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Journal of Chromatography A, 1012 (2003) 57–66
JOURNAL OF CHROMATOGRAPHY A
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Solid-phase microextraction coupled with high-performance liquid chromatography for the determination of phenylurea herbicides in aqueous samples

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Received 13 March 2003; received in revised form 12 June 2003; accepted 30 June 2003

Abstract

Solid-phase microextraction coupled with high-performance liquid chromatography was successfully applied to the analysis of nine phenylurea herbicides (metoxuron, monuron, chlorotoluron, isoproturon, monolinuron, metobromuron, buturon, linuron, and chlorbromuron). Polydimethylsiloxane–divinylbenzene (PDMS–DVB, 60 μm) and Carbowax–templated resin (CW–TPR, 50 μm) fibers were selected from four commercial fibers for further study because of their better extraction efficiencies. The parameters of the desorption procedure were studied and optimized. The effects of the properties of analytes and fiber coatings, carryover, duration and temperature of absorption, pH, organic solvent and ionic strength of samples were also investigated. External calibration with an aqueous standard can be used for the analysis of environmental samples (lake water) using either PDMS–DVB or CW–TPR fibers. Good precisions (1.0~5.9%) are achieved for this method, and the detection limits are at the level of 0.5–5.1 ng/ml.

Keywords: Solid-phase microextraction; Phenylureas; Pesticides

1. Introduction

Phenylurea herbicides are widely used in agriculture for selective or nonselective controls of many annual and perennial weeds. Among the nine herbicides, monuron and linuron are already reported to be possibly carcinogenic in humans [1]; isoproturon, the annual consumption of which in Europe is estimated to be over $1 \cdot 10^6$ kg, has been included in the European ''black list'' [2], and the other six herbicides (metoxuron, chlorotoluron monolinuron, metobromuron, buturon and chlorbromuron) could also cause serious damage to humans [3]. These herbicides are water soluble and their soil-based residues can remain for several months following application. From the soil they can easily migrate to crops and enter the food chain, and, depending on the rainfall pattern, surface run-off, and soil properties, the herbicides can also reach ground waters. Due to the absence of microbial activity, degradation

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0021-9673/03/$ – see front matter
doi:10.1016/S0021-9673(03)01169-5

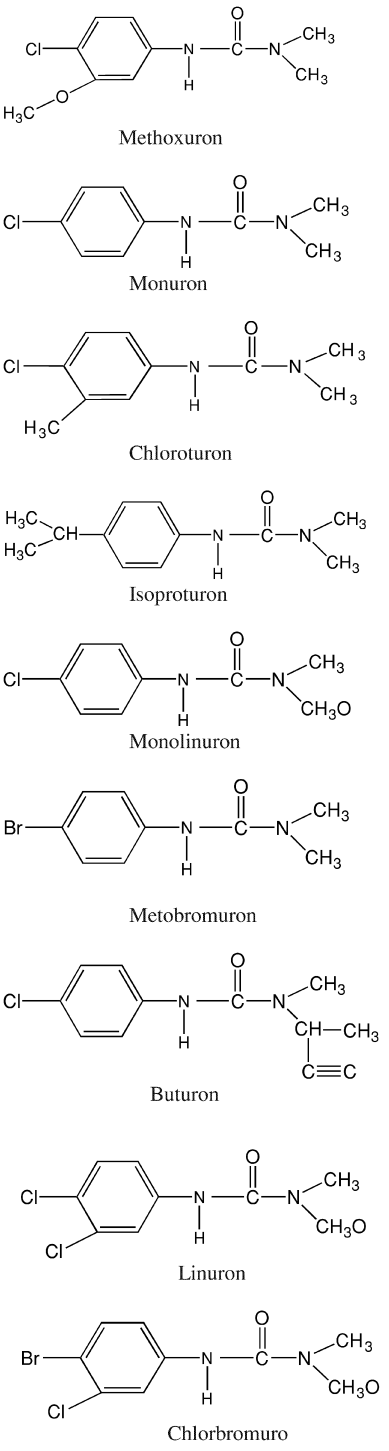

Fig. 1. Structures of phenylurea herbicides.

processes are very slow and accumulation phenomena can easily lead to toxic levels [4]. Under environmental conditions, phenylureas can persist at the mg/l level in ground water [5] for a number of days or weeks depending on temperature and pH. Some properties and the toxicity level of these herbicides can be found in Ref. [6]. The structures of the herbicides are shown in Fig. 1.

For phenylurea herbicides, efficient separations can be realized by either gas chromatography (GC) or liquid chromatography (LC). However, GC analysis of underivatized phenylurea herbicides renders quantification difficult [7] because most of these compounds are thermally labile and therefore thermal degradation products (ascribed to the presence of the amide hydrogen atom [8]) are often detected instead of the molecular herbicides. Moreover, identification of the individual herbicides originally present is often impossible since several different solutes generate identical degradation products [9]. To overcome these problems, derivatization procedures are developed to prevent thermal degradation of the phenylurea herbicides [9,10]. Since sample preparation should be kept as simple as possible, LC analysis is a better choice than GC analysis. At present, LC is widely used for the determination of phenylurea herbicides in aqueous samples [11–13].

Liquid–liquid extraction (LLE) is employed in most methods for the determination of pesticides, including official methods [14–17]. Solid-phase microextraction (SPME) was introduced by Pawliszyn and co-workers (see Ref. [18]). While originally developed as a sample preparation technique for GC [19–22], SPME has been coupled successfully to LC by Chen and Pawliszyn in 1995 [23]. Recently, several applications of SPME–high-performance liquid chromatography (HPLC) were found in the literature, such as polyaromatic hydrocarbons, alkylphenol ethoxylate surfactants, proteins, pesticides, corticosteroids, etc. [23–33].

In this work, we developed a SPME–HPLC method for the analysis of the above nine phenylurea herbicides in aqueous samples. The parameters of the desorption procedure were studied and optimized. The effects of the properties of analytes and fiber coatings, carryover, duration and temperature of absorption, pH, organic solute and ionic strength of samples were also investigated.

2. Experimental

2.1. Materials and apparatus

Analytical-grade reagents: metoxuron, monuron, chlorotoluron, isoproturon, monolinuron, metobromuron, buturon, linuron, chlorbromuron were were purchased from Riedel-de Haën (Germany); acetonitrile and methanol were purchased from Tedia (USA), sodium sulfate was purchased from Showa (Japan). Stock standard solutions were prepared by weighing the phenylureas (0.1 g each) and dissolving them in methanol (100 ml). A working composite standard solution (100 ng/ml) was prepared by combining an aliquot of each stock solution and diluting the mixture with deionized water. Deionized water was prepared from a Milli-Q purification system (Millipore). Lake water from the National Tsing Hua University was used as the environmental sample. 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 (chamber volume 200 μl) which replaces the injection loop of a six-port injection system. SPME fibers (from Supelco) coated with Carbowax–templated resin (CW–TPR, 50 μm), polydimethylsiloxane (PDMS, 100 μm), PDMS–divinylbenzene (DVB) (60 μm), and polyacrylate (PA, 85 μm) were used in this work. The HPLC system, assembled from modular components (Waters), 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. All separations were carried out on a 4 μm C_{18} column (15 cm×3.9 mm, Waters). The mobile phase was acetonitrile–water (40:60, v/v) and the wavelength of UV detection was set at 243 nm.

2.2. SPME–HPLC procedure

Each day prior to sample analysis, the fibers must be conditioned in the interface with mobile phase until they are free from the contaminants. After conditioning, the fiber can be used for extraction. Aliquots of 3 ml of standard solutions or real samples were extracted from 4-ml vials sealed with hole caps and PTFE septa which were punctured to provide apertures to permit passage of the fiber. The depth of immersion was kept constant. The sample solution is stirred with a stirring bar controlled at 550±10 rpm by a Digital/magnetic stirrer (Electrothermal HS 4000/5000). The temperature of the solution was 25±2 °C unless otherwise specified. After samples extraction, the SPME fiber was introduced into the desorption chamber under ambient pressure when the injection valve is in the load position. For static desorption, the fiber was soaked in the desorption chamber (full of mobile phase) for several minutes, then the valve was switched to the inject position and the analytes were delivered to the column. For dynamic desorption, the fiber was not soaked in the desorption chamber, and the analytes were directly removed by a moving stream of mobile phase. The flow-rate was 0.6 ml/min.

To minimize the possibility of analyte carryover, a second desorption was necessary; the fiber was held in the desorption chamber for 5 min, and then flushed twice with 500-μl portions of mobile phase.

3. Results and discussion

3.1. Fiber evaluation

Four commercial fibers were selected for preliminary investigation: PA, PDMS, CW–TPR, and PDMS–DVB fibers. Table 1 shows the absolute recoveries of the phenylureas with various fiber coatings. Obviously, the most polar fiber, PA and the least polar one, PDMS, exhibited the lowest sensitivities for all the nine analytes as compared to PDMS–DVB and CW–TPR fibers; PDMS–DVB and CW–TPR fibers were therefore selected for further investigation due to their better extraction abilities.

3.2. Optimization of the SPME procedure

3.2.1. Extraction time profile

Fig. 2 shows the extraction time profile of extraction for the nine phenylureas using the PDMS–DVB fiber. For all the analytes, the extraction efficiencies of analytes increase as extraction time increases from 0 to 60 min, and the equilibrium was

Table 1
Absolute recoveries of nine phenylurea herbicides[a]

Compound	Absolute recovery (%)			
	PA	CW–TPR	PDMS–DVB	PDMS
Metoxuron	0.13	0.35	0.42	0
Monuron	0.29	0.64	0.68	0.08
Chlorotoluron	0.52	1.45	1.65	0.19
Isoproturon	0.30	0.87	1.58	0.28
Monolinuron	0.62	1.49	4.13	0.26
Metobromuron	1.06	2.57	5.97	0.34
Buturon	6.17	17.18	19.17	1.17
Linuron	3.27	8.39	15.82	1.13
Chlorbromuron	7.67	21.38	33.14	2.80

[a] Percent recoveries(%)=[peak area of SPME÷concentration of compound (100 ng/ml)÷sample volume (3 ml)]/[peak area of direct injection÷concentration of compounds (10 000 ng/ml)÷injection volume (0.01 ml)]·100%=(peak area of SPME/ng)÷(peak area of direct injection/ng)·100%. Concentration: 100 ng/ml, extraction time: 30 min, soaking time: 4 min desorption mode: static, 4 min.

not reached even after 60 min. Since SPME is not an exhaustive extraction, shorter extraction time can be used as long as sufficient sensitivity is achieved and the experimental conditions are well controlled [34]. An extraction period of 40 min was chosen for subsequent experiments with the PDMS–DVB fiber as a compromise between analytical speed and sensitivity. The time profiles of extraction using the CW–TPR fiber are similar to that using the PDMS–DVB fiber; 30 min was chosen as the extraction time.

3.2.2. Desorption mode

All the analytes in the static desorption mode exhibited higher extraction efficiencies than they showed in the dynamic desorption mode using either the PDMS–DVB or CW–TPR fibers. This indicated that the analytes desorbed from the coatings slowly [30]. Peak tailing was found in the dynamic mode, especially with the CW–TPR fiber (as shown in Fig. 3). To achieve better extraction efficiencies and resolution, the static mode was thus used for further study.

3.2.3. Soaking time

Soaking time refers to the time that the fiber

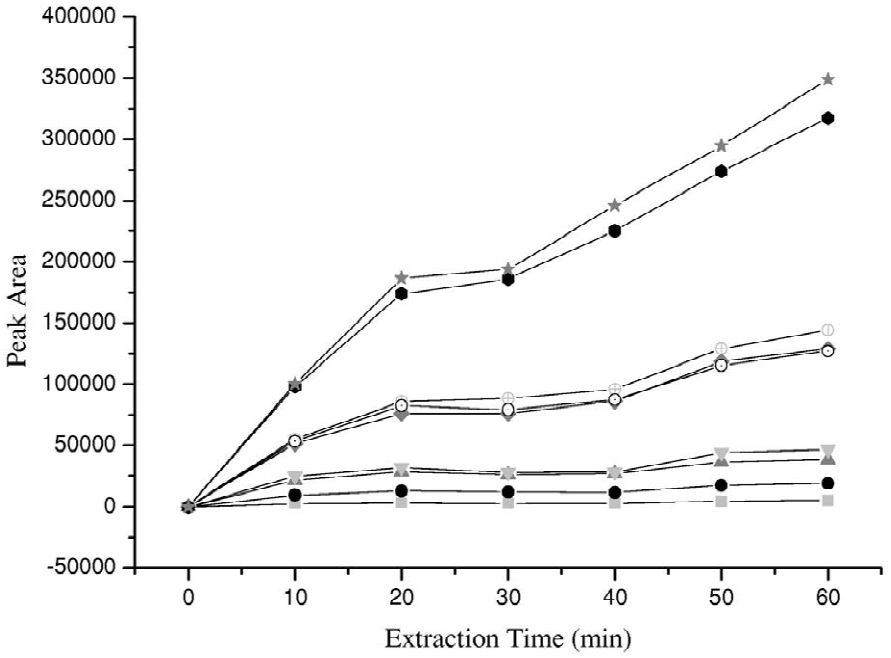

Fig. 2. Extraction time profile for the PDMS–DVB fiber. Concentration: 100 ng/ml, soaking time: 4 min, desorption mode: static, 4 min. Peak notation: (▼) metoxuron, (▽) monuron, (■) chlorotoluron, (□) isoproturon, (+) monolinuron, (×) metobromuron, (●) buturon, (○) linuron, (▲) chlorbromuron.

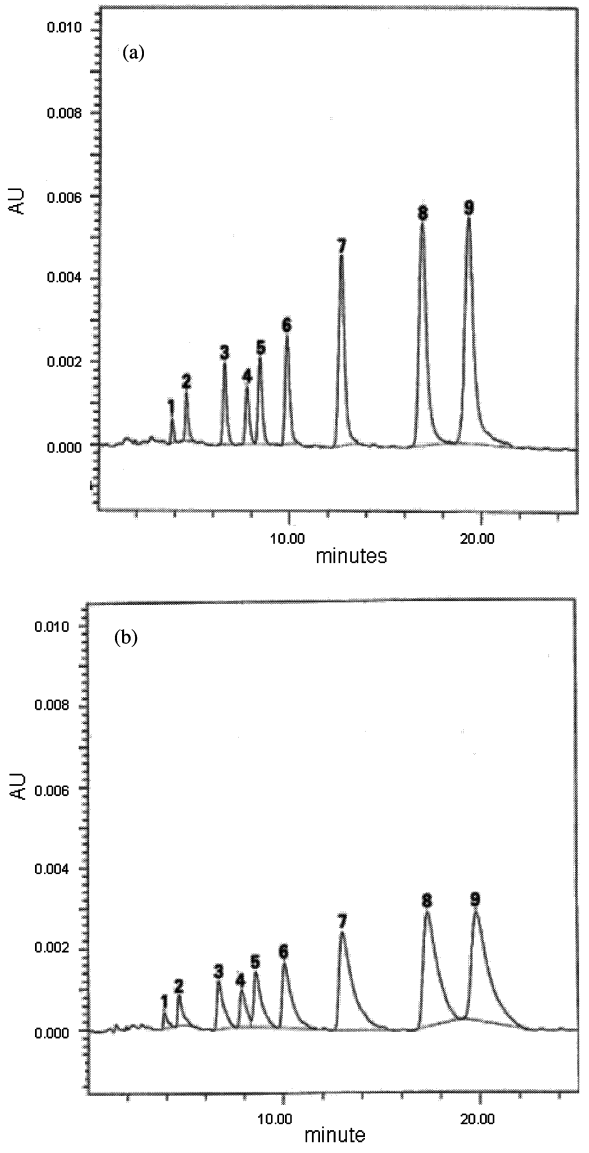

Fig. 3. Chromatograms of phenylureas with different desorption modes (a) static and (b) dynamic mode with the CW–TPR fiber. Concentration: 100 ng/ml, soaking time: 4 min. Absorption time: 40 min for the PDMS–DVB fiber; 30 min for the CW–TPR fiber. Peak assignments: 1=metoxuron; 2=monuron; 3=chlorotoluron; 4=isoproturon; 5=monolinuron; 6=metobromuron; 7=buturon; 8=linuron; 9=chlorbromuron.

soaked in the desorption chamber before it was flushed with the desorption solvent. For the PDMS–DVB fiber, the extraction efficiencies of the analytes increased as the soaking time increased (especially from 0 to 1 min), the maximum desorption was reached at about 4 min. Thus 4 min was used as the soaking time in further work. For the CW–TPR fiber, it seems that soaking time did not affect the extraction efficiencies of the analytes significantly; 3 min was used as the soaking time since it exhibited somewhat better sensitivity than a soaking time at 2 min.

3.2.4. Carryover

Carryovers of metobromuron, buturon, linuron and chlorbromuron were 0.78, 0.91, 0.66, and 0.61%, respectively, for the runs using the PDMS–DVB fiber. That could be eliminated by a second desorption. However, carryover will not be a big concern since SPME is an equilibration method [34]. No carryover was found from the other five analytes. While evaluating the CW–TPR fiber, carryovers of buturon, linuron and chlorbromuron were found to be 1.14, 0.81, and 1.07%, respectively. No carryover was found from the other six analytes. Carryover will not be found following a second desorption.

3.2.5. Desorption solvent

The mobile phase, a mixture of acetonitrile–water (40:60, v/v) is a better solvent to desorb the analytes from the fibers than the other solvents (acetonitrile–water, 30:70 to 55:45, v/v) studied for both the PDMS–DVB and CW–TPR fibers. Besides, using the mobile phase as the desorption solvent eliminates the extra step of inject the desorption solvent into the desorption chamber.

3.2.6. Desorption period

The desorption period refers to the period during which the fiber is washed by the desorption solvent (the mobile phase here) in the desorption chamber. Increasing the desorption period can enhance analyte sensitivities if the desorption rates of analytes are slow. Peak tailing of some analytes was found [29] with increasing desorption period; fortunately it did not occur in this method. Times of 5 min for the PDMS–DVB fiber and 4 min for the CW–TPR fiber were selected as the desorption periods since good extraction efficiencies and resolution were both achieved.

3.2.7. Flow-rate during the desorption period

If the desorption rate of analytes is slow, high flow-rate during desorption might cause band broadening and peak tailing. That problem can be solved by using a lower flow-rate to condense the analytes on the front portion of the column. A higher flow-rate can then be used to desorb the analytes for separation and detection; this is called ''on-column focusing'' [35]. However, no band broadening and peak tailing of these phenylurea herbicides were found at the higher flow-rates (0.6, 1.0 ml/min) for the PDMS–DVB and CW–TPR fibers. No statistical variation in peak area was observed by varying the flow-rate during desorption period from 0.1 to 1.0 ml/min. A flow-rate of 0.6 ml/min (which was also the flow-rate of HPLC) was eventually used for both PDMS–DVB and CW–TPR fibers during the desorption period because changing the flow-rate increased the method instability (bubbles may be produced).

3.2.8. Effect of extraction temperature

The temperature of extraction influences the extraction efficiencies in two different ways: kinetic and thermodynamic. As for kinetics, a higher temperature increases the diffusion rate of the analytes, thus the extraction efficiencies may increase at higher temperature. Thermodynamically, because absorption is generally an exothermic process, the amount of analytes absorbed decreases with increasing temperature [20]. The two effects compete with each other, and different analytes are affected in different ways. Fig. 4a shows the extraction temperature profile using the PDMS–DVB fiber. The extraction efficiencies for all the nine phenylureas increased as the temperature increased from 10 to 55 °C. Obviously, kinetic effect played a more important role under these conditions. The extraction efficiencies decreased in the temperature range 55–70 °C presumably due to decreases in distribution constants [20]. Thus, 55 °C was used for the PDMS–DVB fiber for further study. The extraction temperature profile using the CW–TPR fiber is shown in Fig. 4b. Analytes exhibited different trends with increase in temperature. As a compromise, 25 °C was selected for the CW–TPR fiber.

3.2.9. pH effect

Since the phenylureas are nearly neutral, it is expected that no significant effect of pH would be discovered due to the negligible protonation effects. The pH values of the original sample solutions were about 5.76. The pH ranges 2~10 for the PDMS–DVB fiber and 5~10 for the CW–TPR fiber were evaluated. As expected, there is no significant effect on the extraction efficiencies of phenylureas with either fiber. Therefore, the pH of the sample solutions was not adjusted.

3.2.10. Effect of organic solvent

A series of samples that contained methanol at concentrations ranging from 0 to 20% (v/v) were prepared to evaluate the effect of organic solvent on extraction. The concentration of methanol in the working solution (which containing 100 ng/ml herbicides each) is 0.09% (v/v). The extraction efficiencies of all the analytes decreased dramatically with an increased proportion of methanol in aqueous solutions for both fibers. The extraction efficiencies decreased by 2 (metoxuron)–15% (linuron) for the solution spiked with 1% methanol.

3.2.11. Effect of ionic strength

The effect of ionic strength on the adsorption of phenylureas by either fiber is shown in Fig. 5. The extraction efficiencies of the phenylureas increase 1.5~7.8 times for the PDMS–DVB fiber and 1.5~8.2 times for the CW–TPR fiber at the highest ionic strength of the solutions (20% Na_2SO_4) due to a ''salting-out effect''. But it should be noticed that working at a high salt concentration may facilitate crystal formation thus blocking the fiber protection mechanism and producing a mechanical failure [36,37].

3.3. Detection limits, precision, linearity, and recovery

The limits of detection (LODs), precision (RSDs), linearity correlation coefficient (R), and recovery are studied. LODs (shown in Table 2) were calculated as three times the standard deviation of seven replicate runs, and those based on deionized water and lake water was compared. Four samples (1 l each) were taken from different sites of the lake. No phenylurea herbicides were found in the lake water samples. The detection limits were in the range of 0.5~5.1 ng/ml.

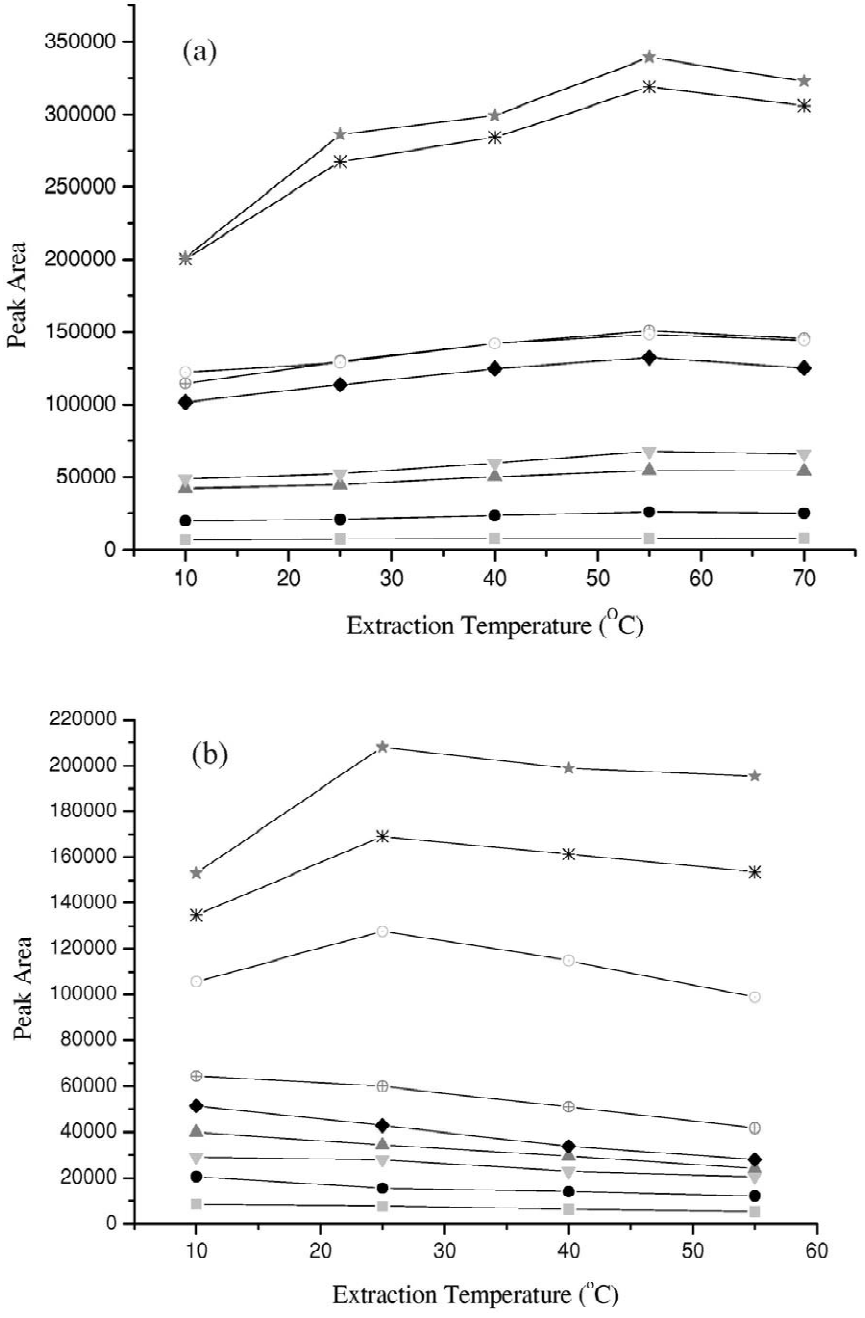

Fig. 4. Absorption temperature profile for (a) PDMS–DVB fiber, (b) CW–TPR fiber. Flow-rate: 0.6 ml/min. Absorption time: 40 min, soaking time: 4 min, desorption mode: static, 5 min for the PDMS–DVB fiber; absorption time: 30 min, soaking time: 3 min, desorption mode: static, 4 min for the CW–TPR fiber. Peak notation and concentration as in Fig. 2.

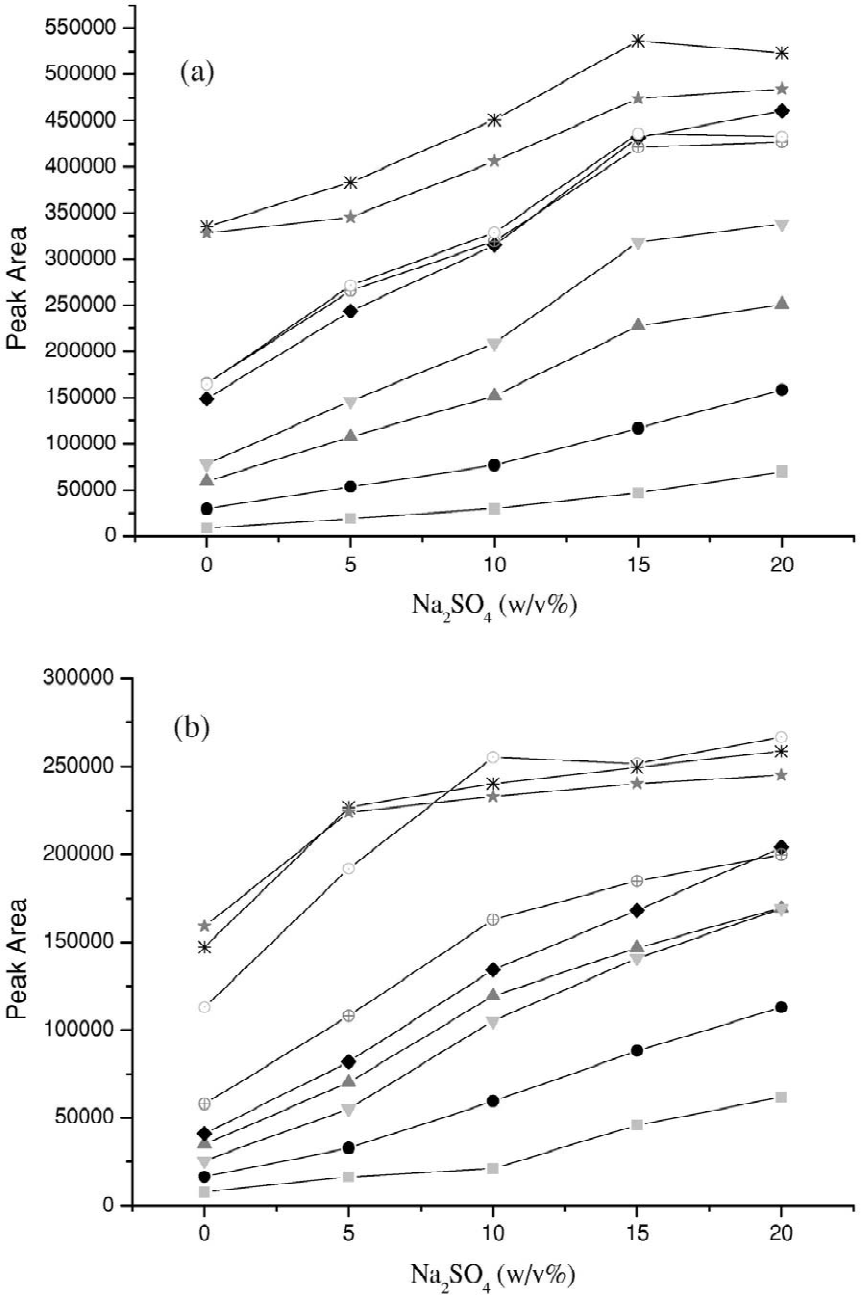

Fig. 5. Effect of ionic strength on absorption of phenylureas by (a) PDMS–DVB fiber, (b) CW–TPR fiber. Other experimental conditions as in Fig. 4. Peak notation as in Fig. 2.

The LOD values were about the same order or lower than the LODs found using the in-tube SPME–HPLC–UV method [27]. Detection limits lower than 9 ng/ml were found without preconcentration steps [12]. These concentrations are higher than those required for drinking water (0.1 ng/ml) [12] but are

Table 2
Method detection limits (LODs) and relative standard deviations (RSDs) for the analysis of phenylureas

Compound	PDMS–DVB		CW–TPR	
	LOD[a] (ppb)	RSD[b] (%)	LOD[a] (ppb)	RSD[b] (%)
Metoxuron	4.6	5.5	5.1	5.5
Monuron	3.8	4.8	2.9	2.3
Chlorotoluron	1.4	4.4	2.2	1.0
Isoproturon	1.2	5.9	1.7	3.0
Monolinuron	0.5	2.4	1.6	2.5
Metobromuron	0.8	3.3	1.4	1.4
Buturon	1.0	2.9	0.9	1.2
Linuron	0.7	5.3	0.8	2.5
Chlorbromuron	0.8	5.6	1.0	3.1

[a] LOD is calculated as three times the standard deviation of seven replicated runs of spiked lake water. Concentrations: metoxuron, monuron: 5 ng/ml; chlorotoluron, isoproturon, monolinuron, metobromuron, buturon, linuron, chlorbromuron: 2 ng/ml.
[b] Data obtained by extraction in seven replicates.

of the same order or lower than those generally reported for surface water, which range between 0.1 and 30 ng/ml [38]. When necessary, higher sensitivities could be achieved by coupling to a more sensitive detector (a mass spectrometer [39,40]), adding salts (20% Na_2SO_4) or using a custom-made fiber [41] or multifibers [42]. No significant difference in limits of detection was found between sample solutions prepared with deionized water and with lake water for both fibers. The RSDs for lake water samples spiked with 20 ng/ml each of the herbicide, ranged from 2.4 to 5.9% for the PDMS–DVB fiber and from 1.0 to 5.5% for the CW–TPR fiber. The linearity of this method for analyzing the phenylureas was investigated over the range 5–1000 ng/ml. The correlation coefficients were better than 0.995 for both fibers. Good recoveries (relative to spiked pure water samples 85~113% for the PDMS–DVB fiber; 85~111% for the CW–TPR fiber) were obtained for the analysis of the phenylurea herbicides in lake water using calibration curves from standard solutions. Fig. 6 shows the chromatogram and the blank using the PDMS–DVB fiber. Since better sensitivity (see Table 1) and lower LODs (see Table 2) were found for most of the herbicides using the PDMS–DVB fiber compared to those using the CW–TPR fiber, the PDMS–DVB fiber was selected as the fiber used in the optimum coatings. The summary of the proposed method is as follows: extraction time 40 min, extraction temperature 55 °C, pH 6, static mode for desorption, soaking time 4 min, desorption solvent (acetonitrile–water, 40:60, v/v), desorption time 5 min, flow-rate during desorption 0.6 ml/min.

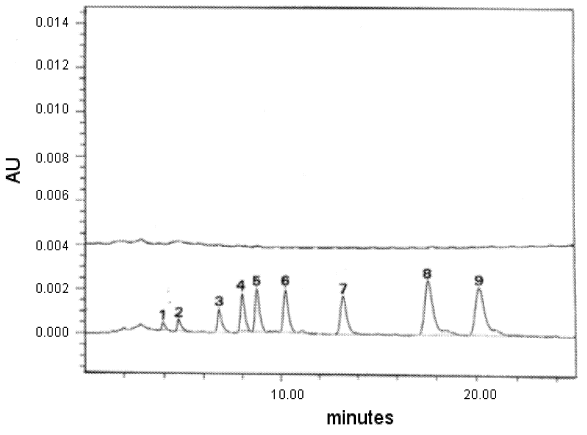

Fig. 6. Chromatograms of phenylureas for the spiked recovery and the blank using the PDMS–DVB fiber. Concentration: 20 ng/ml, which is higher than the LOQ of the least sensitive analyte. Other experimental conditions as in Fig. 4. Peak assignment as in Fig. 3.

4. Conclusion

SPME–HPLC was successfully applied to the analysis of phenylureas in water samples using PDMS–DVB fibers. A simple calibration curve method could be used for quantification and the limits of detection reached were at the level of 0.5–4.6 ng/ml. The results showed that it is im-

portant to optimize both the adsorption and desorption procedure.

Acknowledgements

We gratefully acknowledge the support of the National Science Council of Taiwan (NSC 91-2113-M-007-060).

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