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Monolithic molecular imprinted polymer fiber for recognition and solid phase microextraction of ephedrine and pseudoephedrine in biological samples prior to capillary electrophoresis analysis

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ABSTRACT

A novel capillary electrophoresis (CE) method coupled with monolithic molecular imprinted polymer (MIP) fiber based solid phase microextraction (SPME) was developed for selective and sensitive determination of ephedrine (E) and pseudoephedrine (PE). With *in situ* polymerization in a silica capillary mold and E as template, the MIP fibers could be produced in batch reproducibly and each fiber was available for 50 extraction cycles without significant decrease in extraction ability. Using the MIP fiber under optimized extraction conditions, CE detection limits of E and PE were greatly lowered from 0.20 to 0.00096 μg/mL and 0.12 to 0.0011 μg/mL, respectively. Analysis of urine and serum samples by the MIP-SPME-CE method was also performed, with results indicating that E and PE could be selectively extracted. The recoveries and relative standard deviations (RSDs) for sample analysis were found in the range of 91–104% and 3.8–9.1%, respectively.

1. Introduction

Ephedrine (E) and pseudoepherine (PE) are two alkaloids in clinic for the treatment of asthma and bronchitis [1]. However, ephedrine alkaloids have amphetamine-like properties in high doses and can cause nervousness, tachycar-dias, hypertension, seizures and psychosis [2,3]. On the other hand, because of their stimulating properties to central nervous system [4], these compounds are listed as forbidden substances by the medical commission of the International Olympic Committee. An athlete may be suspected as "positive" if the concentrations of these compounds are too high, e.g., the allowed upper limit of E in the urine of an athlete is 0.01 mg/mL. Furthermore, in the clinic pharmacokinetic studies, the concentrations of E and PE in serum, plasma and salivar are often μg/L level or even lower [5–7]. Therefore, the sensitive monitoring of these compounds in biological samples is of great and continuous interest.

In the past decade, capillary electrophoresis (CE) has been widely adopted for the analysis of ephedrine compounds [8–11], owing to its advantages such as high speed, high separation efficiency and low maintenance cost. However, the application of CE-UV for ephedrine compounds in biological samples is limited by its low detection sensitivity, as their concentrations are generally very low. To address this issue, CE methods coupled with sensitive detection techniques, e.g., laser-induced fluorescence (LIF) [12–16] and MS [17], have been studied for the determination of ephedrine compounds. However, despite their good sensitivity, MS and LIF are still expensive for routine analysis for many laboratories. Also, labeling the analytes by fluorescent reagents is usually essential for LIF detection.

Solid phase microextraction (SPME) is a simple, versatile and cost-effective extraction technique first developed by Pawliszyn's group [18,19]. SPME is based on the partitioning of the analytes between the sample and the stationary extraction phase generally coated on the surface of a fiber. Thus, the coating of the fiber is a key parameter for SPME and the development of fiber coatings receives much attention [20–22]. However, till now only a few types of coating, such as polydimethylsiloxane, divinylbenzene, polyacrylate, Carboxen (CAR; a carbon molecular sieve) and Carbowax (CW; polyethylene glycol), have been commercially available. Furthermore, these commercial coatings are usually used for concentrating analytes without considering the removal of potential interferents from sample matrix, because they only roughly cover the scale of polarity and are non-selective to target compounds.

Incorporation of molecular imprinting polymer (MIP) into SPME can improve selectivity effectively. MIP is a kind of synthesized material in the presence of template compound. After template removal, the left cavity in MIP can rebind the template as well as its structure analogs with good recognition ability and affinity.

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MIPs have been applied as separation materials for LC [23,24], CEC [25,26], solid phase extraction sorbents [27,28], and so on. Combinational application of MIP with SPME has proven to be very promising for sample extraction [29–35], but it has not been adequately studied yet. As regard to ephedrine compounds, reference searching results showed there is only one report on MIP-SPME for the extraction of E and PE [36]. In their work, the fiber coating was prepared by a sol–gel procedure, and the extracted analytes were further concentrated by a field amplified sample injection procedure for sensitive CE analysis.

The goal of this work is to present a novel procedure for the preparation of MIP monolith fibers using E as template for SPME applications prior to CE analysis. A homogenous monomers solution with template was injected into a capillary mold for *in situ* polymerization [31,37,38] under a certain condition to form the fiber. Compared with traditional methods for SPME fiber preparation, this "mold" preparation manner allowed the batch-mode production of MIP fiber, by which the sample handling throughput could be improved by extracting in batch. The lifetime and preparation reproducibility of the MIP fibers and their applicability for SPME purpose, with the template E and its structure analog PE as examples, were tested. Moreover, the applications of the MIP-SPME for concentrating and clean-up of E and PE from complex samples (human urine and serum) were also demonstrated.

2. Experimental

2.1. Chemicals and materials

Methacrylic acid (MAA) and ethylene glycol dimethacrylate (EDMA) are from Sigma–Aldrich (Steinheim, Germany). Ephedrine (E) and pseudoephedrine (PE) as hydrochloride salts are from the National Institute for Control of Pharmaceutical and Biological Product (Chengdu, China). Human urine sample was collected from a healthy volunteer and the serum was obtained from Mingke Biological Product Company (Chengdu, China). All other chemical reagents are of analytical reagent grade and from Kelong Chemical Reagent Factory (Chengdu, China).

The stock solutions of ephedrine and pseudoephedrine at a concentration of 1.0 mg/mL were prepared in methanol and stored at 4 °C. Working solutions were prepared by appropriate dilution of the stock solutions. For MIP preparation, the template compound, ephedrine, was converted from hydrochloride salt to free base by adjust pH to 11. Then ephedrine was extracted with chloroform.

2.2. Equipments

The experiments were performed on a lab-constructed capillary electrophoresis system with a CL 101A high voltage supply and a CL 1020 UV detector from Cailu Scientific Instrument Company (Beijing, China). Fused-silica capillaries of 75 μm i.d. and 530 μm i.d. were obtained from Yongnian Photoconductive Fiber Factory (Hebei, China). The total length of the 75 μm i.d. capillary for separation was 45 cm and the effective length from the inlet to the detection point was 37 cm. New capillary was conditioned sequentially with 1 M HCl, 1 M NaOH and up-water (DDW) for 15 min, respectively. Between runs, the separation capillary was flushed with 1 M NaOH, water and buffer for 1 min, respectively, with the aid of two syringes. The morphology of the ephedrine MIP-fiber was evaluated by using a JSM-5900LV scanning electron microscope (JEOL, Tokyo, Japan).

2.3. Preparation of MIP fiber

Using a silica capillary as mold, the MIP fibers for SPME were prepared by an *in situ* polymerization method according to the previous work [39]. Briefly, the polymerization mixture, consisting of 14.5 mg E template, 28 μL MAA functional monomer, 327 μL EDMA crosslinker, 2.8 mg AIBN initiator and 375 μL porogenic solvent acetonitrile, was thoroughly mixed and degassed by ultrasonication for 10 min to form a homogeneous solution. With the aid of a syringe, the solution was filled into a 30 cm × 530 μm i.d. capillary that was already cleaned and degassed with N_2 stream. The two ends of capillary were sealed with rubbers, and then the capillary was placed in a water bath at 60 °C to react for 24 h. After polymerization, the capillary was cut into pieces with 5 cm for each. Then 1 cm silica wall at one end of the capillary was broken and peeled off mechanically with a blade. Finally, the fibers were immersed in 10% (v/v) acetic acid in methanol to remove the template compound. Due to the limit of our experimental condition, it is at most 7 fibers per batch that can be made.

2.4. Sample preparation

5 mL sample solution, serum or urine, spiked with 0.1 mg/L E and PE standards, was mixed with 7 mL of ethanol, meanwhile 0.25 mL 1 M NaOH was added to adjust the pH to 11. The solutions were sufficiently mixed and then centrifuged for 10 min at 2500 rpm to remove the precipitated proteins. The upper aqueous layer was filtered with 0.45 μm nylon membrane and then dried with mild nitrogen stream for about 1 h. The residues were dissolved in 5 mL toluene for subsequent extraction.

2.5. MIP-SPME procedure

A vial (10 mL capacity, easily obtained in any hospital) sealed with a silicone-rubber septum cap and contained a Teflon stirring bar was used for the extraction. The standard was added in the vial, then NaCl and $NH_3{\cdot}H_2O$ were added to adjust the pH to 11 and then dried with mild nitrogen stream. The residues were dissolved in 5 mL toluene for subsequent extraction. The fiber is flexible which can easily drill through and immobilise at the middle of the silicone-rubber septum cap of the vial. SPME was accomplished by direct immersing a cut portion of the MIP fiber (1 cm) in the standard or samples prepared above for 60 min under a magnetic stirrer operated at 300 rpm. After extraction, the fibers were immersed in toluene for 1 min under stirring in order to remove nonspecific interactions. The fiber was then air-dried (10 min) and put into a 1.5 mL centrifugal tube with 200 μL of 20% (v/v) acetic acid in methanol. The cut portion of the fiber was immersed in the desorption solution for 15 min with ultrasonic treatment. Finally, the desorption solution was dried with N_2 and the extracted compounds were re-dissolved in 5 μL double distilled water for CE analysis. Between two extractions, the fiber was soaked in 20% (v/v) acetic acid (60 min) in methanol and toluene (15 min) for reconditioning.

2.6. CE conditions

All the separations were performed with 25 mM borate buffer (pH 9.2) using a separation voltage of 12.5 kV. The detection wavelength was set at 214 nm, and the sample/standard solutions were injected 10 s by lifting the inlet end of the capillary for 14 cm. Under these conditions, E and PE could be well separated and detected within 4 min.

3. Results and discussion

3.1. Preparation and characterization of MIP fiber

The preparation procedure of the MIP fiber is presented in Fig. 1. Into the capillary mold, a homogenous solution of the monomers with template compound was filled. After the polymerization was

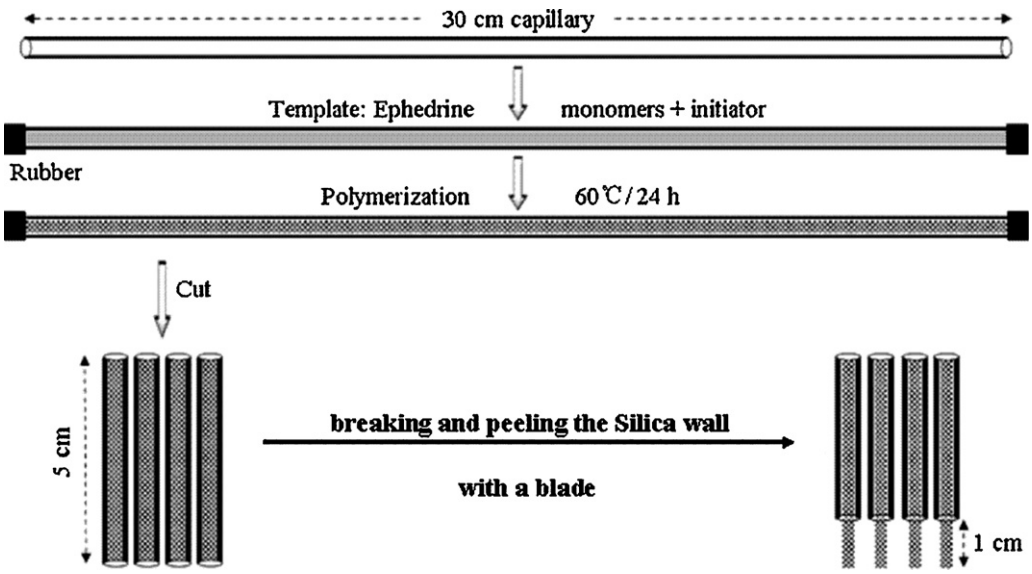

Fig. 1. Schematic illustration of MIP preparation procedure.

completed, the capillary was cut into pieces and the silica wall at the end of each piece was mechanically broken and peeled off from the fiber. The prepared fiber showed good stability and flexibility, even after leaving in the air for two months. This is very important in the view of long-term storage. Removal of silica wall using HF acid, an efficient silica etchant, was also performed. However, HF was eventually excluded for application as special cautions must be taken due to its extreme corrosive nature. In addition, compared with the fiber obtained by the current method, the fiber prepared by HF etching (6 M for 12 h) showed less stability and flexibility, probably HF treatment aged the fiber to some extent.

Fig. 2a shows a photograph of the MIP-fiber prepared. The morphological structure of the MIP fiber was investigated with scanning electron microscopy (SEM) under magnifications of 150 (Fig. 2b) and 15,000 (Fig. 2c). The images show obviously that the formed MIP material is homogeneous and dense. The 15,000 magnification also indicates that the MIP fiber possesses a porous structure, through which the analytes can reach the inner part of the fiber. Thus, the recognition sites on both the surface and inner part of the fiber can be used to affinity separate the analytes, providing high extraction capability and capacity.

A series of ephedrine and pseudoephedrine mixed standard solutions of 0.002–2.0 μg/mL were used to investigate the extraction capacity of the MIP-SPME monolithic prepared. The result shows that the fiber could selectively extract ephedrine and pseudoephedrine. When the concentration arrived at 1.0 μg/mL, the extraction saturation approached and the extraction capacities of ephedrine and pseudoephedrine were about 0.6 and 0.3 μg, respectively.

3.2. Preparation reproducibility and reusability of the MIP fiber

The most important advantage of the current method superior to conventional SPME fiber preparations is that the fibers can be produced in batch reproducibly. A low fiber-to-fiber RSD of extraction efficiency (2.0% for 0.5 μg/mL E) was obtained by 5 fibers prepared in one batch. Batch-to-batch reproducibility was investigated by the fibers prepared in three different batches, of which the RSD of extraction efficiency was determined to be 7.0% for the 0.5 μg/mL E, further implying that the MIP fiber can be produced repeatedly. By this way, a large amount of fibers can be prepared for application, making sample extraction in batch-mode possible. On the other hand, when cross-contamination between different samples needs to be considered, the fibers are even disposable after each extraction owing to its low cost and ease of preparation.

Another important advantage of the current method is that the fiber can be used for many times without loss in their performance.

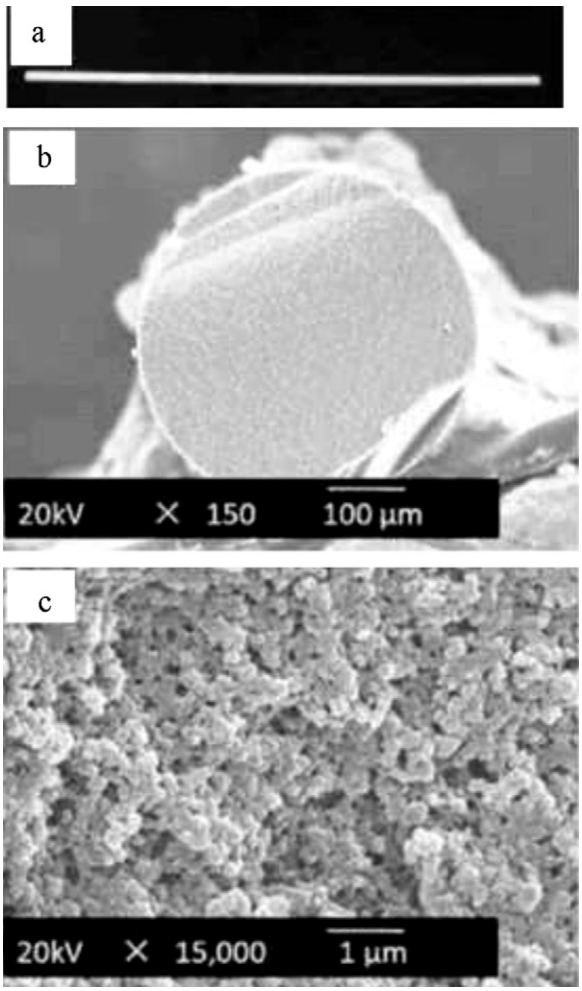

Fig. 2. Photograph (a) and SEM images with 150 (b) and 15,000 (c) magnifications of the MIP fiber.

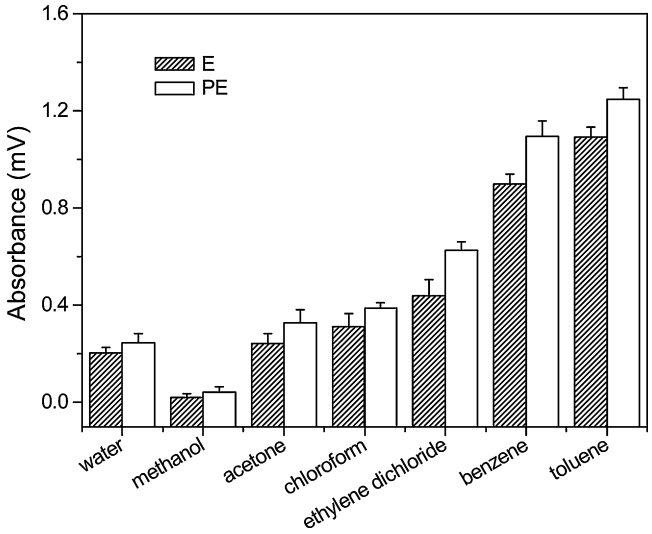

Fig. 3. Effect of extraction solvent on MIP-SPME efficiency of 0.5 μg/mL E and PE. Extraction time: 60 min; desorption time: 15 min, desorption solvent: 20% acetic acid in methanol. CE conditions see Section 2 (the error bars stand for SD for three measurements).

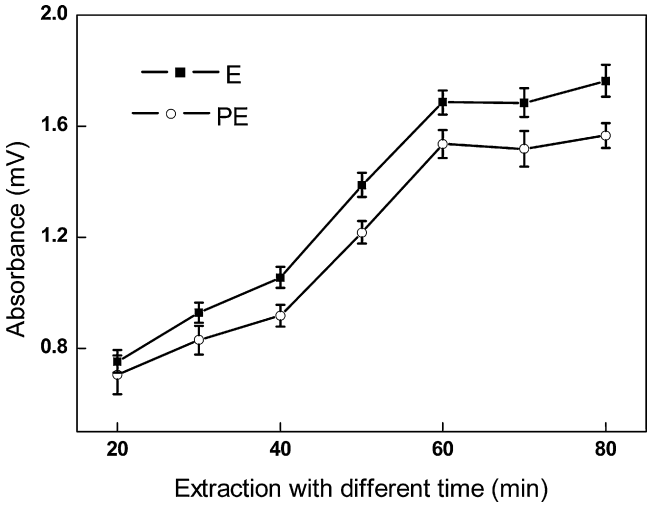

Fig. 4. Dependence of the analytes' signals on extraction time. Concentrations of E and PE: 0.5 μg/mL; extraction solvent: toluene; desorption: 15 min with 20% acetic acid in methanol. CE conditions see Section 2 (the error bars stand for SD for three measurements).

The reusability was investigated as follow, each fiber was labeled by number after preparation and the number was recorded after each extraction. When the extraction efficiency was changed obviously, the times of the same number occurred in the recording at least is 50.

3.3. Optimization of MIP extraction conditions

Because the cross-reactivity, MIP materials are also applicable to recognize the compounds with good structure similarity to the template. In the work herein, the prepared MIP fiber was applied to extract the template E and its structure analog PE and the parameters affecting the extraction efficiency were optimized for CE analysis. The MIP fiber should also be applicable for other E analogs, however, only PE was tested as an example, for no standards available.

The affinity of analytes to the MIP fiber can change much in different media. In order to achieve the best adsorption of analytes onto the MIP, several solvents within a wide range of polarity, including water, methanol, acetone, chloroform, ethylene dichloride, benzene and toluene, were tested as extraction medium. Fig. 3 shows a trend that the extraction efficiency increases with the decrease of solvent polarity. In this work, the MIP fiber was prepared mainly based on the hydrogen bonding of E to MAA. The low extraction efficiency in high polar solvents can be attributed to their strong disturbance to the formation of this hydrogen bond.

Using toluene, which has the lowest polarity among the tested solvents and provided the best extraction efficiency, the dependence of analytes adsorption on extraction time was investigated in the range of 20–80 min with 0.5 μg/mL E and PE mixtures (Fig. 4). It is known that SPME is based on the partition of analytes between extraction fiber and sample solution. The results showed that the extraction efficiency increased rapidly with the increase of the extraction time within 60 min, after which the partition reached equilibrium and the extraction efficiency became almost independent upon the extraction time. Desorption of the analytes elution desorption time was also tested in the range of 5–30 min. The results in Fig. 5 showed that desorption process was much more rapid than adsorption to reach equilibrium. The desorption efficiency could reach the maximum in 15 min. For wash step, no significant change in the extraction efficiency was observed from 1 min to 15 min. So 1 min was chosen in the wash step.

A "poor" solvent for extraction can be a good eluant for desorbing the analytes from the MIP fiber [33]. Thus, several polar solvents were used for desorption (Fig. 6). When a single solvent was used, methanol showed the best desorption yield; but the amount of desorbed analytes was low, suggesting that complete desorption was not achieved. The residual analytes in the MIP fiber after desorption would not only lower the sensitivity in following CE analysis, but also lead to serious a negative effect to the precision and extraction efficiency of subsequent extractions. Ephedrine derivatives are weak basic compounds. At a lower pH, the acid–base equilibrium of the analytes and the hydrogen bonding of E to MAA will be broken. Therefore, adding a certain amount of acetic acid is help for enhancement of the desorption yield. A solution of 20% acetic acid in methanol (V/V) showed the best elution, and the desorption yield was improved almost 2 times compared with pure methanol.

The effect of salty was tested by adding different amount of NaCl into E and PE mixture solutions, but no significant change in the

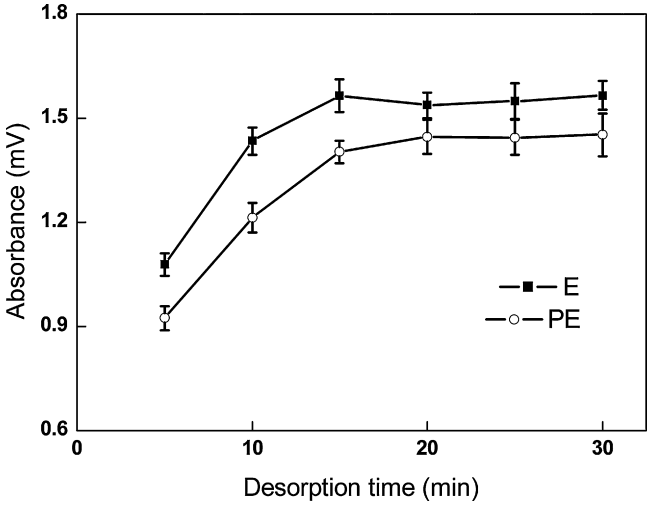

Fig. 5. Dependence of the analytes' signals on desorption time. Concentrations of E and PE: 0.5 μg/mL; extraction: 60 min in toluene; desorption solvent: 20% acetic acid in methanol. CE conditions see Section 2 (the error bars stand for SD for three measurements).

Table 1
Analytical figures of merit obtained by the proposed CE-MIP-SPME.

Compound	Calibration curve[a]	Error (slope)	Error (intercept)	Concentration range (μg/mL)	Correlation coefficient	LOD (μg/mL)	
						After MIP-SPME	Before MIP-SPME
E	$Y = 3.94X + 0.00243$	0.093	0.021	0.005–0.5	0.9986	0.00096	0.20
PE	$Y = 3.47X - 0.00111$	0.083	0.019	0.005–0.5	0.9982	0.0011	0.12

[a] Y and X represent peak height (mV) and analyte concentration (μg/mL), respectively.

Table 2
Relative recoveries of E and PE spiked urine and serum samples ($n = 5$).

Compound	Urine						Serum					
	0.01 μg/mL		0.1 μg/mL		0.4 μg/mL		0.01 μg/mL		0.1 μg/mL		0.4 μg/mL	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
E	95.3	8.3	98.7	7.5	97.9	6.8	94.6	5.3	93.8	3.8	96.8	4.5
PE	91.2	9.1	90.7	8.5	92.4	8.2	101.4	7.0	103.6	6.4	99.7	7.2

extraction efficiency was observed in the range of 0–150 mM NaCl, because the extraction was performed in organic solvent, toluene. The negligible effect of salt on extraction makes the MIP fiber applicable for the affinity separation of target analytes from biological samples, in which salt concentration generally falls in the tested range.

3.4. Analytical performance of MIP-SPME coupled CE

A series of standard mixtures of E and PE at different concentrations were extracted using the MIP fiber under optimized conditions and then subjected to CE analysis. The good linear relationship between peak heights and concentrations (Table 1) in a wide range (0.005–0.5 μg/mL) proved that the established MIP-SPE-CE method is applicable for the quantification of these analytes. The limits of detection (LODs) for E and PE before and after SPME based on signal-to-noise ratio of 3 were calculated and also given in Table 1. The precision of the method was monitored with 0.1 μg/mL E and PE standard solution, and the RSDs for E and PE are 3.2% and 5.4%. The sensitivities of E and PE were improved 200 and 110 times, respectively, by the extraction procedure. Without an expensive instrument or labeling of the compounds, the LODs for E and PE obtained by the MIP-SPME-CE method are comparable with (even higher than) those obtained by CE-LIF [12–16] and CE-MS [17]. Also the sensitivities of E and PE in this work are also higher than those of previously reported CE method coupled with head-space MIP-SPME [34], in which field-amplified sample

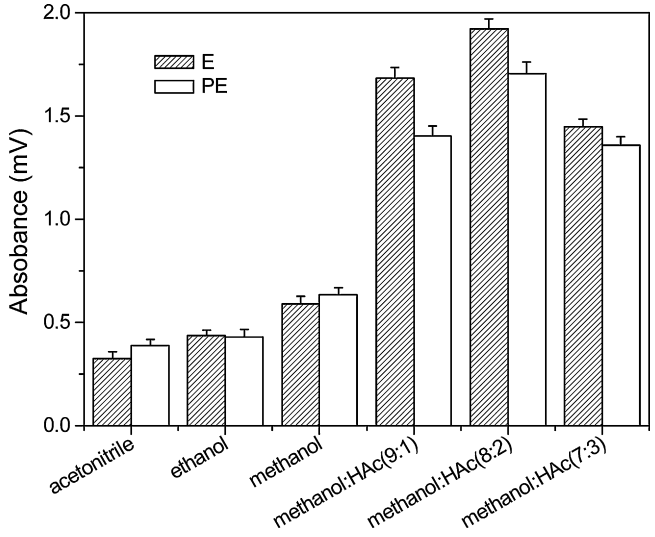

Fig. 6. Desorption efficiency of E and PE in different solvents. Concentrations of E and PE for MIP-SPME: 0.5 μg/mL; extraction: 60 min in toluene; desorption time: 15 min. CE conditions see Section 2 (the error bars stand for SD for three measurements).

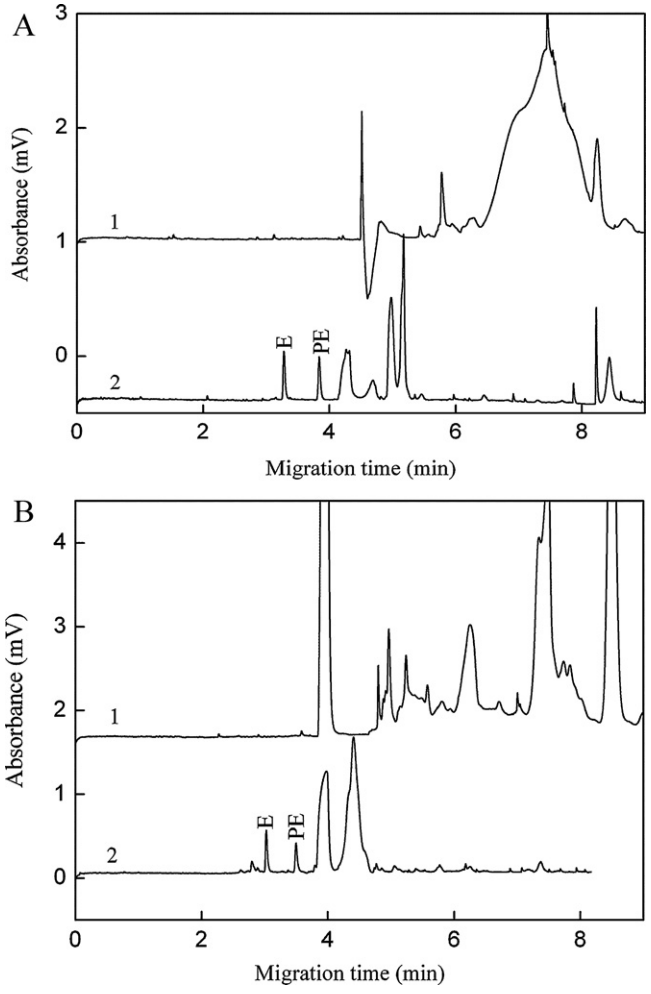

Fig. 7. Electropherograms of serum (A) and urine (B) samples before (line 1) and after (line 2) MIP-SPME. Spiked concentrations of E and PE: 0.1 μg/mL. Extraction: 60 min in toluene; desorption: 15 min using 20% acetic acid in methanol. CE conditions see Section 2.

injection was applied for further concentrating the extracted analytes.

3.5. Analysis of serum and urine samples by MIP-SPME-CE

To demonstrate the applicability of the MIP fiber based SPME for real samples, it was used to extract E and PE spiked in two complex samples, human urine and serum. After simple sample pretreatment as described in Section 2, the resultant solutions were extracted for CE analysis. The electropherograms of the serum and urine samples before (line 1) and after MIP-SPME extraction (line 2) are shown in Fig. 7. It can be observed that the analytes spiked in the samples at 0.1 μg/mL are not detectable and complex peak profiles for the samples were obtained by direct injection. In contrast, after the samples were subjected to the MIP-SPME procedure, the sensitivities for E and PE were greatly enhanced and most co-existing components in the sample matrix were cleared away owing to the good selectivity of the MIP fiber. The accuracy of the MIP-SPME-CE method was evaluated by recovery test. The relative recoveries and corresponding RSDs ($n = 5$) for serum and urine samples (spiked levels of analytes are 0.01 μg/mL, 0.1 μg/mL and 0.4 μg/mL, respectively) were in the range of 91–104% and 3.8–9.1% (Table 2), respectively. The absolute recoveries and corresponding RSDs ($n = 5$) were also calculated and were in the range of 11.3–20.7% and 7.5–8.8%.

4. Conclusions

With silica capillaries as mold, monolith MIP fibers of ephedrine for SPME purpose were prepared by *in situ* polymerization. The MIP fiber based SPME was successfully coupled to CE for the extraction and sensitive determination of ephedrine and its structure analog, pseudoephedrine. The results indicated that the MIP fibers can be prepared in batch reproducibly. Thus, a large number of fibers can be produced rapidly and conveniently without using hazardous materials (e.g. HF). Using the prepared fibers, the samples can be pretreated in batch mode, by which the handling throughput of samples can be improved. In addition, with the advantages of low cost and easy preparation, the fibers can also be used for disposable purpose in order to avoid the cross-contamination of different complex samples. The preliminary applications of this method for urine and serum demonstrated that the fibers can extract and clean-up ephedrine and pseudoephedrine from complex sample matrix with good recoveries and reproducibility.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2011.11.016.

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