction or conventional off-line SPE. However, when SPME–HPLC is compared to on-line SPE–HPLC, with similar or less sample volumes and time of analysis, on-line SPE is more sensitive (since SPE–HPLC is an exhaustive procedure and the total amount of extracted material is transferred onto the HPLC column). The precisions of these two techniques are comparable.

Acknowledgements

This work was supported by the National Science Council of the Republic of China (NSC 87-2113-M-007-042).

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