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Poly(methacrylic acid-ethylene glycol dimethacrylate) monolith in-tube solid phase microextraction coupled to high performance liquid chromatography and analysis of amphetamines in urine samples

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Abstract

In-tube solid-phase microextraction (SPME) based on a poly(methacrylic acid-ethylene glycol dimethacrylate) monolithic capillary column was investigated for the extraction of amphetamine, methamphetamine and their methylenedioxy derivatives. The monolithic capillary column showed high extraction efficiency towards target analytes, which could be attributed to its larger loading amount of extraction phase than conventional open-tubular extraction capillaries and the convective mass transfer procedure provided by its monolithic structure. The extraction mechanism was studied, and the results indicated that the extraction process of the target analytes was involved with hydrophobic interaction and ion-exchange interaction. The polymer monolith in-tube SPME-HPLC system with UV detection was successfully applied to the determination of amphetamine, methamphetamine and their methylenedioxy derivatives in urine samples, yielding the detection limits of 1.4–4.0 ng/mL. Excellent method reproducibility (RSD < 2.9%) was found over a linear range of 0.05–5 μg/mL, and the time for the whole analysis was only ∼25 min. The monolithic capillary column was reusable in coping with the complicated urine samples.

Keywords: Poly(methacrylic acid-ethylene glycol dimethacrylate); Monolithic capillary; In-tube SPME; Liquid chromatography; Amphetamine

1. Introduction

Amphetamine, methamphetamine and their methylenedioxy derivatives are among the list of abusing drugs and popular in many regions these years. The increasing popularity of amphetamines abuse arises a series of social problems and imperils the public security seriously. Therefore, many research works involving GC and LC procedures have been concentrated on their determination [1]. In analyzing these drugs, urine sample has always been involved since it can reflect the consumption or exposure during the preceding 1–4 days [2] and a suitable sample pretreatment step is usually inevitable. Generally, liquid–liquid extraction (LLE) and solid phase extraction (SPE) are applied for preconcentration of the analytes and get rid of the sample matrix [1,3–5]. However, most of these pretreatment methods involving multi-steps are time-consuming and may lead to analytes losing. Therefore, the development of the pretreatment method that holds advantages such as convenient manipulation, easy automation, high sensitivity and specificity towards amphetamines in biological samples is required.

In-tube solid phase microextraction (in-tube SPME) coupled to HPLC is the on-line mode of SPME coupling to liquid chromatography, which was put forward by Eisert and Pawliszyn in 1997 [6] and received wide acceptance since then [7]. Since it requires small volume of the samples and the whole manipulation can be easily automated, in-tube SPME-HPLC is especially suitable for biological sample analysis [8–10], and has also been used for amphetamine analysis in urine and hair samples [11,12].

Since the volume of extraction sorbent in in-tube SPME is generally small, developing sorbent with high extraction efficiency is always an attractive task and therefore, the

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"packed" format of extraction capillaries more than the inner wall coated open-tubular ones are brought forward, including molecularly imprinted polymer (MIP) particles [13] or alkyl-diol-silica (restricted access material, RAM) [14] packed PEEK tubes, Zylon fiber-in-tube capillaries [15,16] and silica monolithic capillaries [17]. However, only MIP, RAM and the Zylon fibers are employed in analysis of biological samples. Thus, further developing the extraction capillaries with both biocompatibility and specificity towards a certain kind of analytes will be useful.

The interest in synthesis and application of the organic polymer monolithic materials to chromatography and related technologies has increased in recent years [18–22]. The polymer monolithic material can be easily in situ synthesized and is able to provide tunable monolithic structures and tailored functional groups for specific purposes. Many of these materials are also able to provide biocompatibility and pH stability, which enables them to deal with the biological samples and be used even at extreme pH values [23]. Moreover, the monolithic porous structure offers convective mass transfer procedure [24], which is preferable in extraction process. In respect of these attractive merits of polymer monolithic materials, we recently introduced a poly(methacrylic acid-ethylene glycol dimethacrylate) (MAA-EGDMA) monolithic capillary column into in-tube SPME-HPLC system for extraction of basic analytes from serum and urine samples [25,26]. High extraction efficiency was achieved and the column was proved to be robust in biological sample analyses.

In this study, in-tube SPME-HPLC system based on the poly(acrylic acid-ethylene glycol dimethacrylate) monolithic capillary column was investigated for the extraction of amphetamine, methamphetamine and their methylenedioxy derivatives, 3,4-methylenedioxyamphetamine and 3,4-methylenedioxymethamphetamine, from urine samples. An investigation of the extraction mechanism was also involved in this paper, which indicated that the hydrophobic and ion-exchange interactions are dominant in the extraction process. Finally, urine samples from amphetamines abusers were also analyzed under the optimized conditions.

2. Experimental

2.1. Chemicals and materials

Ethylene glycol dimethacrylate (EGDMA) was purchased form Acros (Sweden). Methacrylic acid (MAA), 2,2′-azobis(2-methylpropionitrile) (AIBN), dodecanol and toluene were obtained from Shanghai Chemical Co. Ltd. (Shanghai, China) and were of analytical reagent grade. The poly(MAA-EGDMA) monolithic column was synthesized by a polymerization method described previously [25]. Double distilled water was used for all experiments.

Amphetamine (PA), methamphetamine (MPA), 3,4-methylenedioxyamphetamine (MDA) and 3,4-methylenedioxymethamphetamine (MDMA) were obtained from China National Ministry of Public Security (Beijing, China). Their molecular structures are shown in Fig. 1. A stock standard solution of 1 mg/mL for each analyte was prepared in methanol. The composite standard containing 50 μg/mL of each analyte was prepared by diluting the stock solution with double distilled water.

2.2. Instrument and analytical conditions

The in-tube SPME-HPLC system consisted of the pre-extraction segment, which included a Shimadzu LC-4A six-port valve (valve 1), a Jasco PU-1580 pump (pump A) (Tokyo, Japan) and a PEEK tube (0.03 in. i.d., 0.7 mL total volume), and the analytical segment, which included a Jasco PU-1580 pump (pump B) (Tokyo, Japan), Rheodyne 7725i six-port valve (valve 2) with a 20 μL loop (Cotati, CA, US) and a Unimicro UV-detector (Unimicro Technologies, CA, USA). The extraction manipulation has been detailed in our previous work [25]. The extraction flow rate was set to 0.04 mL/min. The desorption of the analytes was carried out by directing the mobile phase to flow through the capillary at 0.02 mL/min for 5 min.

The analytical column was 250 mm × 4.6 mm, i.d. packed with Kromasil ODS (5 μm), which was purchased from Eka Chemicals (Bohus, Sweden). The optimized mobile phase consisted of 12.5% acetonitrile and 87.5% buffer solution (v/v) that containing 0.02 mol/L Na_2HPO_4 and 0.02 mol/L methanesulfonic acid, with pH adjusted to 2.9. The flow rate was 1.0 mL/mim and the detection was performed at 210 nm with the UV detector for the four analytes.

2.3. Sample preparation

Urine samples were collected from drug-free, healthy volunteers. Any precipitated material was removed by centrifuging the sample at 5000 rpm for 10 min. The supernatant of urine was directly spiked with four amphetamines and then

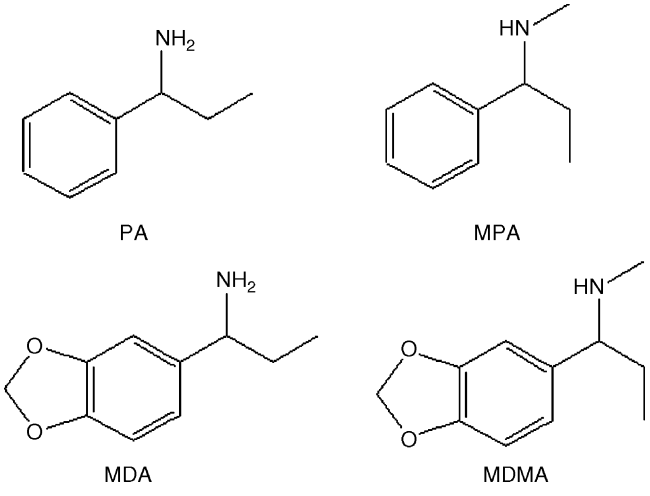

Fig. 1. Structures of amphetamines studied.

diluted with equal volume of 10 mmol/L phosphate buffer solution to adjust the pH to 5. The obtained samples at the concentration range of 50–5000 ng/mL were used directly for analysis. The urine samples from suspected addicts, donated by Wuhan Public Security Bureau (Wuhan, China), were prepared in the same way without spiking.

3. Results and discussion

3.1. Desorption of the analytes from poly(MAA-EGDMA) monolithic capillary

In manipulating the in-tube SPME-HPLC system, the desorption of the analytes can be achieved by simply directing the mobile phase to flow through the capillary with once valve switch. The introduction of the additional desorption solvent is unnecessary. In our experiment, the optimized mobile phase performed well in desorption of PA, MPA, MDA and MDMA from the monolithic column. This could be confirmed by the blank analysis performed after extraction without finding carryover. Besides, the addition of the ion-pair reagent methanesulfonic acid to the mobile phase did not show any negative influence on the extraction and desorption.

3.2. Optimization of the in-tube SPME conditions

When applying in-tube SPME with poly(MAA-EGDMA) monolithic capillary column to determination of amphetamines, great improvement in sensitivity was achieved in comparison to that of the direct injection, as can be seen from Fig. 2. In order to further access the extraction ability of poly(MAA-EGDMA) monolithic capillary column towards amphetamines and also achieve the best extraction efficiency, several parameters, including extraction time profile, pH of the sample matrix and the concentration of inorganic salt, were optimized.

The extraction time profiles of the poly(MAA-EGDMA) monolithic capillary column for extraction of PA, MPA, MDA and MDMA were monitored by increasing the extracting time at constant extraction flow rate of 0.04 mL/min in extracting 1 μg/mL of standard sample solution. As shown in Fig. 3, the amount of the amphetamines extracted, presented as the peak area, increased rapidly with the increasing of the extraction time from 0 to 16 min. The sharp slopes of the profiles indicated that the monolithic column showed remarkable extraction capacity towards these analytes. Thus, the extraction time can be chosen according to the sensitivity required and the time acceptable for a whole analysis. Generally, further prolonging the extraction time was not desirable for routine analysis and an extraction time of 10 min was selected for subsequent analyses with satisfactory sensitivity achieved.

As to SPME, the pH of the samples relates closely to the interactions between analytes and the extraction phase. The

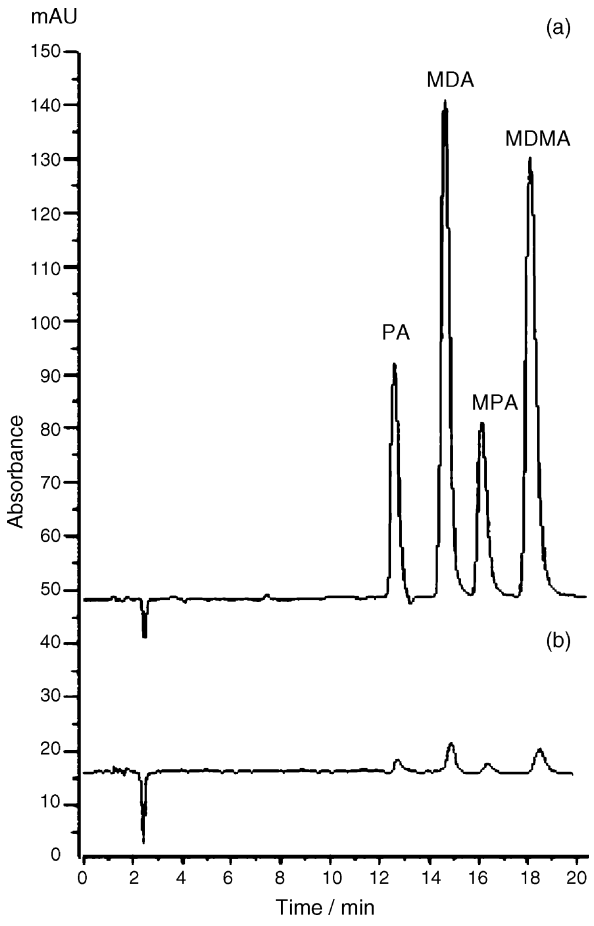

Fig. 2. HPLC chromatograms of PA, MPA, MDA, and MDMA by (a) in-tube SPME-HPLC with the monolithic column and (b) direct injection of the standard sample. Amphetamines were spiked at 1 μg/mL. The volume for direct injection was 20 μL. In-tube SPME conditions: the flow rate was 0.04 mL/min. Extraction time was 10 min. HPLC conditions outlined in Section 2.

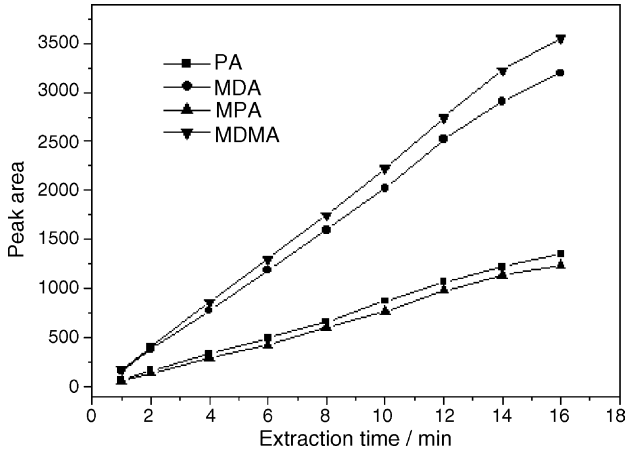

Fig. 3. In-tube SPME-HPLC extraction time profile of PA, MPA, MDA and MDMA. Sample solution consisted of four amphetamines spiked at 1 μg/mL. Extraction flow rate was 0.04 mL/min. HPLC conditions outlined in Section 2.

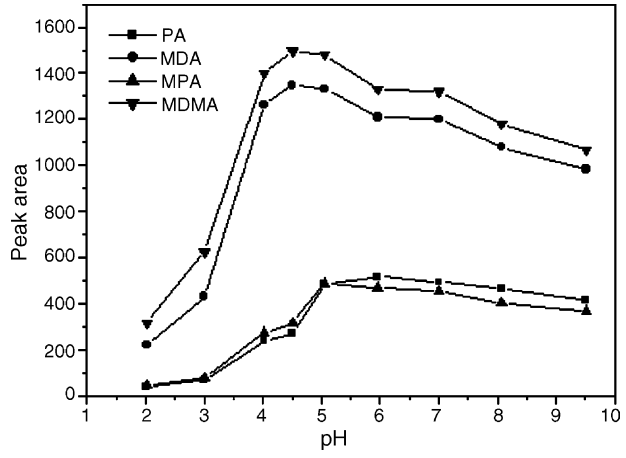

Fig. 4. Optimization of pH of the sample matrix. Four amphetamines were spiked in 0.01 mol/L phosphate buffer solution at different pH at 1 μg/mL. Extraction flow rate was 0.04 mL/min. Extraction time was 6 min. HPLC conditions outlined in Section 2.

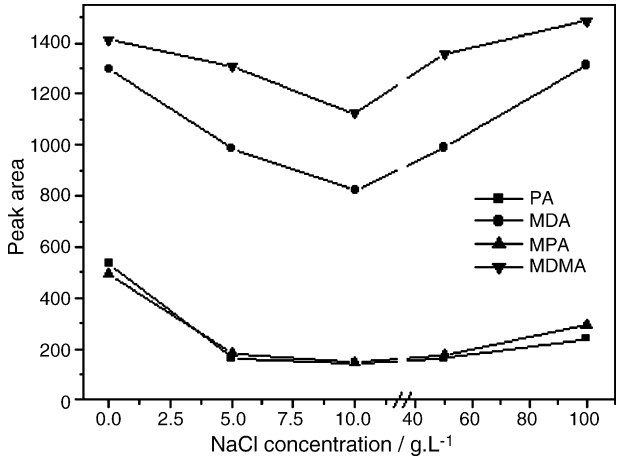

Fig. 5. Effect of the NaCl added to the sample matrix on the extraction. Amphetamines were spiked at 1 μg/mL. In tube SPME conditions: the flow rate was 0.04 mL/min. Extraction time was 6 min. HPLC conditions outlined in Section 2.

pH optimization results for extraction of amphetamines by poly(MAA-EGDMA) monolithic column are found to be interesting. As can be seen from Fig. 4, the extraction efficiency is highest at pH around 5 and decreases at pH below or higher than 5. This triangle-like trend indicates that the ion-exchange interaction is involved in the extraction process [27]. Considering the acid–base equilibrium of the analytes and the poly(MAA-EGDMA) column, the amphetamines are likely to exist in positively charged forms at pH below 5 because their p*K*a values are in the range of 9.6–10.4 [28]; while for poly(MAA-EGDMA), the amount of the ionized carboxylic groups decreases with the decreasing of the matrix pH, resulting in the weakening of ion-exchange interaction between the polymer and the amphetamines and thus poor extraction performance. For pH higher than 5, the carboxyl groups are ionized efficiently while the amphetamines tend to be their neutral forms with the increasing of the pH, also resulting in the decrease of the ion-exchange interaction. However, the hydrophobic interaction between the amphetamines and the polymer main chains is intensified with the increasing of the pH, which compensates for the reduction of the ion-exchange interaction between the polymer and the analytes, leading to only slight decrease of the extraction efficiency. As a result, the highest extraction efficiency was achieved at pH 5, where the ion-exchange interaction and hydrophobic interaction both contributed to the extraction.

Generally, the addition of inorganic salt to aqueous samples increases the extraction efficiency for neutral organic molecules, especially for those polar ones [29]. In our experiment, NaCl was added to the sample solution in the range of 0–100 g/L. The relationship between the extraction efficiency and the salt concentration is displayed in Fig. 5 with the "V"-like curves obtained. The decrease trend of the curves can be attributed to the existence of the ion-exchange interaction, which is sensitive to the inorganic salt concentration. In respect of the extraction efficiency increasing with the increasing of the NaCl concentration, the salting-out effect is thought to be responsible for, which is also commonly found in the extraction process involving hydrophobic interaction. This phenomenon further confirmed the existence of the mix-mode mechanism for the monolithic column.

3.3. Extraction mechanism for SPME with poly(MAA-EGDMA) monolithic column

In the above discussion, the mixed-mode interactions were thought to be involved in the extraction with poly(MAA-EGDMA) monolithic capillary and therefore, a consideration of the adsorption controlled extraction process was generated and further validating experiment was carried out.

The extraction efficiency for PA and MDA obtained by extracting a sample containing only PA or MDA was compared to that achieved by extracting a mixture sample containing all the four amphetamines by constructing the calibration curves, respectively. As a result, the slopes of the calibration curves of the latter at high sample concentrations were smaller than those of the former. Therefore, the competing effect was confirmed when mixture samples were used. However, at lower concentration ranges, the phenomenon was not found and the calibration curves for extraction of sole or mixture samples showed almost the same slopes. This is in accordance with the extraction behavior of the sorbent based on adsorption mechanism: at low sample concentration, the amount of the active adsorption sites of the sorbent is able to satisfy the adequate retention of all the analytes; while at high concentration, the amount of the analyte molecules is larger than that of the available active sites and the competition between the different analytes occurs [30,31]. Therefore, when applying such kind of monolithic column to perform extraction of the

Table 1
log *P* and p*K*a values of the basic analytes

Compound	log *P*	*pK*a
Amphetamine	1.76	9.9
Methamphetamine	2.07	9.87
3,4-Methylenedioxyamphetamine	1.64	9.67
3,4-Methylenedioxymethamphetamine	2.12	10.38
Caffeine	−0.07	10.4
Theophylline	−0.02	8.8
Theobromine	−0.78	9.9
Ketamine	3.12	7.8
Nicotine	1.17	7.9
Chloramphenicol	1.14	11.03

The log *P* (octanol/water partition coefficient) and p*K*a values were obtained from web site: http://chemfinder.cambridgesoft.com and web databases from Syracuse Research Corporation.

mixture samples, the linear range of the sample concentration that the quantification can be taken efficiently should be considered carefully.

In order to further investigate the interactions dominating the extraction process, the extraction behavior of several other basic analytes was also taken into account. The analytes spiking at 1 μg/mL individually were extracted under the same conditions with the same column, and the adsorption constants calculated thereby were taken for comparison. The analytes investigated and their molecular parameters are listed in Table 1.

Generally, when adsorption of the analyte happens in the surface of the extraction sorbent, the complex of the analyte A and the active site S_{ac} can be expressed as [31]

$$A + S_{ac} \rightarrow A_{ad}$$

where A_{ad} is the adsorbed analyte A on the active site in the sorbent. Defining the adsorption constant of analyte A as K_A, we obtain the following equation

$$C_{pA} = C_{pmax}\frac{K_A C_{sA}}{1 + K_A C_{sA}} \quad (1)$$

where C_{pA} is the concentration of analyte A in the sorbent (polymer monolithic column), C_{pmax} is the maximum concentration of active sites on the sorbent, and C_{sA} is the analyte concentration in the sample, and a rearrangement of Eq. (1) results in

$$C_{sA} = \frac{C_{pA}}{K_A(C_{pmax} - C_{pA})} \quad (2)$$

According to the mass balance equation,

$$C^0_{sA} V_s = C_{sA} V_s + C_{pA} V_p, \quad (3)$$

where C^0_{sA} is the initial concentration of analyte A in the sample solution, V_s and V_p are the volumes of the sample solution and the polymer sorbent, respectively. Combining Eqs. (2) and (3), we can obtain the following equation as

$$n_A = C_{pA} V_p = \frac{K_A V_p V_s C^0_{sA}(C_{pmax} - C_{pA})}{V_s + [K_A V_p (C_{pmax} - C_{pA})]} \quad (4)$$

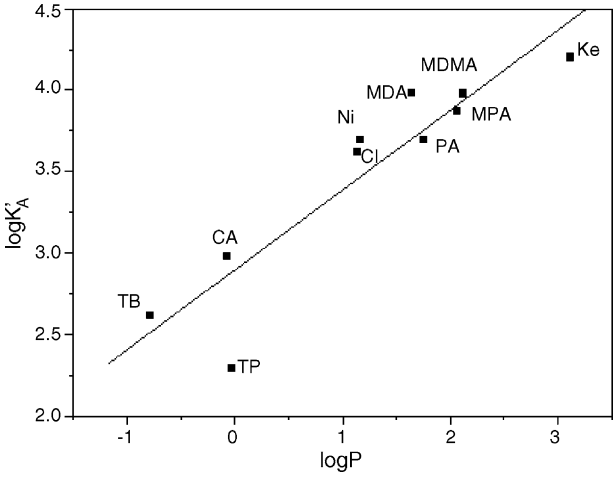

Fig. 6. $\log K'_A \sim \log P$ relationship. The sample solution for extraction contained only one analyte spiked at 1 μg/mL. The extraction flow rate was 0.04 mL/min. Analysis conditions for TB, TP, CA and Ke were detailed in refs. [25,26]. HPLC conditions for nicotine: mobile phase consisted of 20% methanol and 80% 0.025 mol/L NaAc buffer solution (pH 5.5) in volume ratio. The flow rate for chromatographic separation was 1.0 mL/min; UV detection was performed at 260 nm. For chloramphenicol, the mobile phase consisted of 55% methanol and 45% 0.025 mol/L NaAc buffer solution (pH 4.5) in volume ratio. The flow rate for chromatographic separation was 1.0 mL/min; the detection wavelength was 278 nm. HPLC conditions for amphetamines outlined in Section 2. TP, theophylline; TB, theobromine; CA, caffeine; Ke, ketamine; Cl, chloramphenicol; Ni, nicotine.

where n_A is the amount of analyte A extracted. When the sample concentration is low enough, the Eq. (4) can be simplified by assuming $C_{pmax} \gg C_{pA}$ and K_A can be expressed as

$$K_A = \frac{n_A V_s}{C_{pmax} V_p (C^0_{sA} V_s - n_A)} \quad (5)$$

Generally, C_{pmax} is hard to access, while n_A and V_p are measurable and V_s and C^0_{sA} are known. Therefore, we can define the revised adsorption constant K'_A, representing $K_A C_{pmax}$, to compare the different retention behavior of the various analytes on the monolithic column under the same extraction conditions. After calculation, we plotted $\log K'_A$ as the function of the octanol/water partition coefficient, $\log P$ (see Fig. 6). After linear fitting the plots, we can figure out that almost all the plots locate around the line, indicating that the hydrophobic interaction do work during the extraction process. And the deviation of the plots from the line also indicated the existence of other interactions. For example, the extraction efficiency for the three xanthines (theophylline, theobromine and caffeine) were obviously smaller than that of other investigated analytes, which could be attributed to their small hydrophobicity represented by the negative $\log P$ values. And for theophylline, which possesses similar $\log P$ value to that of caffeine but shows the lowest adsorption constant of the three, its low extraction efficiency should be attributed to its weak basic character represented by the

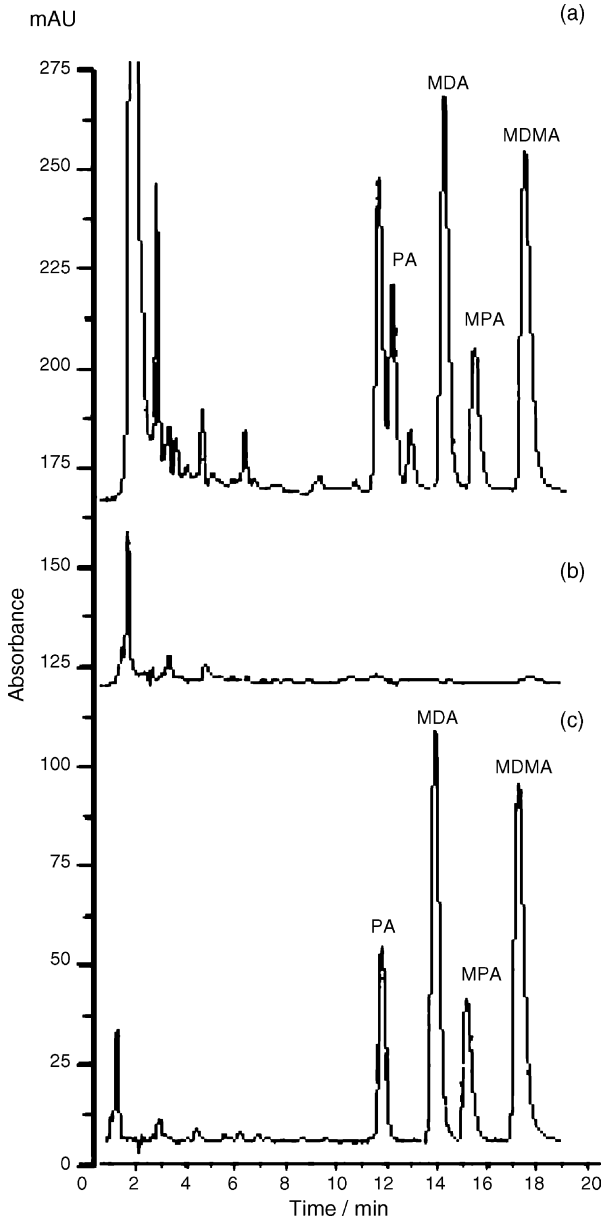

Fig. 7. Chromatograms obtained by in-tube SPME of (a and c) spiked urine sample at 1 μg/mL and (b) blank urine sample, (a) with 75 s of washing; (b and c) with 3 min of washing. The extraction flow rate was 0.04 mL/min. Extraction time was 10 min; HPLC conditions outlined in Section 2.

smallest p*K*a value, which results in weak ion-exchange interaction with the poly(MAA-EGDMA) monolithic column.

3.4. Urine samples analysis

Under the optimized conditions, the poly(MAA-EGDMA) monolithic column was applied for determination of amphetamines in urine samples. Fig. 7 shows the chromatograms obtained by in-tube SPME of the urine sample with the four amphetamines spiked at 1 μg/mL. Unexpectedly, the sample matrix was coextracted from the urine and interfered the analysis of the amphetamines, especially for PA, as shown in Fig. 7a. Therefore, a washing step after extraction was optimized. The washing step could be realized by allowing the carrier solution, phosphate buffer solution, to flow through the capillary after valve one reswitched to LOAD position. The components adsorbed weakly to the monolithic column were expected to be removed by the washing step. By prolonging the washing time from 75 s to 3 min, the matrix peaks were suppressed obviously. This could be proved by extracting the blank urine sample with a washing step of 3 min, showing a clean chromatogram depicted in Fig. 7b. Applying the same washing step to the spiked urine sample, satisfactory results was achieved for the four amphetamines: no decrease of the peak height was found for the analytes in comparison to that obtained by extracting the standard samples and the matrix peaks could hardly be seen from the chromatogram, as displayed in Fig. 7c.

The in-tube SPME of the four amphetamines spiked in urine samples in the range of 0.05–5 μg/mL was successfully accomplished under the optimized conditions. The results are listed in Table 2. The regression coefficients were better than 0.999 and the detection and quantification limits were also calculated with the signal-to-noise ratio set at 3 and 10, respectively, which were found to be adequate for practical analyses. The extraction recovery was also calculated by comparing the extraction efficiency obtained by extracting 1 μg/mL urine sample to that of the standard sample with the results obtained as 98.4, 101.9, 99.1 and 99.3% for PA, MDA, MPA and MDMA, respectively, which confirmed again that the urine matrix hardly affected the extraction. The precision of the constructed in-tube SPME method was evaluated with the results also listed in Table 2; very good reproducibility of the analysis was achieved with the RSD values better than 2.9%.

Urine samples from suspected amphetamines abusers were extracted with the chromatograms shown in Fig. 8a–c. The detected amphetamines were mainly MDA and MDMA and small amount of MPA, indicating that the addicts might be “Ecstasy” abusers [32]. There were also some undefined peaks appearing in the chromatograms, which were thought to be the metabolites of the MDMA after digestion and had not been identified for the moment. The results confirmed that the in-tube SPME method based on poly(MAA-EGDMA) monolithic column could be directly applied to real sample analysis.

Generally, a routine method dealing with biological samples, such as serum and urine, requires acceptable reusability of the extraction sorbent. In the experiment, the decrease of the extraction efficiency for the poly(MAA-EGDMA) monolithic column towards amphetamines was not observed even after hundreds of usages and abnormal fluctuation of the column backpressure was also not observed, which can be attributed to the biocompatibility of the monolithic column.

Table 2
Calibration curves and the precision data for in-tube SPME of PA, MPA, MDA and MDMA from urine samples

	Linear range (μgmL^{-1})	Calibration curves			LOD ($ngmL^{-1}$)	LOQ ($ngmL^{-1}$)	Precision	
		Slope	Intercept	r			Intraday RSD (%)	Interday RSD (%)
PA	0.05–2.5	803.3	45.3	0.9990	2.9	9.7	1.9	2.8
MDA	0.05–5	1978.3	128.1	0.9992	1.4	4.6	2.3	1.8
MPA	0.05–5	821.7	1.7	0.9995	4.0	13.3	2.9	2.3
MDMA	0.05–5	2198.3	154.6	0.9990	1.6	5.2	1.9	1.3

Number of data point for calibration curves is 6. The extraction flow rate was 0.04 mL/min. Extraction time was 10 min. The intraday precisions were calculated by performing four extractions of independently prepared urine samples with amphetamines spiked at 1 μg/mL over a day. Interday precision was accessed by performing extraction of independently prepared urine samples with amphetamines spiked at 1 μg/mL for continuous 5 days. HPLC conditions outlined in Section 2.

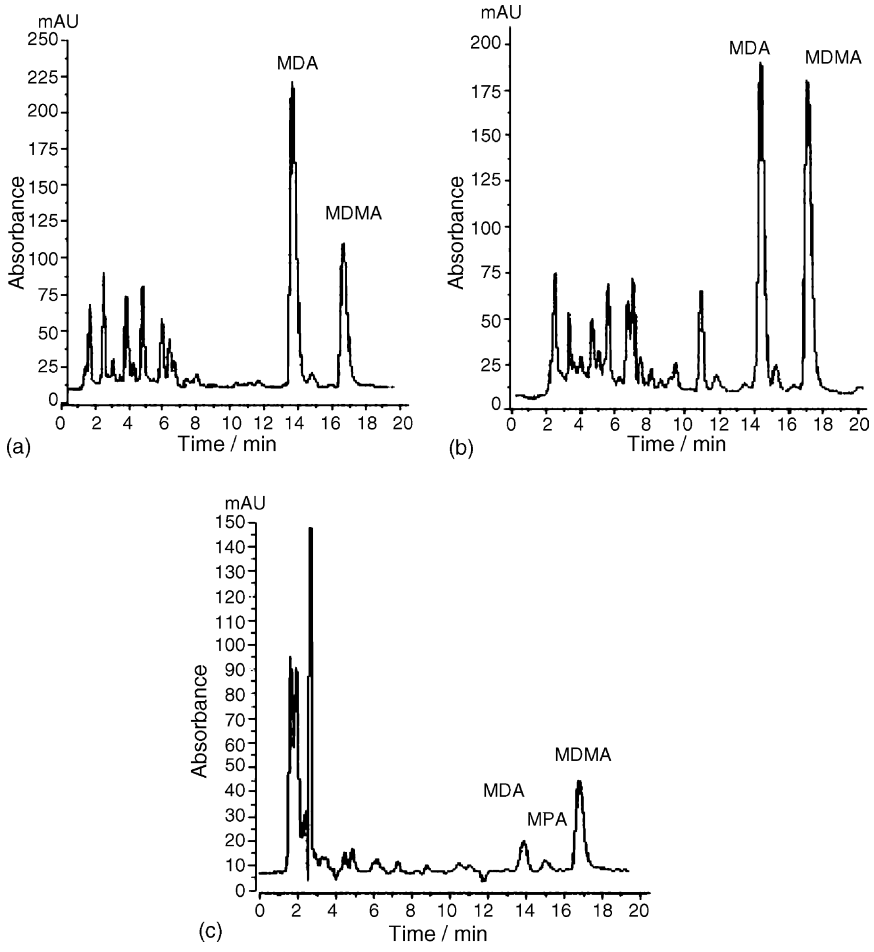

Fig. 8. Chromatograms from in-tube SPME-HPLC of abusers' urine samples. In-tube SPME conditions: the flow rate was 0.04 mL/min. Extraction time was 10 min. HPLC conditions outlined in Section 2.

4. Conclusions

Poly(methacrylic acid-ethylene glycol dimethacrylate) monolithic capillary column was introduced successfully into in-tube SPME coupled to HPLC for direct determination of amphetamine, methamphetamine and their methylenedioxy derivatives in urine samples. High extraction efficiency and great improvement in sensitivity were confirmed. The washing step after extraction was found to be effective for sample matrix removal, which favored the practical analysis well.

The mechanism for poly(MAA-EGDMA) extracting the basic analytes was investigated and an adsorption process was thought to be involved in the extraction procedure. The ion-exchange (acid–base) interaction and the hydrophobic interaction were regarded as the two main factors that dominated the retention of the analytes on the monolithic column.

Since such kind of polymer monolithic column shows good compatibility in deal with biological sample and can be easily obtained, we believe that application range of the constructed in-tube SPME-HPLC method can be easily ex-

tended to other kinds of biologically and clinically important analytes. And for the moment, this method can also be used to other groups of basic analytes with little modification.

Acknowledgements

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References

[1] T. Kraemer, H.H. Maurer, J. Chromatogr. B 713 (1998) 163.
[2] M.A. Huestis, R.E. Choo, Forensic Sci. Int. 128 (2002) 20.
[3] S. Pichini, R. Pacifici, M. pellegrini, E. Marchei, J. Lozano, J. Nurillo, O. Vall, O. Garcia-Algar, Anal. Chem. 76 (2004) 2124.
[4] H.P. Hendrickson, A. Milesi-Hallé, E.M. Laurenzana, S.M. Owens, J. Chromatogr. B 806 (2004) 81.
[5] M.R. Moeller, S. Steinmeyer, T. Kraemer, J. Chromatogr. B 713 (1998) 91.
[6] R. Eisert, J. Pawliszyn, Anal. Chem. 69 (1997) 3140.
[7] H. Kataoka, Anal. Bioanal. Chem. 373 (2002) 31.
[8] W.M. Mullett, K. Levsen, J. Borlak, J. Wu, J. Pawliszyn, Anal. Chem. 74 (2002) 1695.
[9] H. Kataoka, S. Narimatsu, H.L. Lord, J. Pawliszyn, Anal. Chem. 71 (1999) 4237.
[10] Y. Saito, M. Kawazoe, M. Hayashida, K. Jinno, Analyst 125 (2000) 807.
[11] H. Kataoka, H.L. Lord, J. Pawliszyn, J. Anal. Toxicol. 24 (2000) 257.
[12] J. Wu, H. Lord, J. Pawliszyn, Talanta 54 (2001) 655.
[13] W.M. Mullett, P. Martin, J. Pawliszyn, Anal. Chem. 73 (2001) 2383.
[14] W.M. Mullett, K. Levsen, D. Lubda, J. Pawliszyn, J. Chromatogr. A 963 (2002) 325.
[15] Y. Saito, Y. Nakao, M. Imaizumi, T. Takeichi, Y. Kiso, K. Jinno, Fresenius J. Anal. Chem. 368 (2000) 641.
[16] K. Jinno, M. Kawazoe, Y. Saito, T. Takeichi, M. Hayashida, Electrophoresis 22 (2001) 3785.
[17] Y. Shintani, X. Zhou, M. Furuno, H. Minakuchi, K. Nakanishi, J. Chromatogr. A 985 (2003) 351.
[18] E.F. Hilder, F. Svec, J.M.J. Fréchet, J. Chromatogr. A 1044 (2004) 3.
[19] T. Ikegami, N. Tanaka, Curr. Opin. Chem. Biol. 8 (2004) 527.
[20] Y. Ueki, T. Umemura, J. Li, T. Odake, K. Tsunoda, Anal. Chem. 76 (2004) 7007.
[21] F. Svec, J. Sep. Sci. 27 (2004) 1419.
[22] C. Yu, F. Svec, J.M.J. Frechet, Electrophoresis 21 (2000) 120.
[23] F. Svec, E.C. Peters, D. Sýkora, J.M.J. Fréchet, J. Chromatogr. A 887 (2000) 3.
[24] S. Xie, F. Svec, J.M.J. Fréchet, Chem. Mater. 10 (1998) 4072.
[25] Y. Fan, Y.Q. Feng, S.L. Da, Z.G. Shi, Anal. Chim. Acta 523 (2004) 251.
[26] Y. Fan, Y.Q. Feng, S.L. Da, X.P. Gao, Analyst 129 (2004) 1065.
[27] O. Rbeida, B. Christiaens, P. Hubert, D. Lubda, K.-S. Boos, J. Crommen, P. Chiap, J. Chromatogr. A 1030 (2004) 95.
[28] Obtained from Web site: http://chemfinder.cambridgesoft.com and web databases from Syracuse Research Corporation.
[29] Y. Gou, C. Tragas, H. Lord, J. Pawliszyn, J. Microcolumn Sep. 12 (2000) 125.
[30] J.C. Wu, J. Pawliszyn, Anal. Chem. 73 (2001) 55.
[31] T. Górecki, X. Yu, J. Pawliszyn, Analyst 124 (1999) 643.
[32] F. Sadeghipour, J.L. Veuthey, J. Pharm. Biomed. Anal. 17 (1998) 801.