Journal of Chromatography A, 1218 (2011) 3952–3957

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

An unbreakable on-line approach towards sol–gel capillary microextraction

Habib Bagheri*, Hamed Piri-Moghadam, Ali Es'haghi

Environmental and Bio-Analytical Laboratories, Department of Chemistry, Sharif University of Technology, P.O. Box 11365-9516, Tehran, Iran

ARTICLE INFO

Article history:
Received 14 February 2011
Received in revised form 17 April 2011
Accepted 22 April 2011
Available online 7 May 2011

Keywords:
Self assembled monolayers (SAMs)
Sol–gel technology
In-tube solid phase microextraction
Capillary microextraction (CME)
High performance liquid chromatography-fluorescence detector (HPLC-FD)
On-line approach

ABSTRACT

In this work a novel unbreakable sol–gel-based in-tube device for on-line solid phase microextraction (SPME) was developed. The inner surface of a copper tube, intended to be used as a high performance liquid chromatography (HPLC) loop, was electrodeposited by metallic Cu followed by the self assembled monolayers (SAM) of 3-(mercaptopropyl) trimethoxysilane (3MPTMOS). Then, poly (ethyleneglycol) (PEG) was chemically bonded to the –OH sites of the SAM already covering the inner surface of the copper loop using sol–gel technology. The homogeneity and the porous surface structure of the SAM and sol–gel coatings were examined using the scanning electron microscopy (SEM) and adsorption/desorption porosimetry (BET). The prepared loop was used for online in-tube SPME (capillary microextraction) of some selected polycyclic aromatic hydrocarbons (PAHs), as model compounds, from the aquatic media. After extraction, the HPLC mobile phase was used for on-line desorption and elution of the extracted analytes from the loop to the HPLC column. Major parameters affecting the extraction efficiency including the sample flow rate through the copper tube, loading time, desorption time and sample volume were optimized. For investigating the sorbent efficiency, four loops based on the copper tube itself, the copper tube after electrodeposition with Cu and the tubes with the SAMs and SAMs-sol–gel coating were made and compared. The SAMs-sol–gel coated loop clearly shows a prominently lead of at least 20–100 times of higher efficiency. The linearity for the analytes was in the range of 0.01–500 $\mu g\,L^{-1}$. Limit of detection (LOD) was in the range of 0.005–0.5 $\mu g\,L^{-1}$ and the RSD% values ($n = 5$) were all below 8.3% at the 5 $\mu g\,L^{-1}$ level. The developed method was successfully applied to real water samples while the relative recovery percentages obtained for the spiked water samples were from 90 to 104%. The prepared loop exhibited long life time due to its remarkable solvent and mechanical stability. Different solvents such as methanol, acetonitrile and acetone were passed through the loop for many days and it was also used for more than 100 extractions/desorption of the selected analytes and no decrease in the peak areas was observed.

1. Introduction

Nowadays, SPME is regarded as a rather rapid, solvent free and economical technique which is an alternative to traditional extraction techniques such as liquid–liquid extraction (LLE) and solid phase extraction (SPE) [1,2]. These traditional techniques are time consuming and laborious with large consumption of toxic and expensive solvents. In SPME, a sorbent which could be liquid or solid is usually placed onto a solid support such as fused silica. Although, SPME has increasingly becoming popular, but their fibers possess relatively low recommended operating temperatures and exhibit instability and swelling in organic solvents (greatly restricting their use with HPLC), while the conventional fibers could be broken easily and their coatings are stripped when they are exposed to high temperatures and organic solvents. Apart from the fiber breakage, most of the problems are due to the physical bonds between the solid supports and the coated extracting media. The fibers instability problem was obviated in 1997, when the sol–gel technology was used to coat sorbents onto the solid supports [3]. Applications of the SPME fibers have been increased ever since the sol–gel technology was used for environmental and biological analytes in conjunction with gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS) [4–15]. The coupling of SPME and HPLC with the use of a LC loop could be automated [16–19]. Automation of sol–gel-based SPME technique with HPLC still has some limitations. This is due to the fact that the LC loop which, is usually made of stainless steel, could not be functionalized and adhesion of the coating on the inner surface of the metallic tubes are prominently physical. Malik et al. were used a capillary column as a HPLC loop for coupling the sol–gel-based CME with HPLC [20–23]. Although the prepared capillary microextraction (CME) loop using the sol–gel coating resolved some issues but the extracting loop remained breakable and needed to be handled carefully. According to our knowledge, as far as the conjunction of SPME and HPLC is concerned, no report on the unbreakable sol–gel-based CME, or so-called in-tube SPME, has been published.

* Corresponding author. Tel.: +98 21 66165316; fax: +98 21 66012983.
E-mail address: bagheri@sharif.edu (H. Bagheri).

0021-9673/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2011.04.059

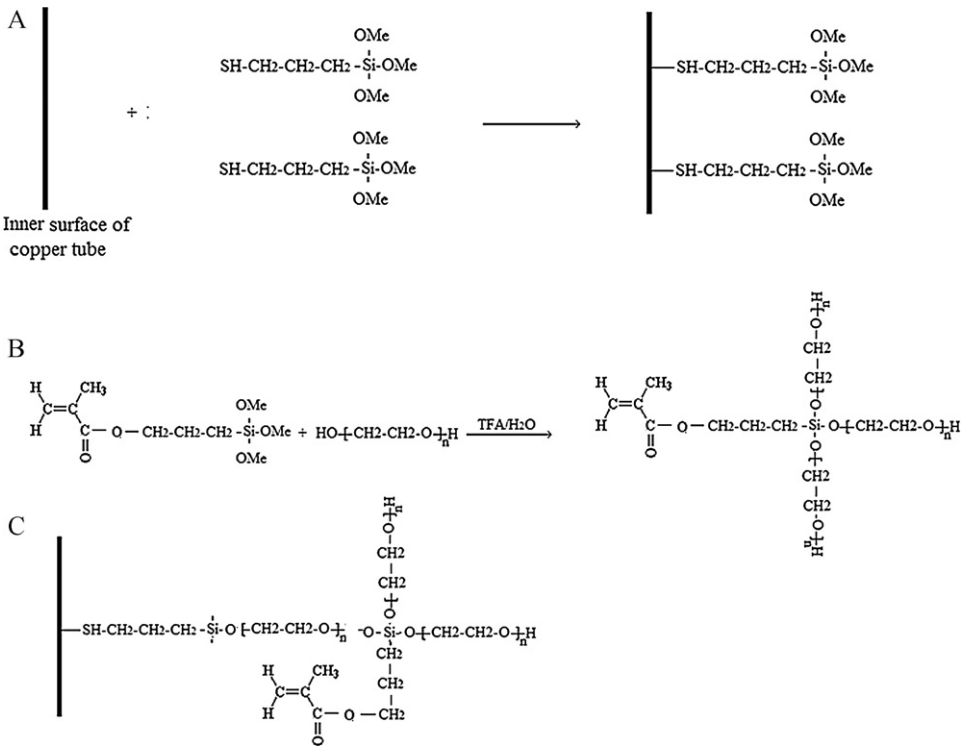

Fig. 1. Preparation of the sol–gel coated HPLC loop. (A) Functionalization of the inner surface of copper tube (HPLC loop), (B) preparation of sol solution, (C) coating of the sol–gel sorbent on the inner surface of the prepared loop.

SAMs are ordered monomolecular films, which are spontaneously formed from immersing a solid substrate into a solution containing amphifunctional molecules. The amphifunctional molecule has a head group, which usually has a high affinity for the solid surface, a tail (typically an alkyl chain) and a terminal group that can be used to control the surface properties of the resultant monolayer. The molecular forces between the tails are prominently responsible for the order of the monolayer. The most extensively studied SAMs are silanes, which are used to modify hydroxyl terminated surfaces, and organosulfur compounds. The affinity of sulfur for gold, platinum, copper and silver could be therefore justified [24]. For formation of SAMs, the thiol groups are chemisorbed on the inner surface of the copper tube via the formation of the copper-thiol bond to produce a densely packed highly ordered monolayer.

In this work a novel unbreakable sol–gel-based in-tube device for on-line SPME was developed. The self assembled monolayers (SAMs) technique was used to functionalize the inner surface of a copper tube. The LC loops are stainless steel and they cannot be used as a support for sol–gel based SPME. For obviating this problem, a copper tube was used as a LC loop and for functionalizing the inner surface, alkanthiol with –OH terminal group was employed. Then, the appropriate sorbent was coated into the loop using the sol–gel technology.

2. Experimental

2.1. Reagents and standards

Naphthalene (NPH), fluorene (FLU), acenaphthylene (ACY), acenaphthene (ACE) and anthracene (ANT) were obtained from Merck (Darmstadt, Germany). Poly(ethyleneglycol) (PEG), 3-(mercaptopropyl)trimethoxysilane (3MPTMOS) and 3-propylmethacrylate trimethoxysilane (3PMTMOS) with purity higher than 98% were purchased from Aldrich (Darmstadt, Germany). Methanol, acetone, sulfuric acid, copper sulfate and trifluoroacetic acid (TFA) were supplied from Merck (Darmstadt, Germany). The stock solution was prepared in methanol at concentration of 1000 mg L^{-1} and stored at 4 °C.

2.2. Instrumental

A Knauer (Berlin, Germany) HPLC system including a k-1001 HPLC pump, a K-1001 solvent organizer, an on-line degasser, a dynamic mixing chamber and a fluorescence detector model RF-10XL was used for separation and determination of analytes. The separation was performed on the Waters C_{18} (4.6 × 250 mm) column (particle size: 3 μm). The solvents used as mobile phase were acetonitrile HPLC-grade and three-distillated water at flow rate of 1 mL min^{-1}. The analysis was started with 50% acetonitrile, which was increased linearly up to 80% in 15 min and this percentage was maintained until end of the run. The fluorescence detection was performed at 226 nm as excitation wavelength and 330 as emission wavelength.

2.3. The CME device

The CME device preparation included three major steps. At the beginning it was necessary to be sure that the inner surface of the copper tube (12 cm length × 0.7 mm i.d.) is as clean as possible and no chemical residues remained. The copper tube was placed in the electrolyte solution containing of H_2SO_4 (20%, v/v) and $CuSO_4$ (10%, w/v) acting as cathode and a piece of aluminum foil was used as anode. A peristaltic pump was used to deliver the electrolyte through the copper tube and while a potential of −0.3 V was applied for 15 min for electrodeposition of pure Cu on the inner surface of the copper tube.

The copper tube was, then, placed in a solution of 0.001M of 3MPTMOS for performing the functionalization. A peristaltic pump was used to deliver the 3MPTMOS solution through the copper tube

expecting to be adsorbed on the inner surface of the copper tube spontaneously. This process was performed for 15 h [25–27].

At this stage it was essential to prepare the sol by adding 400 mL of 3-propylmethacrylate trimethoxysilane (precursor) to 500 mg of poly (ethyleneglycol) and sonication for 10 min. Then 100 μL TFA (100%) was added and sonicated for another 3 min. Afterward 30 μL distilled water was added for initiating the hydrolysis process [28]. After 5 min of sonication, the sol was ready to be used. A peristaltic pump was used to pass the prepared sol through the copper tube for 20 min in order to form the gel into the copper tube. The copper tube was placed into a desiccator for 24 h for further aging and eventually to increase the number of bonds between the colloids. To complete the polycondensation step, the prepared loop was placed in an oven with a temperature of 50 °C for 30 min, and then the temperature was raised to 200 °C during 1 h and maintained at this temperature for 30 min, finally it was returned to initial temperature during 1 h. After drying, a xerogel of amorphous silica was obtained (Fig. 1).

2.4. Extraction–determination procedure

The prepared loop was conditioned daily prior to the first extraction by pumping the HPLC mobile phase through it. The prepared loop was used for online in-tube SPME (capillary microextraction) of some selected PAHs, as model compounds, from the aquatic media. Extraction was performed by passing the spiked aqueous samples through the loop. After extraction, the HPLC mobile phase was used for on-line desorption and elution of the extracted analytes from the loop to the HPLC column. In all experiments, distilled water was spiked with 10 ng mL^{-1} standards of PAHs. Fig. 2 shows a typical HPLC-FD chromatogram obtained after extraction of a distilled water sample spiked with the selected PAHs under the optimum conditions.

3. Results and discussion

3.1. Characteristics and efficiency of the prepared in-tube SPME

Formation of sol–gel composite on the surface of metals is possible only when functional OH groups are available on the metals surface. The formation of self monolayers, to impart this type of functionality, is one of the possibilities. The use of alkanethiol appeared to be an efficient way to functionalize the inner surface of the copper tube. The details of the bond formation between the copper and the sulfur is still unclear, but in the case of alkanethiols it can be considered as an oxidative addition of the S–H bond to the copper surface followed by a reductive elimination of hydrogen [29]:

$$R\text{–}S\text{–}H + Cu_n^0 \rightarrow R\text{–}S^-Cu^+ \cdot Cu_n^0 + \frac{1}{2}H_2$$

Evidence for H_2 leaving has been hard to observe, but the presence of a thiolate has been confirmed by different instrumentations [30–38]. Typically alkanethiols are assembled into copper surfaces from dilute mM solutions. Two distinct adsorption stages are reported in the process. A rapid stage within the first few minutes by which time the contact angle is close to its limiting value and the thickness is 80–90% of the maximum [25]. The length of this stage is dependent on the alkanethiol concentration, taking only a few minutes at a concentration of 1 mM [26,27]. The latter stage occurs over several hours as the contact angle and thickness reach their final value [17,39]. Due to the slow reorganization of the SAM, many workers typically allow a time interval of 12–24 h for SAM formation prior to use. In this work, a time interval of 15 h was used for formation of SAMs in order to have rather organized and complete monolayers. Then the PEG sol–gel composite was

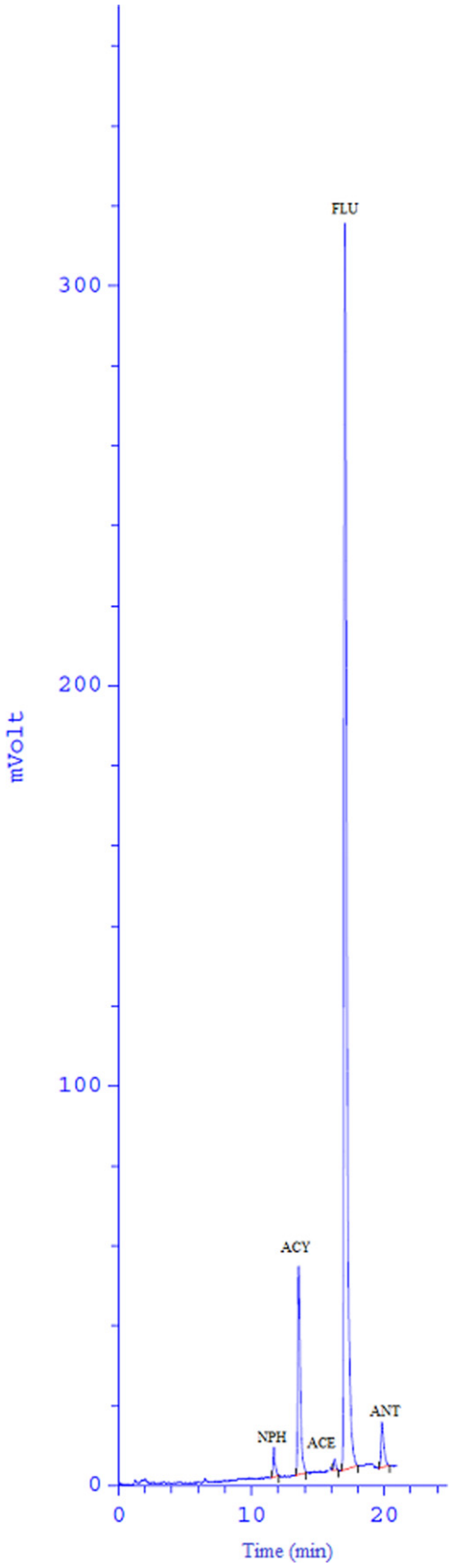

Fig. 2. A typical HPLC-FD chromatogram obtained after extraction of a distilled water sample spiked with the selected PAHs under the optimum conditions.

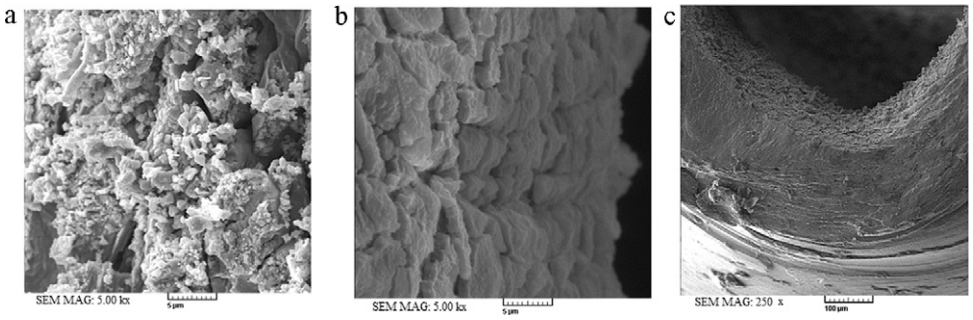

Fig. 3. Scanning electron microscopy (SEM). (a) The SAMs-sol–gel coated copper loop (5000×), (b) the SAMs coated copper loop (5000×), (c) the cross section of the sol–gel coated copper loop (250×).

chemically formed via the hydrolysis process. The surface characteristics of the polymer coatings were investigated by SEM. Fig. 3 shows the micrographs of the SAMs and SAMs-sol–gel coatings along with the cross section of the SAMs-sol–gel coating. The thickness of the coating obtained under this condition was 150 μm according to the SEM study. Also, the images taken from different parts of the prepared loop proved that the PEG sol–gel-based coating was thoroughly homogenous and porous. In order to evaluate the porosity of the prepared sorbent, the adsorption/desorption porosimetry (BET) test was performed. The results revealed that the mean pore diameter of the sorbent is 14.202 nm, an indication of possessing a rather high degree of porosity, and consequently high extraction efficiencies.

In order to examine the efficiency of the method for extracting organic compounds from water and transferring them into a HPLC system, a number of two-, three- and four-ring PAHs were selected as model compounds. The extraction was performed using a water sample spiked with 10 μg L^{-1} standard solution. Differences in peak sizes in the chromatogram could be attributed to different concentration, various fluorescence quantum yields of the analytes or response factors and using not-optimized excitation and emission wavelengths for each individual compound. This primary test revealed that the method is feasible.

For investigating the sol–gel coating efficiency, four loops based on the copper tube itself, the copper tube after electrodeposition with Cu and the copper tubes with the SAM before and after synthesizing the sol–gel coating were made and compared. A peristaltic pump was used to deliver the standard solution containing the selected analytes through four prepared loops. As it is shown in Fig. 4, the copper tubes could not extract NPH and ACE, although they managed to extract ACY, FLU and ANT slightly. Apparently, the copper loop containing the SAMs exhibits higher extraction efficiency which might be due to the presence of propyl and ethoxy groups in 3MPTMOS and the involved Van Der Waals forces. The SAMs-sol–gel coated loop clearly shows a prominently lead of at least 20–100 times of higher efficiency.

3.2. Optimization

After successful preliminary results, important and influential parameters including the sample flow rate through the loop, the loading time, desorption time and the sample volume are needed to be optimized. The chromatographic peak area, which is related to the number of extracted moles of analytes, was used to evaluate the extraction efficiency under different experimental conditions.

3.2.1. The sample flow rate through the loop

It is known that the required time to obtain extraction equilibrium is proportional to the length of the loop, the analyte distribution constant and the volume of the coating, while it is inversely proportional to the extraction flow rate [40,41]. Generally, the loading flow rate is optimized by keeping the total sample solution volume and concentration constant. Thus for the loop used here, the extraction flow rate was initially optimized to obtain high extraction efficiency while still offering a reasonable analyzing time.

For doing so, a range of flow rates from 0.15 to 2 mL min^{-1} were considered to be investigated. As Fig. 5 shows the higher extraction efficiencies were achieved at flow rates above 0.5 mL min^{-1} as a result of improved mass transfer during more extraction cycles. However, it was found that at very high flow rates the precision is affected, possibly owing to the formation of air bubbles at the edges of the loop [42]. A flow rate of 1.5 mL min^{-1} was chosen as the optimum value.

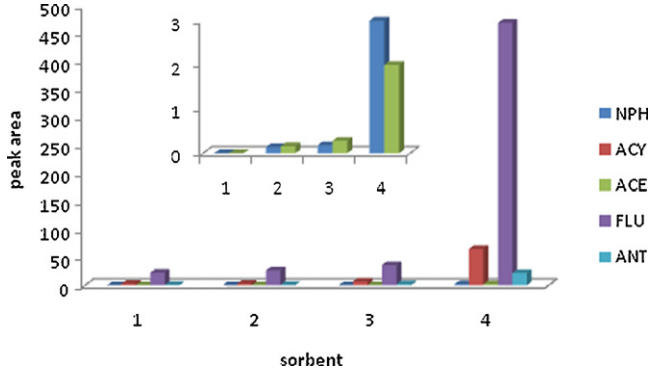

Fig. 4. Extraction efficiency of the prepared sol–gel loop. (1) The bare copper tube, (2) the Cu electrodeposited into the copper tube, (3) the SAMs coated copper tube, (4) the SAMs-sol–gel coated copper tube. The insert shows the comparison of NPH and ACE.

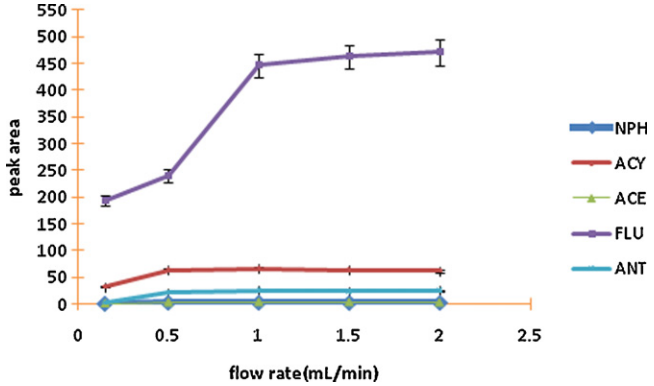

Fig. 5. Sample flow rate through the loop. Loading time: 20 min, desorption time: 10 min; sample volume: 8 mL; analytes concentration: 10 μg L^{-1}.

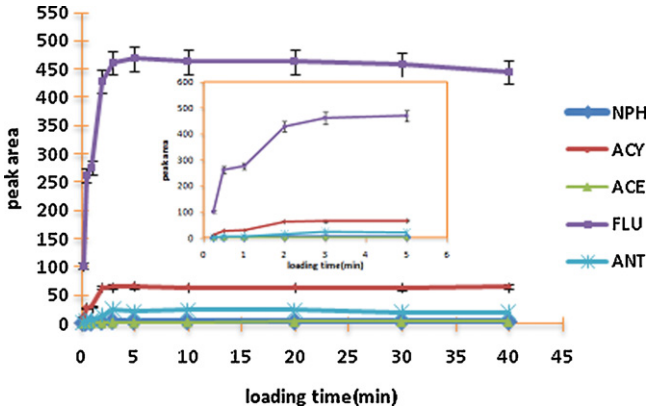

Fig. 6. Loading time. Flow rate: 1.5 mL min^{-1}; desorption time: 10 min; sample volume: 8 mL; analytes concentration: 10 μg L^{-1}. The insert shows the first 5 min of the extraction time.

3.2.2. Loading time

The amount of analyte adsorbed by a sorbent is dependent on the distribution constant between sorbent and solution, thickness of an adsorbing phase and diffusion coefficient of analytes. SPME is an equilibrium based method in which the extraction efficiency is expected to increase with time until the equilibrium is reached. As shown in Fig. 6, the extraction efficiency of analytes improved almost linearly as the sample loading time increased. A loading time of 3 min was selected as for most analytes the equilibrium time was almost achievable.

3.2.3. Desorption time

In SPME, desorption of analytes should be performed as fast as possible to avoid any possible peak broadening. In GC, the rapid desorption happens inside the high temperature injection port, while in HPLC the fast desorption is achievable using the mobile phase with strong eluting power. As Fig. 7 shows whenever the extraction through the loop is completed, on-line desorption of analytes could be simply accomplished by switching the sampling valve from the load position to the inject mode. Thus the mobile phase composition should provide complete desorption of the extracted analytes, while still maintaining the proper separation of the analytes in the analytical column. According to Fig. 8, the desorption was almost complete when desorption time of 30 s was used. However, to avoid any possible carryover effect, a time interval of 5 min was chosen for all further experiments.

3.2.4. Sample volume

The mass of an analyte extracted by the polymeric coating is related to the overall equilibrium of the analyte in the two phases. Mass of the analyte absorbed by the coating can be expressed as:

$$n = \frac{K_{fs} V_f V_s C_0}{K_{fs} V_f + V_s} \quad (1)$$

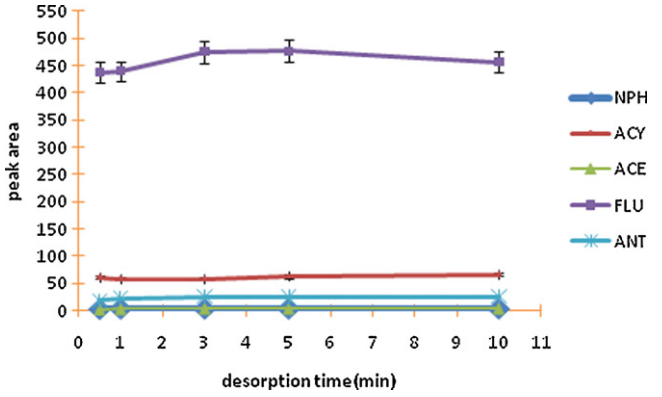

Fig. 8. Desorption time. Flow rate: 1.5 mL min^{-1}; sample volume: 8 mL; loading time: 3 min; analytes concentration: 10 μg L^{-1}.

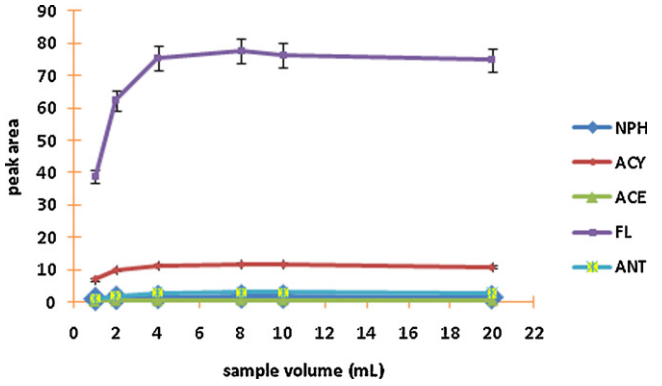

Fig. 9. Sample volume. Flow rate: 1.5 mL min^{-1}; desorption time: 10 min; loading time: 3 min; analytes concentration: 2 μg L^{-1}.

Above equation describes the mass absorbed by the polymeric coating after equilibrium has been reached in the system. Also it can be inferred that n is increased as long as sample volume (V_s) increased, until $K_{fs} V_f \ll V_s$; At this point amount of analyte extracted is independent of sample volume:

$$n = K_{fs} V_f C_0 \quad (2)$$

The effect of sample volume was investigated from 1 to 20 mL. As Fig. 9 shows, the extraction efficiency was increased up to 4 mL of the sample, and then it was independent of sample volume. Apparently by the use of 4 mL sample, the equilibrium is easily reachable and the rise of sample volume has no effect on the extraction efficiency.

3.3. Method validation

Based on the developed method, a sampling flow rate of 1.5 mL min^{-1}, loading time of 3 min, desorption time of 5 min

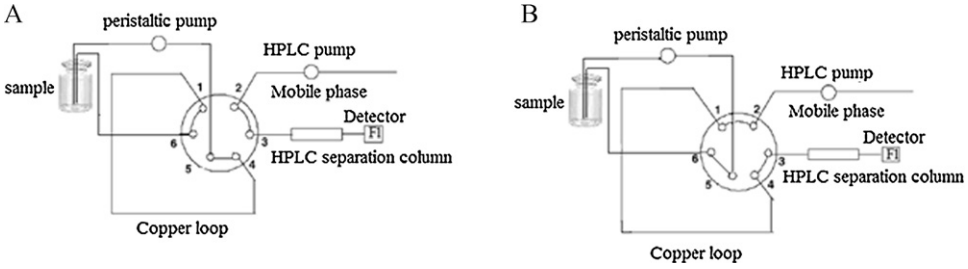

Fig. 7. Schematic diagram of the on-line in tube solid phase microextraction coupled with HPLC. HPLC injector valve position: (A) load and (B) inject.

Table 1
Figures of merit of the method.

Compounds	LDR ($\mu g\,L^{-1}$)	LOD[a] ($\mu g\,L^{-1}$)	LOQ[b] ($\mu g\,L^{-1}$)	R^2	Regression equation	RSD, % ($n=5$)[c]
Naphthalene	1–500	0.5	1	0.9929	$y=0.2094x-1.7261$	2.8
Acenaphthylene	0.05–10	0.01	0.05	0.9996	$y=6.52x+0.2249$	4.5
Acenaphthene	1–100	0.5	1	0.9938	$y=0.1063x+0.3346$	8.3
Fluorene	0.01–10	0.005	0.01	0.9956	$y=47.237x+8.9457$	4.3
Anthracene	0.5–500	0.1	0.5	0.9955	$y=0.6673x+8.9064$	6.1

[a] S/N = 3.
[b] S/N = 10.
[c] $C_{anlytes} = 5\,\mu g\,L^{-1}$.

Table 2
Relative recoveries for tap water spiked with $5\,\mu g\,L^{-1}$ of analytes.

Analyte	Relative recovery, %*	RSD, % ($n=4$)*
Naphthalene	104	6.1
Acenaphthylene	103	11.3
Acenaphthene	90	9.3
Fluorene	103	6.2
Anthracene	93	5.2

* $C = 5\,\mu g\,L^{-1}$.

and sample volume of 4 mL were chosen as the optimum set of conditions. Distilled water spiked with the selected PAHs was used to evaluate the precision of the measurements, LOD and the dynamic range of method. The linearity of the method was tested by preparing the calibration curve for each analyte with 5–7 points. The linearity for the analytes was in the range of 0.01–500 μg^{-1}. The regression coefficient obtained for each analyte was rather satisfactory ($R^2 > 0.9938$). The values of LOD (S/N = 3) was in the range of 0.005–0.5 $\mu g\,L^{-1}$ and LOQ (S/N = 10) was between 0.01 and 1 $\mu g\,L^{-1}$. The precision of the method was determined by performing five consecutive extractions from the aqueous solutions. The standard deviation of the peak areas of analytes, spiked at the concentration level of 5 $\mu g\,L^{-1}$, was in the range of 2.8–8.3% (Table 1). To evaluate the applicability of the proposed method, extraction and analysis was performed on tap water. The water sample was spiked at a concentration level of 5 $\mu g\,L^{-1}$ and the analysis was carried out under the optimized conditions. As Table 2 shows good relative recoveries were achieved for the selected PAHs ranging from 90 to 104%.

4. Conclusion

In this work, an unbreakable online SPME-HPLC method was developed by preparing a sol–gel coated copper loop. Functionalizing the inner section of the copper tube, intended to be used as the LC loop, could be facilitated by the SAM technique. The sol–gel coating technology led to a solvent resistant and unbreakable loop due to the formation of a chemical bond between the sorbent and the inner section of the loop. The developed method showed good linearity and repeatability while rather low LOD values could be achieved. Homogeneity and porosity of the prepared sol–gel coated loop seem to be responsible for good repeatability and high extraction efficiency. The extraction and desorption in this technique are rather rapid. Also, good relative recoveries for the selected analytes from the tap water samples were obtained. The prepared loop could easily provide the possibility of on-line coupling between the sol–gel-based SPME and HPLC.

Acknowledgments

The Research Council and Graduates School of Sharif University of Technology (SUT) are thanked for supporting the project. Also M. Naderi is greatly appreciated for her assistances.

References

[1] R.P. Berladi, J. Pawliszyn, Water Pollut. Res. J. Can. 24 (1989) 179.
[2] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145.
[3] S.L. Chong, D. Wang, J.D. Hayes, B.W. Wilhite, A. Malik, Anal. Chem. 69 (1997) 3889.
[4] L. Yun, Anal. Chim. Acta 486 (2003) 63.
[5] T.P. Gbatu, K.L. Sutton, J.A. Caruso, Anal. Chim. Acta 402 (1999) 67.
[6] D. Wang, J. Xing, J. Peng, C. Wu, J. Chromatogr. A 1005 (2003) 1.
[7] T.-Y. Kim, K. Alhooshani, A. Kabir, D.P. Fries, A. Malik, J. Chromatogr. A 1047 (2004) 165.
[8] H. Bagheri, A. Aghakhani, A. Es-Haghi, Chromatographia 66 (2007) 779.
[9] M.A. Azenha, P.J. Nogueira, A.F. Silva, Anal. Chem. 78 (2006) 2071.
[10] S.S. Segro, M. Tran, S. Kesani, A. Alhendal, E.B. Turner, A. Malik, J. Sep. Sci. 33 (2010) 3075.
[11] W.A. Wan Ibrahim, H. Farhani, M.M. Sanagi, H.Y. Aboul-Enein, J. Chromatogr. A 1217 (2010) 4890.
[12] S. Sungkaew, C. Thammakhet, P. Thavarungkul, P. Kanatharana, Anal. Chim. Acta 664 (2010) 49.
[13] H. Bagheri, Z. Ayazi, E. Babanezhad, Microchem. J. 94 (2010) 1.
[14] A. Sarafraz-Yazdi, H. Piri Moghadam, Z. Es'Haghi, S. Sepehr, Anal. Methods 2 (2010) 746.
[15] Y. Wang, Z. Zeng, M. Liu, J. Chromatogr. Sci. 49 (2011) 29.
[16] D. Djozan, M. Amir-Zehni, Chromatographia 62 (2005) 127.
[17] H. Bagheri, A. Salemi, Chromatographia 59 (2004) 501.
[18] D. Djozan, M. Amir-Zehni, Chromatographia 60 (2004) 567.
[19] J. Wu, H. Lord, J. Pawliszyn, Talanta 54 (2001) 655.
[20] S. Bigham, J. Medlar, A. Kabir, C. Shende, A. Alli, A. Malik, Anal. Chem. 74 (2002) 752.
[21] S.S. Segro, A. Malik, J. Chromatogr. A 1205 (2008) 26.
[22] S.S. Segro, A. Malik, J. Chromatogr. A 1200 (2008) 62.
[23] S.S. Segro, Y. Cabezas, A. Malik, J. Chromatogr. A 1216 (2009) 4329.
[24] R.G. Nuzzo, D.L. Allara, J. Am. Chem. Soc. 105 (1983) 4481.
[25] C.D. Bain, E.B. Troughton, Y.-T. Tao, J. Evall, G.M. Whitesides, R.G. Nuzzo, J. Am. Chem. Soc. 111 (1989) 231.
[26] H. Schessler, D.S. Karpovich, G.J. Blanchard, J. Am. Chem. Soc. 118 (1996) 9645.
[27] W. Pan, C.J. Durning, N.J. Turro, Langmuir 12 (1996) 4469.
[28] H. Bagheri, E. Babanezhad, F. Khalilian, Anal. Chim. Acta 616 (2008) 49.
[29] A. Ulman, Chem. Rev. 96 (1996) 1533.
[30] R.G. Nuzzo, F.A. Fusco, D.L. Allara, J. Am. Chem. Soc. 109 (1987) 2358.
[31] M.M. Walczak, C. Chung, S.M. Stole, C.A. Widrig, M.D. Porter, J. Am. Chem. Soc. 113 (1991) 2370.
[32] M.D. Porter, T.B. Bright, D.L. Allara, C.E.D. Chidsey, J. Am. Chem. Soc. 109. (1987) 3559.
[33] C.D. Bain, H. Biebuyck, G.M. Whitesides, Langmuir 5 (1989) 723.
[34] R.G. Nuzzo, B.R. Zegarski, L.H. Dubois, J. Am. Chem. Soc. 109 (1987) 733.
[35] Y. Li, J. Huang, McIver R.T. Jr., J.C. Hemminger, J. Am. Chem. Soc. 114 (1992) 2428.
[36] R.G. Nuzzo, L.H. Dubois, D.L. Allara, J. Am. Chem. Soc. 112 (1990) 3145.
[37] M.A. Bryant, J.E. Pemberton, J. Am. Chem. Soc. 113 (1991) 3629.
[38] M.A. Bryant, J.E. Pemberton, J. Am. Chem. Soc. 113 (1991) 8284.
[39] D.S. Karpovich, H. Schessler, G.J. Blanchard, Self-assembled Monolayers of Thiols, Academic Press, New York, 1998, p. 44.
[40] H. Lord, J. Pawliszyn, J. Chromatogr. A 885 (2000) 153.
[41] R. Eisert, J. Pawliszyn, Anal. Chem. 69 (1997) 3140.
[42] J. Wu, W. Xie, J. Pawliszyn, Analyst 125 (2000) 2216.