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Solid-phase microextraction from small volumes of sample in a glass capillary

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Abstract

A new sampling method is proposed for solid-phase microextraction (SPME), in which the extraction is carried out in a glass capillary containing a few microliters of sample. When an adsorption-type fiber is used for SPME, the equilibrium between aqueous sample and coating can be described by a Langmuir isotherm. Since the total amount of analytes and coexisting substances stays at a low level in a small volume of sample, the linear concentration range of analytes will be extended for SPME to be applied in quantification and the interference caused by sample matrix will be reduced. In addition, sampling in a capillary has a short diffusion distance and extraction equilibrium is established in 5–10 min. It is important in clinical analysis and therapeutic drug monitoring to be able to analyse sample volumes of samples. The feasibility of the new sampling method is demonstrated by the extractions of *p*-hydroxybenzaldehyde and a synthetic solution containing 1-naphthol, paeonol and 1-naphthylamine.
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Keywords: Solid-phase microextraction; Sample preparation; Hydroxybenzaldehyde; Aldehydes; Naphthol; Paeonol; Naphthylamine

1. Introduction

Since its introduction in 1990 [1], solid-phase microextraction (SPME) as a technique for sample preparation has made progress theoretically and practically. Now SPME is used for the analysis of various samples, such as food, natural products, biological fluids, water, soil, etc. [2–4].

A piece of fused-silica fiber is coated with 1 cm length and 10–100 μm thickness of stationary phase and another is bound to the stainless steel plunger in a device that looks like a syringe. Left unused, the fiber is held in the needle of the syringe. The fiber can be moved outside the needle by depressing the plunger and dipped into the solution to be analyzed or the headspace above the sample. The analytes adsorbed in the fiber coating are desorbed in the injection port and introduced into a GC or HPLC system.

The equilibrium and kinetics of SPME have been discussed, including two-phase (sample solution–stationary phase coating) and three-phase (sample solution–headspace–stationary phase coating) systems [5–11]. In the SPME practice, the following points are required for its application in quantification:

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(i) The extraction equilibrium of analytes can be reached quickly to shorten the sampling time.
(ii) The amount of each analyte adsorbed in the stationary phase is proportional to its initial concentration, giving a linear calibration curve for quantification.
(iii) Other components existing in the matrix do not interfere with the extraction process of analytes.

Usually, sampling is carried out in a vial containing 1–5 ml of sample solution. With the sample stirred, it takes about 30 min or more to reach the extraction equilibrium. The fiber coatings are divided into two categories: absorption- and adsorption-type SPME coatings [10]. The former consists of liquid polymer and the latter is made up of porous solids. If the extraction of analytes on the surface of the adsorption-type coating is considered as the process where analytes interact with the adsorption sites to form complexes, we might describe the relationship between the adsorbed amount of an analyte and its concentration at equilibrium in the sample by the Langmuir isotherm [12]. In the case of SPME, the phase ratio (coating/sample) is quite small so that the adsorption sites on the surface of the coating might be saturated even with low initial concentration of analytes. As a result, the concentration of analytes is restricted in the use of SPME. Secondly, other components coexisting in sample can also be adsorbed on the coating surface. They might produce a significant impact on the extraction of analytes owing to the competition for adsorption sites.

In this work, a new sampling method is proposed for SPME, in which the extraction is carried out in a capillary containing a small volume of sample solution. Based on the kinetics, the short diffusion path favors the establishment of equilibrium. Next, even if the concentration of analytes is at a high level, the total amount of analytes in the small volume is still low and the linear range of the calibration curve obtained by SPME will extend to higher concentrations. Finally, the small volume of sample also reduces the possible interference coming from the components in the matrix. The adsorption sites on the coating surface are definite. The components in the matrix may compete with analytes to affect the recovery of the analytes. The purpose of this work is to examine the feasibility of the new sampling mode. We used several compounds in testing the method. The application of the sampling method is under way.

2. Experimental

2.1. Instrumentation

2.1.1. Chromatographic system

Chromatographic experiments were carried out on a system consisting of an automatic gradient controller, 501 and 510 HPLC pumps (Waters, Milford, MA, USA), a SPME–HPLC interface (Supelco, Bellefonte, PA, USA), and an LC-95 UV–Vis spectrophotometric detector (Perkin-Elmer, Norwalk, CT, USA). An Anastar chromatographic working station (Autoscience, Tianjin, China) was connected to the 1 V output of the detector.

The SPME–HPLC interface consists of a six-port Rheodyne valve and desorption chamber that replaces the loop in the valve.

2.1.2. SPME device

A SPME fiber holder for the SPME–HPLC interface and SPME fiber assemblies were purchased from Supelco. The SPME fibers used in this work included polydimethylsiloxane–divinylbenzene (PDMS–DVB, 60 μm, partially crosslinked) and Carbowax–templated resin (CW–TPR, 50 μm, partially crosslinked). Before use, the fibers were conditioned by the relevant mobile phases in the desorption chamber until a flat baseline was obtained.

2.2. Materials

The chemicals were obtained from a variety of suppliers. Methanol (No. 2 Chemical Reagent Factory, Tianjin, China) was distilled to prepare the mobile phase. Water purified by a Milli-Q water system (Millipore, Bedford, MA, USA) was used for preparing solutions.

2.2.1. Standard solutions

p-Hydroxybenzaldehyde (p-HBA) (1.0 mg/ml): dissolve 10 mg of p-HBA into 10 ml of methanol or 1% (v/v) methanol in water to prepare the stock solutions.

1-Naphthol, paeonol, 1-naphthylamine (1.0 mg/

ml): dissolve 10 mg of 1-naphthol, paeonol, 1-naphthylamine into 10 ml of methanol, respectively.

2.2.2. Working solutions

Working solutions were prepared by diluting the corresponding stock solutions with water or with a 25% (w/v) aqueous solution of NaCl.

2.3. Sampling

The procedures are shown in Fig. 1:

1. Take a 5-cm length and 0.65 or 1.00 mm I.D. glass capillary and suck 0.9–1.0 cm length of liquid column from the sample vessel.
2. Fix the capillary in a vial with the aid of a septum.
3. Insert the needle of the SPME fiber holder into the capillary.
4. Depress the plunger to expose the fiber to the sample solution.
5. Retract the fiber and withdraw the needle from the vial after adsorption equilibrium is attained.

2.4. Desorption

The needle of the SPME fiber holder is introduced into the SPME–HPLC interface, where the adsorbed analytes are desorbed and then delivered to the HPLC column. There are two ways to desorb analytes: dynamic and static. In the former, the fiber contacts with the moving mobile phase and the analytes removed from the fiber are delivered to the column.

When desorbing statically, the fiber is first immersed with mobile phase or other solvents in the desorption chamber for a short period. Then, the desorbed analytes go into the column along with the moving mobile phase when the six-port valve is switched from ''Load'' to ''Injection'' position.

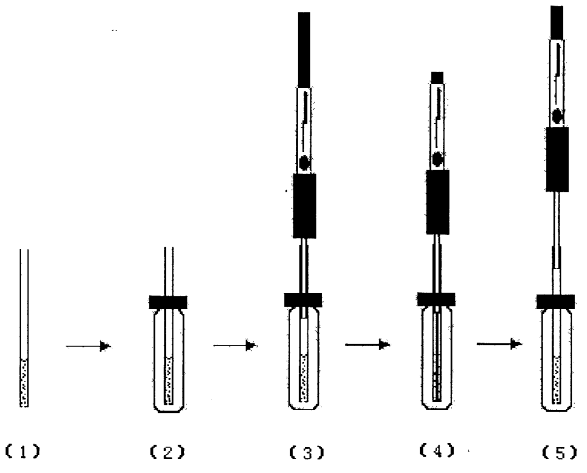

Fig. 1. Procedures of SPME in capillary (see the text for details).

2.5. Determination of recovery

In order to obtain the recovery of the analytes extracted from the sample by SPME, the response (peak area) per mass unit of analytes is determined first. A certain amount of standard solution is manually injected by syringe. The amount of the injected standard solution is given by the mass difference of syringe before and after injection. The peak area is measured from the chromatogram. The amount of sample taken for SPME is obtained by the mass increment of the capillary after sucking. The recovery can be calculated according to:

$$\text{Recovery}\ (\%) = (A_{\text{SPME}} W_{\text{STD}} / A_{\text{STD}} W_{\text{SPME}}) \times 100$$

where W_{STD} and A_{STD} are the masses of analyte and peak area for the direct injection of standard solution, respectively, W_{SPME} is the mass of analyte containing in the sample for SPME, and A_{SPME} is the peak area of analyte in the chromatogram obtained after SPME.

3. Results and discussion

3.1. Sampling in small volume of solution

When equilibrium is developed between aqueous sample and the coating of porous adsorbent, the amount of adsorbed analyte, n_{A}, can be expressed by the following equation [5]:

$$n_{\text{A}} = kV_{\text{A}}V_{\text{S}}C_{\text{S, init}} / (kV_{\text{A}} + V_{\text{S}}) \quad (1)$$

where k is the distribution coefficient, V_{S} is the volume of sample, V_{A} is the volume of coating, and $C_{\text{S, init}}$ is the initial concentration of the analyte in the sample. The total amount of analyte is equal to:

$$n_{total} = V_S C_{S,\,init} \quad (2)$$

Recovery of SPME is defined as

$$R = n_A / n_{total} = kV_A / (kV_A + V_S) \quad (3)$$

According to Eq. (3), the recovery decreases with the increasing V_S. It can be seen from Eq. (2) that a small volume of sample also makes n_{total} decrease. With V_S reduced, however, the increasing rate of R is less than the declining one of n_{total}. That means less analyte will be adsorbed from a small volume of sample although recovery rises in the situation. When sampling in small volume, therefore, a wider concentration range of sample will be allowed before adsorption sites on the surface of the coating are saturated.

The sensitivity of SPME depends on the adsorbed amount of analytes on the coating, n_A. From Eq. (3), $n_A = Rn_{total}$. Although n_{total} decreases in a small volume of sample, the increasing R compensates the loss in sensitivity to a certain extent.

3.2. SPME of p-HBA

3.2.1. Chromatographic conditions

The pK_a of p-HBA is 7.62 (25 °C, water), quite close to the pH of pure water. To start with, it was examined whether unbuffered acetonitrile (ACN)–water and MeOH–water systems could be used as the mobile phase for the chromatographic separation of p-HBA. The solute was strongly retained on the C_{18} column with both mobile phases. In circumstances of ACN–water, however, a tailing peak of p-HBA was present so that MeOH–water solvent was selected as the mobile phase to elute p-HBA.

3.2.2. Selection of SPME fibers

Two kinds of fibers supplied by Supelco, PDMS–DVB (60 μm) and CW–TPR (50 μm) were tested for SPME–HPLC sampling. Both have partially crosslinked coating and extract analytes via the adsorption mechanism [10].

In the preliminary test, it was observed that the fiber coated with CW–TPR gave a higher recovery for p-HBA than that with the PDMS–DVB coating. We used the CW–TPR fiber for SPME of p-HBA later.

3.2.3. Optimizing desorption

To study the new extraction method, the desorbing conditions were optimized at the beginning. A fiber on which p-HBA had been extracted was inserted into the SPME–HPLC interface. The adsorbed analyte was removed into the column by kinetic desorption. The fact that a tailing peak developed in this condition made us try the static method of desorption.

With the six-port valve of the SPME–HPLC interface set at the ''Load'' position, the CW–TPR fiber with adsorbed p-HBA was inserted into the desorption chamber and immersed in desorbing solvent for a given period (immersion time). Then, the six-port valve was switched to the ''Injection'' position and returned back to the ''Load'' position upon rinsing for a while (rinsing time). As the p-HBA peak was eluted from the column, switching the valve to the ''Injection'' position, the fiber was rinsed once again to determine if there was p-HBA left on the fiber after the first desorption.

The ratio of the peak area for each desorption to the total area of the two desorptions is referred to as the desorption percentage. The effect of desorption conditions on it is shown in Table 1, and this indicates that the solvent strength for desorption and immersion time are critical to desorb the adsorbed analyte from the SPME fiber completely.

Table 1
Desorption of p-HBA

Desorbing agent	MeOH–water (40:60)	MeOH–water (50:50)			MeOH–water (50:50)
Immersion time (min)	2.0	2.0	5.0	7.0	5.0
Mobile phase	MeOH–water (40:60)	MeOH–water (50:50)			MeOH–water (50:50)
Rinsing time (min)	0.5	0.5	1.0	0.5	1.0
Flow-rate (ml/min)	1.0	1.0	1.0	1.0	0.8
First desorption (%)	83.6	88.1	100	100	100
Second desorption (%)	16.5	11.9	0	0	0

With the desorbing solvent and immersion time being 40% methanol and 2 min, respectively, the percentage of the first desorption is 83.55%, lower than that in 50% methanol, which was 88.1%. When the immersion time is extended to 7 min, no residue of p-HBA is found in the second desorption. In fact, 5 min of immersion time is long enough to desorb the analyte with 50% methanol.

A long rinsing time is not necessary. The data in the fourth column of Table 1 show that the desorbed analyte can be rinsed into the chromatographic system with 500 μl of mobile phase (1.0 ml/min flow-rate for 0.5 min). This means that the volume of eluent is sufficient to sweep the desorption chamber.

According to the results in Table 1, the conditions for the desorption of p-HBA are: mobile phase and desorption solvent, 50% methanol; immersion time, 5 min; flow-rate, 0.8 ml/min; rinsing time, 1 min. To simplify the procedures, a mobile phase identical to the desorption solvent is used. The p-HBA samples injected directly and handled by SPME yield the chromatograms shown in Fig. 2. The p-HBA peaks obtained in two cases have the same retention time and peak shape.

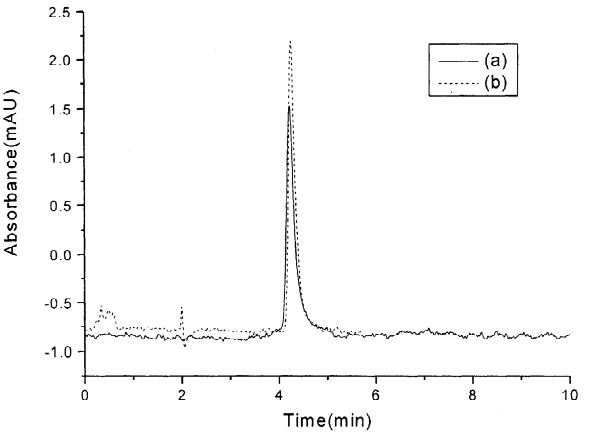

Fig. 2. Chromatograms of p-HBA obtained (a) by direct injection and (b) after SPME. Chromatographic conditions: column, Kromasil C_{18}, 15×0.46 cm; mobile phase, 50% MeOH in water; flow-rate, 0.8 ml/min; detection, UV 280 nm; sample, 1.0 ppm p-BHA. Desorption conditions: desorbing agent, 50% MeOH in water; immersion time, 5 min; rinsing time, 1 min.

3.2.4. Factors influencing extraction recovery

3.2.4.1. Sample volume

The capillaries 0.65±0.02 and 1.00±0.02 mm I.D. replaced the sample vials usually used in SPME to suck p-HBA solution in 0.1% methanol 0.90 and 1.00 cm in length, respectively. The volumes of the liquid column were 3.0±0.2 and 7.5±0.3 μl for each of them separately. The study on the effect of extraction time on recovery was carried out, and the results are shown in Fig. 3. With 3.0 μl of p-HBA solution extracted (Fig. 3A), the time required to attain the equilibrium is about 5 min. Fig. 3B is for 7.5 μl of p-HBA solution, and in the case, it takes about 20 min for equilibrium to be established.

The speed to achieve equilibrium depends on the moving distance and the diffusion coefficients of solute in aqueous phase, the mass transfer in coating. Comparing between the experimental conditions of Fig. 3A,B, among the factors, the difference is only moving distance in aqueous phase. Inserting a fiber 100 μm in diameter with a coating 50 μm in thickness into a capillary 0.65 mm in internal diameter, the moving distance of solute can be calculated to be ~0.2 mm. It is ~0.4 mm for the capillary with 1.0 mm I.D. and the same SPME fiber.

Fig. 3C demonstrates the variation of recovery with extraction time when the liquid column in the capillary has 10.0 μl volume and is 1.3 cm in length. Since the length of coating on fiber is only 1 cm, the solute molecules in the bottom of the liquid column

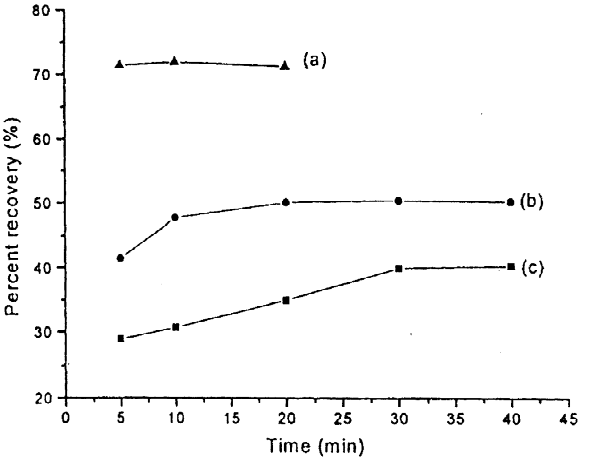

Fig. 3. Plot of recovery versus extraction time for different volumes of sample, (a) 3.0 μl, (b) 7.5 μl, (c) 10.0 μl. SPME conditions: sample, 1.0 ppm p-BHA; fiber, CW–TPR, 50 μm.

should move a much longer distance to reach the surface of the coating. This slows down the equilibrium process, its development requiring at least 30 min.

Now let us to look at the variation of recovery with the sample volume for SPME. With the equilibrium attained, the recoveries of 3.0, 7.5 and 10.0 μl samples are 71.4, 50.0 and 40.4%, respectively. It is pointed out from the results that recovery increases with decreasing sample volume. That is consistent with Eq. (3) in Section 3.1.

SPME is an adsorption (or partition) process. As the equilibrium is established between sample and coating, the adsorbed amount of analyte will not change with the extraction time. Usually, the volume of coating on the fiber is only $\sim 10^{-4}$ ml, but the solution in the sample vial is 1–5 ml. The small phase ratio could lead to low recovery for SPME. The situation can be improved by either increasing the coating volume or decreasing the sample volume. The former is restricted by such factors as coating technique, slow mass-transfer and interface coupling between HPLC or GC and SPME. The simple way to increase recovery is by means of reducing sample size.

As shown in the SPME of p-HBA in capillary, it is not assured for the analyte to be extracted completely, even though a small volume of sample solution is involved. There are two possibilities resulting in the incomplete extraction: (1) the coating has been saturated already and cannot adsorb the analyte further; (2) a small distribution coefficient prevents p-HBA from being fully extracted. Thus, an experiment was done where the recoveries were measured at the different levels of p-HBA.

3.2.4.2. Sample concentration

In order to ascertain if the CW–TPR coating had been saturated by p-HBA in SPME of 3.0 μl of 1 ppm p-HBA solution, the same volume of 10 ppm p-HBA solution was taken and the recovery was measured under the same SPME conditions. The plot of recovery versus extraction time is given in Fig. 4. The results for 1 and 10 ppm solution are consistent with each other. The recoveries in both cases reach about 70% when the extraction time is longer than 5 min. This indicates that recovery less than 1 in SPME of 3.0 μl of 1 ppm p-HBA solution results from the distribution property of p-HBA other than the saturation of the coating. Or the recovery of 10 ppm p-HBA sample would obviously decrease.

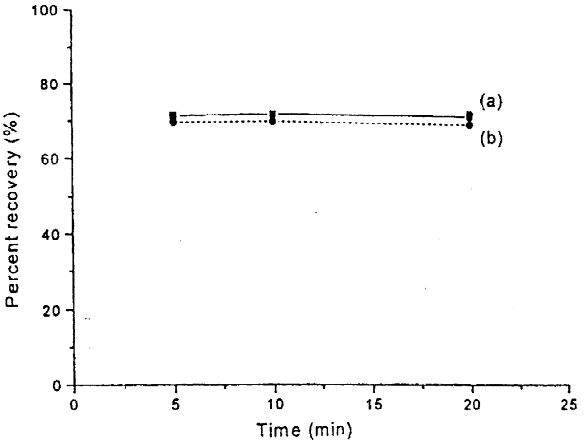

Fig. 4. Plot of recovery versus extraction time for different concentrations of sample, (a) 1 ppm p-HBA (in 0.1% MeOH in water), (b) 10 ppm (in 1% MeOH in water). SPME conditions: sample volume, 3 μl; fiber, CW–TPR, 50 μm.

To verify the conclusion further, the recoveries of p-HBA were determined with 3.0 μl of solution and 10-min extraction time in a concentration range from 1 to 100 ppm, as shown in Table 2. Roughly the same recovery values were obtained in the whole range of concentrations.

3.2.4.3. Salt in matrix

Generally, the increase in ionic strength of sample matrix favors the distribution of analytes to coating. Using NaCl as ionic strength adjusting agent, the effect of the coexisting salt on recovery was examined. When p-HBA was extracted from 3.0 μl of its 10 ppm solution containing 25% (w/v) NaCl, the recovery increased from 70% for the solution without NaCl to 97%. The variation of recovery with NaCl in the matrix is illustrated in Fig. 5.

Table 2
SPME recovery of p-HBA at different concentrations

p-HBA concentration (ppm)	Sample matrix	Recovery (%)
1.0	0.1% MeOH in H_2O	71.9
10	1% MeOH in H_2O	70.0
100	10% MeOH in H_2O	71.5

Sample volume: 3 μl.

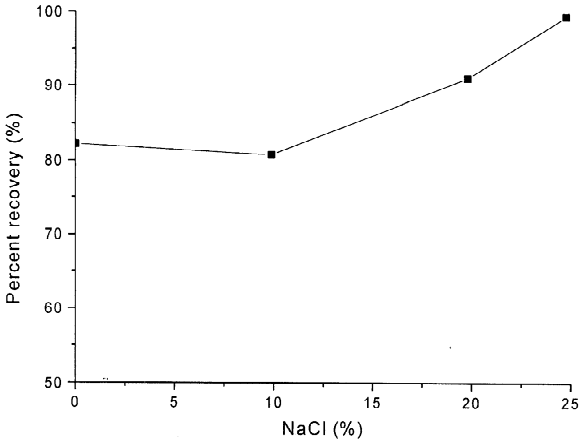

Fig. 5. Effect of NaCl concentration in sample on recovery. SPME conditions: sample, 10 ppm p-HBA in 0.1% MeOH in water containing different concentrations of NaCl; sample volume, 3 μl; fiber, CW–TPR, 50 μm.

3.2.4.4. Organic solvent in matrix

The effect of methanol existing in matrix on recovery is summarized in Table 3. With 3.0 μl of 1 ppm p-HBA extracted, the recovery is 70.0% for the solution containing 1% methanol, compared with 82.2% for the 0.01% methanol matrix. When NaCl exists in the matrix, the same trend is also observed.

3.3. Simultaneous SPME of a few analytes in the capillary

As seen in the above section, p-HBA is extracted with a certain recovery in the wider concentration range when SPME is carried out in a capillary. This being the case, the total amount of p-HBA is quite low even if its initial concentration in the capillary may be high. The extraction system still remains within the linear range of the Langmuir isotherm after equilibrium is attained. The advantage of performing SPME in a capillary extends its applications to samples having a high concentration of analytes. This also suggests sampling in a small volume of sample should have more tolerance to the interfering substances that could also be extracted.

Table 3
Effect of organic solvent on SPME recovery

Sample matrix	Recovery (%)
0.01% MeOH in H_2O	82.2
1% MeOH in H_2O	70.0
0.01% MeOH in H_2O, 24% NaCl	100.4
1% MeOH in H_2O, 24% NaCl	97.9

Sample: 3 μl of 10 ppm p-HBA.

A synthetic sample was made which contained 1-naphthol, paeonol and 1-naphthylamine. With 60–70% methanol in water as mobile phase, the three compounds can be separated from each other on a C_{18} column. In the same way as described in Section 3.2, the conditions for static desorption were optimized as follows: mobile phase and desorption solvent, 65% methanol; immersion time, 5 min; flow-rate, 0.8 ml/min; rinsing time, 1 min. Under the optimized conditions for desorption in the SPME–HPLC interface, the synthetic samples injected directly and handled by SPME give the chromatograms shown in Fig. 6. The peaks of the three components obtained in two cases have the same retention time and peak shape.

Recoveries were determined for the synthetic samples in which the concentrations of 1-naphthol, paeonol and 1-naphthylamine were 10 and 100 ppm each and different levels of methanol existed, and the results are listed in Table 4. We can see that no

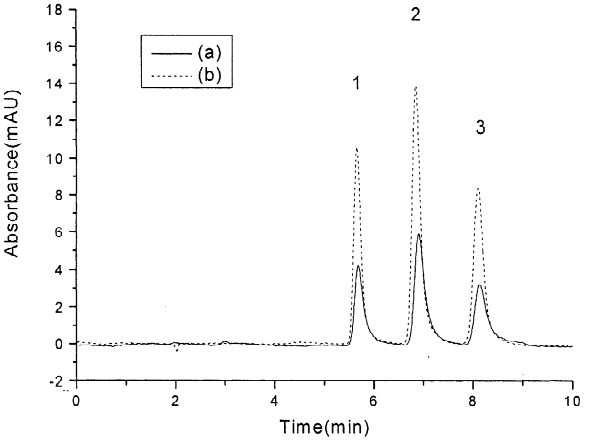

Fig. 6. Chromatograms of synthetic sample containing 1-naphthol, paeonol and 1-naphthylamine obtained (a) by direct injection and (b) after SPME; 1, 1-naphthol; 2, paeonol; 3, 1-naphthylamine. Chromatographic conditions: column, Kromasil C_{18}, 15×0.46 cm; mobile phase, 65% MeOH in water; flow-rate, 0.8 ml/min; detection, UV 280 nm; sample, 10 ppm 1-naphthol, paeonol, 1-naphthylamine each. Desorption conditions: desorbing agent, 65% MeOH in water; immersion time, 5 min; rinsing time, 1 min.

Table 4
Simultaneous SPME of 1-naphthol, paeonol and 1-naphthylamine

Concentration of each analyte (ppm)	10	10	100
Sample matrix	3% MeOH in water	0.3% MeOH in water	3% MeOH in water
Immersion time (min)	10	10	10
Recovery (%)			
1-Naphthol	95.1	97.4	95.7
Paeonol	95.2	96.2	95.3
1-Naphthylamine	98.2	95.3	96.4

Sample volume: 3 μl.

influence on the recoveries of the three components is observed when they coexist. They are almost completely extracted even at 100 ppm concentration.

4. Conclusion

The project is carried out in a SPME–HPLC system. Except for the extraction being completed in a glass capillary, desorption in the SPME–HPLC interface and chromatographic separation remain as usual. Of course, the sampling procedures could also be coupled with GC. The results obtained in this study demonstrate that sampling by SPME in a capillary is feasible. With the fiber coated with porous polymer such as CW–TPR used for SPME–HPLC, the equilibrium of analytes between the aqueous sample and stationary phase (coating) can be described by the Langmuir isotherm. The concentration of analytes in the sample must be low enough for the extraction equilibrium to be located in the linear part of the isotherm. This is necessary to apply SPME to quantification. The total amount of analytes in a small volume of sample is quite low despite their initial high concentration. Upon establishing equilibrium, the stationary phase still remains in the unsaturated state. Thus, the application of SPME can be extended to samples with a high concentration of analytes or a complex matrix. In addition, sampling with the small volume of sample has other advantages:

1. Sampling in capillary reduces the diffusion distance. Without stirring, the equilibrium can be established in 5–10 min.
2. The large phase ratio (coating/sample) favors the complete extraction of the analytes having lower distribution coefficient.
3. The technique is less affected by the experimental conditions and is more reproducible.
4. Only a few microliter of sample is needed for sampling. That is particularly suitable for clinical analysis and therapeutic drug monitoring. Meanwhile, the short diffusion distance in a capillary is favorable to the achievement of equilibrium. This is quite important to the samples with high viscosity such as plasma.
5. The device for SPME is simplified and the consumables are only capillaries.

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