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Application of the polysilicone fullerene coating for solid-phase microextraction in the determination of semi-volatile compounds

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Abstract

Solid-phase microextraction using polysilicone fullerene (PF) coating has been applied for the determination of semi-volatile compounds. Detection limits at the $10 \text{ ng l}^{-1} \sim \mu\text{g l}^{-1}$ level were achieved using flame ionization detection. A wide linear range was obtained with precision below 7% relative standard deviation. Parameters that affect the extraction process were investigated, which included sampling time, desorption time, sampling temperature, and salting out effect. Compared to the non-polar commercial polydimethylsiloxane (PDMS) coating, the PF coating has higher extraction efficiency, better selectivity and greater sensitivity for aromatic compounds. The experimental results revealed the thermal stability and life span are superior to commercially available PDMS. The PF coating has been demonstrated to possess planarity molecular recognition. The theoretical study confirmed that quantification is feasible under non-equilibrium conditions by use of the PF coating. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Polysilicone fullerene coating; Solid-phase microextraction; Headspace analysis; Polynuclear aromatic hydrocarbons; Naphthalenes; Biphenyl; Hydrocarbons, aromatic; Xylenes; Benzenes; Toluene

1. Introduction

Solid-phase microextraction (SPME) which uses a polymeric-coated fused-silica fiber to extract organic compounds from the sample matrix, is a simple, fast, solvent-free, efficient, convenient, sensitive, easily automated and portable technique [1,2]. Headspace (HS) SPME has been demonstrated to be an excellent solvent-free sampling method for compounds [3–6]. One of the major factors contributing to the success of HS-SPME is the concentrating effect of the fiber coating towards organic compounds. SPME

is predominantly performed on fibers coated with non-polar polydimethylsiloxane (PDMS) stationary phase [7,8]. A significant drawback of such fibers is that their recommended operating temperatures are relatively low and generally remain within the range of 200–270°C [9], and the life span of the commercial fiber is short, it can only be used 50 to 100 times. It is evident that future advancements in SPME technology would greatly depend on seeking a new coating that has high efficiency, good thermal stability and special selectivity to solve the serious problems concerning environmental pollution.

In this paper, the polymeric fullerene was prepared and used as the coating for SPME with the intention of increasing the selectivity and concentrating effect

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for aromatic and conjugated compounds. The reasons that polysilicone fullerene (PF) was chosen as the coating of SPME may be attributed to the following:

First, fullerene used as chromatographic material has shown wide operational temperature (80~360°C), good thermal stability and good selectivity for aromatic compounds [10,11].

Second, the properties of fullerene, such as the unique spherical shape, conjugated three-dimensional π -electronic system, and the ability to exhibit donor-acceptor or π - π interactions, promise it to be an attractive candidate for coating material.

Furthermore, polymeric fullerene is easier to coat on fused-silica fibers.

Fullerene is difficult to coat because of its high melting point and poor solubility. Crown ether polysiloxanes are good stationary phases for capillary column gas chromatography (GC). These materials provide good diffusion of solution and have excellent thermal stability [12,13]. This fact suggests that a fullerene molecule attached to a polysiloxane backbone may overcome the disadvantages of fullerene. In this article, the polysiloxane-containing azide group has been synthesized. Then, the reaction between polyazidosilicone and C_{60} was accomplished, and the target compound was characterized. The method used in this study is simple, fast, and the molecules mass of the target compound can be controlled.

We have coated two fibers by employing the PF and the mixed stationary of PDMS (OV-1) and PF (OV-1/PF) (ratio 4:1). The properties of the two new-coated fibers containing C_{60} have been investigated comprehensively for the extraction of two kinds of sample, BTEX (benzene, toluene, ethylbenzene, *o*-xylene, and *p*-xylene) and naphthalene congeners (naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, 2,3-dimethylnaphthalene, 2,6-dimethylnaphthalene), from the headspace of a water sample. Also studied were extraction time to reach equilibrium, desorption time, extraction amount, selectivity, detection limits, linear range, thermal stability and the life span of coatings. The OV-1/PF coating has been described [14] previously. In this article, the preparation of PF is presented, and the property of this PF coating is investigated. The application in determination of polycyclic aromatic hydrocarbons (PAHs) in a water sample is performed.

2. Experimental

2.1. Equipment and reagents

SPME devices were obtained from Supelco (Bellefonte, PA, USA). To compare the extraction efficiencies of different extraction phases, the commercially available PDMS fiber, and laboratory-prepared OV-1 were examined. The separations were carried out in a Wenling 9790 GC system equipped with a flame ionization detection (FID) system (Zhejiang, China) and a Shimadzu Chromatopac Model CR3A data processor. Nitrogen was used as the carrier gas at a linear velocity of 13–14 cm s^{-1} . The injection split ratio was 15:1. The temperatures of the injector and detector were maintained at 250~320°C and 250°C or 280°C, respectively. BTEX analysis was performed with a 25 $\text{m} \times 0.32$ mm I.D. capillary column coated with 0.25- μm film thickness crown ether. For naphthalene congeners and PAHs (naphthalene, biphenyl, acenaphthylene, fluorene, phenanthrene, fluoracene, *m*-terphenyl, *p*-terphenyl), a 25 $\text{m} \times 0.32$ mm I.D., 0.25- μm film thickness HP-5 coating capillary column (Hewlett-Packard) was employed. To analyze PAHs, the oven temperature was maintained at 100°C for 1 min after injection, then programmed at 8°C min^{-1} to 280°C, which was held for 10 min.

Fullerene (C_{60}) was purchased from Wuhan University Chemical Reagent. All solvents used in this study were analytical-reagent grade. Three stock solutions, BTEX, naphthalene congeners and PAHs were prepared by dissolving each compound in methanol in a volumetric flask. Stock and working standards were stored at 4°C in the refrigerator. The aqueous solutions were prepared daily by diluting standard solution with deionized water to give the corresponding solution for extraction.

2.2. The synthesis of polysilicone fullerene

The fullerene polymers were prepared by reaction of excess of fullerene (C_{60}) with ω -azido-undecylpolymethylsiloxane in refluxing chlorobenzene for 24 h under a nitrogen atmosphere. Then the solvent was removed. Dichloromethane was added to the reaction vessel when it was cooled to ambient temperature, and insoluble C_{60} was filtered off. IR analysis revealed that the absorption band at 2096

cm^{-1} (for the azide group) disappeared and a peak at 524 cm^{-1} appeared due to the appearance of the fullerene group. The UV–Vis spectrum of this compound in dichloromethane solution gave peaks at about 231, 258, and 325 nm. The nuclear magnetic resonance (NMR) spectrum of the target compound showed peaks at δ 1.9–2.1 and δ 1.5–1.7 for CH_2 , δ 0.1–0.2 for SiCH_3 .

2.3. Preparation of fiber

In this study, the fibers used are commercially available PDMS of 100 μm thickness and polymeric fullerene of 33 μm thickness.

Before coating the stationary phase of polymeric fullerene, the fiber was treated with 98% sulfuric acid and washed thoroughly with methanol. An electric dryer dried the bare fused-silica fiber. Then it was drilled at a uniform rate through a pore in a vial filled with a coating liquid containing 5% photosensitive reagent (dicumyl peroxide, DCP) in polymeric fullerene dissolved in heptane solution. The fiber was illuminated through UV radiation for 15 min. After that, it was cut to a 1-cm length and stuck on the inner needle of the SPME probe by high-temperature epoxy resin. The fiber was conditioned in the GC injection port at 300°C for 1–2 h.

2.4. Headspace extraction procedure

The sample vial containing a magnetic spin bar was sealed with a septum in order to prevent evaporation of volatile organic compounds. The vial was placed in a heating bath for a given time before the SPME sampling to reach thermal equilibrium. During extraction, the vial septum was pierced with the protecting needle and the fiber exposed to the headspace above the condensed phase.

3. Results and discussion

SPME is especially suitable for headspace sampling. Chemicals in the headspace over a condensed phase are directly extracted and concentrated in the SPME polymer film, which makes this technique advantageous over conventional techniques for headspace analysis.

The coating is designed aiming at π – π interaction

between aromatic compounds and fullerene, so two groups of analytes were selected to investigate the performance of the PF coating. BTEX is always used to evaluate the properties of coating as standard compounds. To the naphthalene congeners and biphenyl, the number of aromatic rings increase and is more similar to the fullerene molecule to some degree. It can be expected that effective interaction would be strengthened. So the above-mentioned compounds are chosen for evaluation of the PF coating properties.

The extraction equilibration is affected by various factors, such as the nature of the coating on fiber, the extraction time, the extraction temperature. It is important to optimize the extraction conditions for each compound. Extractions of BTEX and naphthalene congeners were performed at 30°C . The solution was vigorously mixed with a magnetic stirrer, the speed of which was kept constant for all extractions.

Once sampling is terminated, the fiber is drawn back into the syringe needle and then ready for thermal desorption in the GC injector, where the analytes are desorbed from the coating and enter the GC column for separation and analysis.

3.1. Equilibrium extraction time and desorption time

The headspace of solution was exposed for times that ranged from 1 to 15 min while undergoing vigorous agitation. Under agitation conditions, the experimental results indicated that the equilibrium time was short, approximately 3 min for benzene, toluene and ethylbenzene, 5 min for *p*-xylene and 8 min for *o*-xylene. Stirring may be beneficial for HS-SPME for it facilitates the mass transfer from the condensed phase to the gaseous phase.

For BTEX, the desorption process took much less time than extraction and can be completed within 0.5 min at 250°C . After the desorption step, the fiber was desorbed once again to avoid carryover effects in subsequent analyses. The experimental results indicated that analytes had been completely removed from the fiber.

Fig. 1 shows the extraction time profiles of the naphthalene congeners by use of the PF coating. The time to reach equilibration is about 90 min for the five naphthalene congeners. However, an absorption

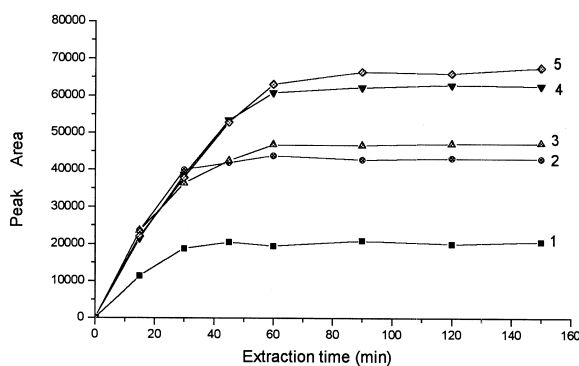


Fig. 1. Response: extraction time profiles of the naphthalene congeners for the PF coating. 1=Naphthalene, 2=2-methylnaphthalene, 3=1-methylnaphthalene, 4=2,6-dimethylnaphthalene, 5=2,3-dimethylnaphthalene. Concentration of each compound, 1 mg l^{-1} , exposure temperature, 30°C .

time of 10 min was selected for subsequent analysis so that the analysis time was shortened and the response was acceptable. For chemicals with relatively low volatility, it takes a long time to reach partition equilibrium during HS-SPME. Quantitative measurements before reaching the equilibrium will save a lot of experimental time. The desorption of naphthalene congeners was carried out at 280°C . With an increase of the injection temperature from 250 to 280°C , the high-boiling-point chemicals can also be completely desorbed in 0.5 min.

3.2. Extraction quantity and selectivity

3.2.1. Extraction temperature

The extraction temperature is the next parameter to be optimized. The effect on the amount of analytes absorbed was studied by exposing the fiber to the sample for 10 min at temperatures ranging from 20 to 50°C . From Fig. 2, an increase in the peak area of naphthalene congeners can be observed when temperature increases. Increasing the extraction temperature enhances the diffusion of the analytes. However, at a temperature over 30°C , there is a decrease in the amount of naphthalene, biphenyl and 1-methylnaphthalene extracted. This is because the absorption of the analytes by the fiber is an exothermic process and high temperatures can decrease the amount extracted. For this reason, the plot of the area peak versus the absorption temperature

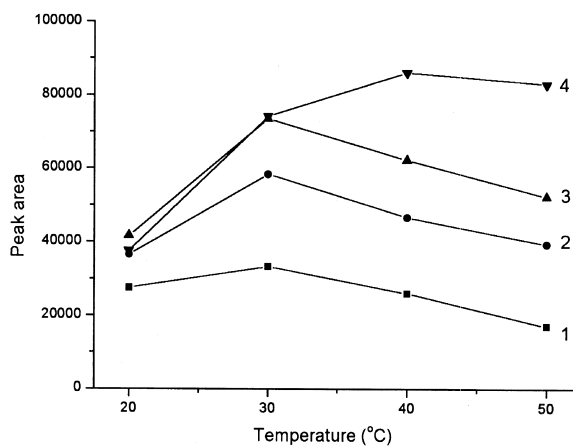


Fig. 2. Response: the influence of temperature for the PF coating. 1=Naphthalene, 2=biphenyl, 3=1-methylnaphthalene, 4=2,6-dimethylnaphthalene, Concentration of each compound, 1 mg l^{-1} , extraction time, 10 min.

usually exhibits a maximum for some analytes. An extraction temperature of 30°C was selected since at this temperature the peak area for most compounds was a maximum.

3.2.2. Agitation and NaCl addition

The “salting out” effect is widely used to increase the effectiveness of an organic solvent to extract organic compounds dissolved in water. NaCl is often added to the sample in order to increase the ionic strength and enhance the amount of analyte extracted by the fiber. The results obtained show that the peak areas increase significantly when salt is added compared with agitation (Fig. 3). NaCl has a distinct effect on each compound. The maximum peak areas of these compounds were obtained when the sample solution was saturated with NaCl and stirred with a magnetic stirrer bar, so this condition was selected for subsequent experiments.

3.2.3. Comparison of extraction quantities per unit volume

The comparison different fibers are shown in Fig. 4. The PF coating has the maximal extraction quantities per unit volume for BTEX though the four coating revealed similar tendency for selectivity.

Fig. 5 reports the comparison of the different coatings for the quantities of naphthalene congeners and biphenyl. The PF coating has the maximal

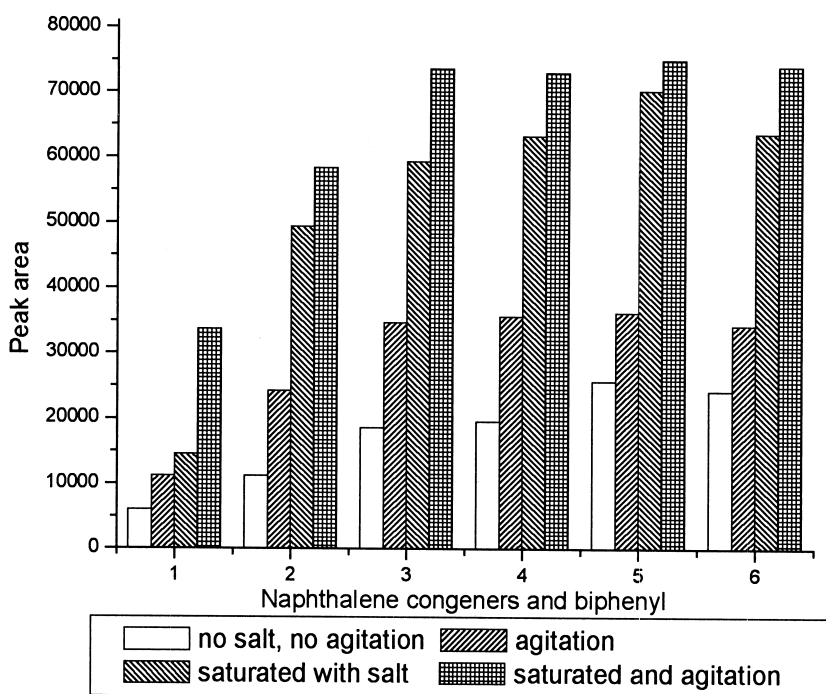


Fig. 3. Response: the influence of salt-out effect and agitation for the PF coating. 1=Naphthalene, 2=biphenyl, 3=2-methylnaphthalene, 4=1-methylnaphthalene, 5=2,6-dimethylnaphthalene 6=2,3-dimethylnaphthalene. Concentration of each compound, 1 mg l^{-1} , exposure temperature, 30°C , extraction time, 10 min.

extraction quantity per unit volume. The PF coating extract of naphthalene congeners gave results superior to those of the non-polar commercial PDMS-coated fiber. As can be seen from Fig. 5, the extracted amount of analyte increases as aromatic ring number increases.

To BTEX and naphthalene congeners, the PF coating exhibited a high extraction efficiency in contrast to the other three coatings.

Once the SPME parameters were optimized, the quantities of PAHs extracted per unit volume by the PF coating are significantly superior to that of the commercial PDMS coating (Fig. 6). It has a minimum peak area for naphthalene, which has the lowest boiling point. Perhaps it has a smaller partition coefficient than the other aromatic compounds at 60°C as well as benzene in BTEX. However, for the PF coating the ratio of the naphthalene peak area against biphenyl is 0.367, for commercial PDMS it is 0.235. This indicated that the coating containing C_{60} possesses selectivity for planar naphthalene. It is well known that the dispersion forces play a key role

in the extraction process by using non-planar coating. In this case, the π - π interaction between the phenyl rings of the analyte molecule and those of the bonded C_{60} molecule took place effectively.

The F number is one of the molecular size descriptors for organic aromatic compounds, defined as:

$$F = (\text{number of double bonds}) \\ + (\text{number of primary and secondary carbons}) \\ - 0.5 \times (\text{number of non-aromatic rings})$$

The response of planar acenaphthylene extracted by the PF coating was higher than non-planar biphenyl even though they have same F number. The results suggests that the PF coating has a special selectivity for planar molecules. As can be observed from Fig. 6, acenaphthylene, fluorene, phenanthrene, fluoranthene have the maximum amount extracted by the PF coating. It should be noted that these compounds are a kind of the planar PAH isomers which contain a partial structure similar to that of the C_{60}

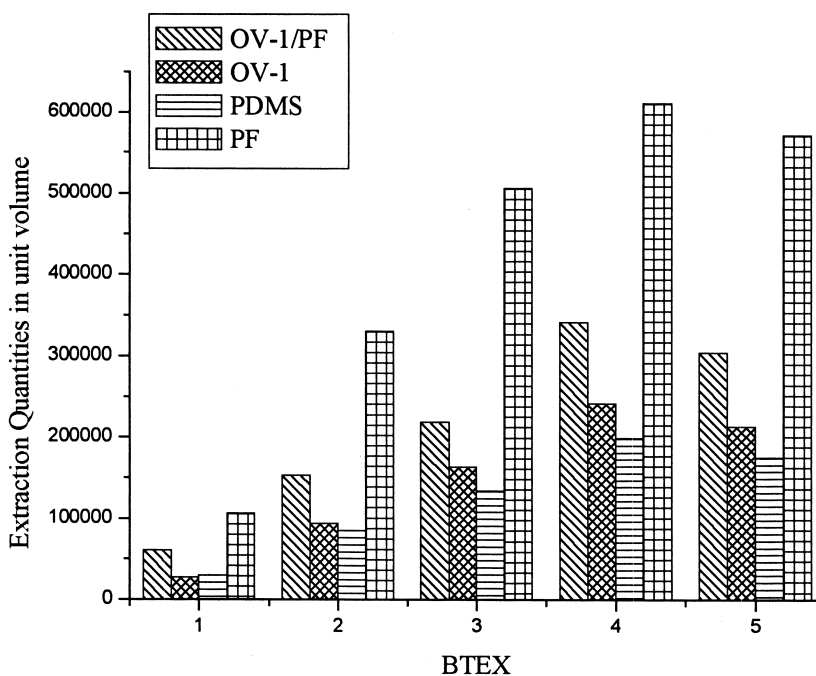


Fig. 4. Comparison of the quantities of BTEX extracted per unit volume by the four different coatings. 1=Benzene, 2=toluene, 3=ethylbenzene, 4=*p*-xylene, 5=*o*-xylene. Concentration of each compound, 10 mg l^{-1} ; exposure time, 10 min; exposure temperature, 30°C .

molecule. The configuration of phenanthrene takes on a horn shape and the π -electron pair is confined in the middle ring. The property of the phenanthrene middle bond resembles the character of alkenes. The interaction between the C_{60} moiety and phenanthrene is strong so that the response of phenanthrene is the highest among the eight PAHs. As has been mentioned, the coatings containing C_{60} have demonstrated good recognition ability for planar molecules. Because biphenyl and terphenyl are non-planar molecules, their peak areas are small. As a non-polar molecule, *m*-terphenyl has the highest response among the three compounds. It may be considered a result of a small curvature of configuration.

PAHs are high boiling point, low volatility and conjugated compounds. The chromatographic separation results indicate that the PF coating achieves the special selectivity and performance for concentration of PAHs. Based on the interaction mechanism of π - π complex interaction or unique ball shaped combination, PAHs undergo more pronounced interaction with the C_{60} ligand. It is also showed that thin

fibers are more suitable for extraction of high-molecular-mass PAHs.

3.2.4. Linearity, sensitivity, precision and lifetime of the fiber

Limits of detection (LODs), linearity and precision were investigated and summarized in Table 1. Linearity extended in the range of $5000\sim 10 \mu\text{g l}^{-1}$ for BTEX and correlation coefficients were above 0.99. The LODs calculated via three times the background noise level are between $0.8\sim 2.21 \mu\text{g l}^{-1}$. The precision of the method, expressed as the relative standard deviation (RSD), was ideal and less than 5%.

Linear calibration curves could be obtained for concentrations ranging from 0.1 to $100 \mu\text{g l}^{-1}$ with a correlation coefficient of 0.998 for naphthalene congeners. Detection limits depend on instrumentation, the film thickness of coating, extraction under the optimum condition, and can be as low as $0.04 \mu\text{g l}^{-1}$. The RSDs are below 6.8%, which shows acceptable precision.

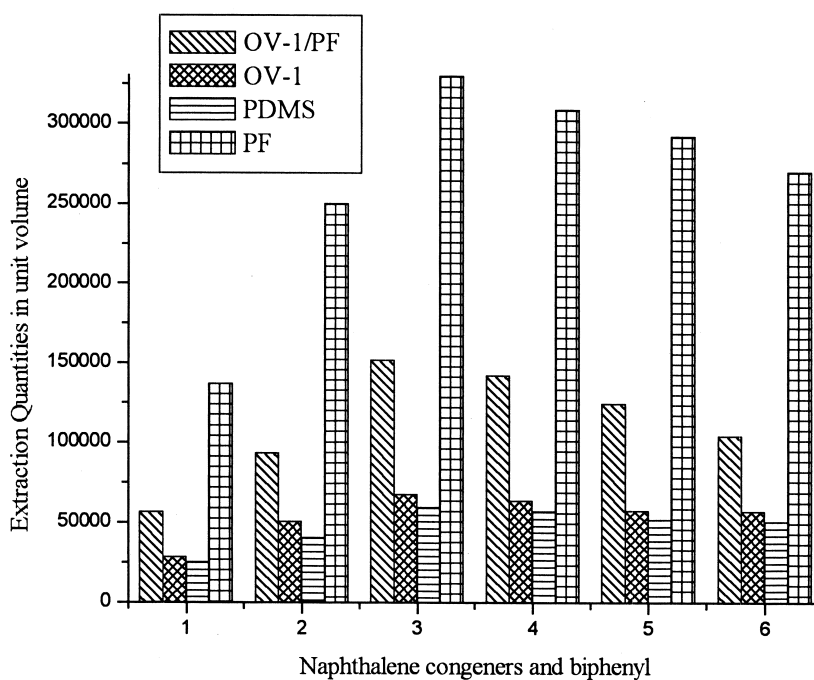


Fig. 5. Comparison of the quantities of naphthalene congeners and biphenyl extracted per unit volume by use of four different coatings. 1=Naphthalene, 2=biphenyl, 3=2-methylnaphthalene, 4=1-methylnaphthalene, 5=2,6-dimethylnaphthalene, 6=2,3-dimethylnaphthalene. Concentration of each compound, 1 mg l^{-1} ; exposure time, 30 min; exposure temperature, 30°C .

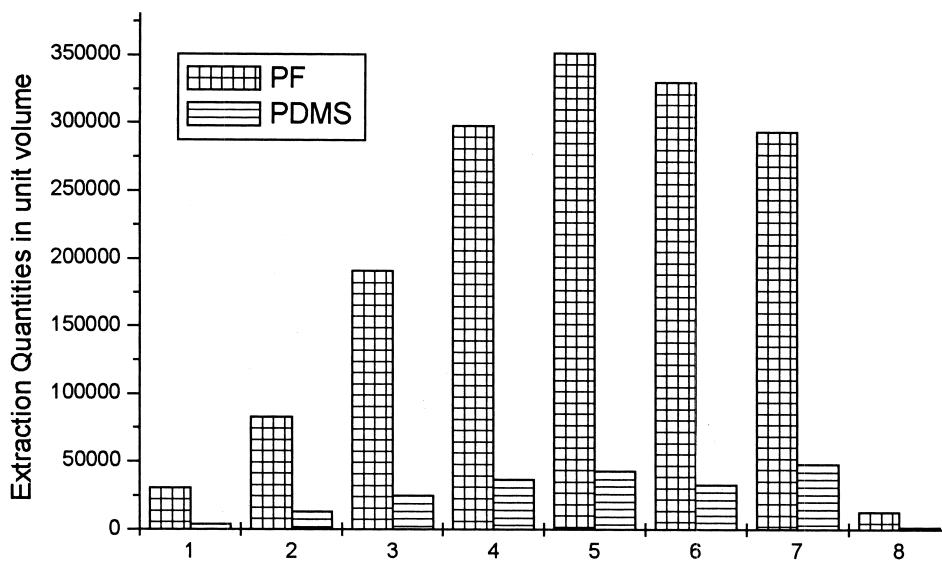


Fig. 6. Comparison of the quantities of PAHs extracted per unit volume by the PF coating and the PDMS coating. 1=Naphthalene, 2=biphenyl, 3=acenaphthylene, 4=fluorene, 5=phenanthrene, 6=fluoranthene, 7=*m*-terphenyl, 8=*p*-terphenyl. Concentration of each compound, 0.1 mg l^{-1} , exposure temperature, 60°C , exposure time, 30 min.

Table 1
BTEX, naphthalene congeners and biphenyl's linear range and detection limits by HS-SPME at 30°C for PF coating

Compound	Linear range ($\mu\text{g l}^{-1}$)	Correlation coefficient	Detection limits ($\mu\text{g l}^{-1}$)	RSD ($n = 6$) (%)
Benzene	5000~10	0.9974	2.21	4.20
Toluene	5000~10	0.9971	0.63	1.52
Ethylbenzene	5000~10	0.9996	1.20	4.60
<i>p</i> -Xylene	5000~10	1	0.80	3.72
<i>o</i> -Xylene	5000~10	1	0.83	2.68
Naphthalene	100~0.1	0.9983	0.04	4.14
2-Methylnaphthalene	100~0.1	0.9986	0.1	6.80
1-Methylnaphthalene	100~0.1	0.9987	0.08	5.97
Biphenyl	100~0.5	0.9986	0.3	5.35
2,6-Dimethylnaphthalene	100~0.5	0.9989	0.4	3.64
2,3-Dimethylnaphthalene	100~0.5	0.9987	0.33	4.70

The thermal stability and life span are the crucial characters of coating in practical application. An important operation in SPME fiber technology is the creation of a stable stationary phase coating at the fiber end. Generally, for most commercial PDMS fibers, the thermal stability of such coating is less than 270°C which limits the molecular mass range of analytes that can be handled by SPME–GC, and the lifetime of commercial fibers is short in the range of 50~100 times. After use of the two coatings containing C_{60} more than 150 times at 280°C it was still stable and reusable. The amount of coatings on the fiber did not change apparently. The RSDs of the PF coating are less than 3% for the same compound during different periods. It should be pointed out that the PF-coated fiber did not show any sign of bleeding even exceeding the 170th operation at 280°C. It means the fiber containing C_{60} can be used in the analysis of high-molecular-mass compounds at higher temperature. The thermal stability and lifetime of PF coatings are better than that of the

OV-1/PF coating [14]. The content of C_{60} in the coating increasingly enhances the thermal stability of fiber and prolongs its lifetime (Table 2).

The interfiber comparison study was performed with compound concentrations of 1 mg l⁻¹. The data is shown in Table 3. An interfiber estimation of method precision for the different fibers of the same PF coating yield less than 4% RSD. The reproducibility of interfiber for the OV-1/PF coating is less than 7% RSD. The reproducibility of the coating containing C_{60} is better than the data published in the literature, which is less than 9% for the commercially available PDMS. The precision of interfiber for the OV-1/PF coating is inferior to that of the PF coating. The mixing process of the two different stationary phases is not completely uniform, that leads to the results.

3.3. Theory

According to the theoretical treatment for the HS-

Table 2
The extraction quantities and precision of the PF coating at 280°C under different periods

Compound	Peak area						
	No. of extraction procedures						
	50	100	RSD (%)	150	RSD (%)	181	RSD (%)
Naphthalene	18 258	18 042	0.84	18 360	0.89	15 341	8.26
2-Methylnaphthalene	33 468	33 998	1.11	35 163	2.53	32 055	3.83
1-Methylnaphthalene	34 335	34 912	1.18	34 937	0.98	32 460	3.42
2,6-Dimethylnaphthalene	29 918	28 468	3.51	29 074	2.50	26 308	5.42
2,3-Dimethylnaphthalene	28 709	29 014	0.75	29 003	0.60	26 211	4.80

Table 3
The comparison of interfibers

Compound	Fiber	The OV-1/PF coating		The PF coating		RSD ($n=4$) (%)	
						OV-1/PF	PF
Naphthalene	1	9686	9842	17 258	17 963	5.36	2.35
	2	10 211	10 856	18 301	18 125		
Biphenyl	1	14 345	17 367	24 466	25 555	5.35	3.14
	2	15 642	13 759	25 308	26 987		
2-Methylnaphthalene	1	20 467	21 754	32 487	33 012	6.73	2.63
	2	22 648	23 789	33 468	34 512		
2,6-Dimethylnaphthalene	1	25 783	26 791	29 918	31 125	2.34	2.17
	2	28 197	26 143	29 074	30 128		

SPME dynamic process proposed by Ai [15–17], it is investigated whether the quantities of the HS-SPME method are feasible under non-equilibrium situations by using of the PF coating. The equations we will discuss in this paper are:

$$n = [1 - \exp(-a_h t)] n_e \quad (1)$$

$$n = \alpha \cdot [1 - \exp(-at)] + \beta \cdot [1 - \exp(-bt)]$$

$$\alpha + \beta = n_e = \frac{K_2 K_1 V_f V_s}{K_2 K_1 V_f + K_1 V_h + V_s} \cdot C_0 \quad (2)$$

where n is the amount of analyte extracted by the coating before partition equilibrium, n_e is the amount of analyte extracted by the SPME coating when partition equilibrium is attained, C_0 is the initial concentration of analyte, K_1 and K_2 are equilibrium partition constants for the analyte between the condensed phase and its headspace and between the headspace and the coating, t is the extraction time, a_h , a and b are complicated parameters that determine how fast the equilibrium can be reached. Eqs. (1) and (2) are proposed in the non-equilibrium situation of the steady-state and non-steady-state mass transfer for HS-SPME, respectively.

There is an exponential term between the amount of extracted analyte in the coating before partition equilibrium and extraction time. On the other hand, once the conditions of extraction process and time are held constant, the extracted amount of analytes before partition equilibrium in coating has a directly proportional relationship with its initial concentration

in the condensed phase. The lower-boiling-point compounds, which include BTEX and naphthalene congeners, exhibited good linear relationship in the range of concentration investigated. To higher analytes of interest, for instance, acenaphthylene and phenanthrene, it is important to study the linear relationship for the purpose of quantitation under non-equilibrium conditions.

A set of aqueous solutions were prepared with the stock solution aimed at studying the relationship between the extracted amount n and the initial solution concentration C_0 before reaching partition equilibrium. Fluorine is used as internal standard. The data in Fig. 7 were obtained via fluorine at a 10 min sampling time. Solid and dashed straight lines were attained after a linear fitting. Linear correlation coefficients (r) are better than 0.99 for acenaphthylene and phenanthrene. The linearly proportional relationship between n and C_0 verifies that quantification is feasible using the PF coating when the sampling time was far shorter than that required partition equilibrium.

4. Conclusions

The coating containing C_{60} used in SPME is simple and convenient method for determination of semi-volatile compounds. It affords high sensitivity and selectivity for aromatic compounds. Compared with laboratory-prepared OV-1 and commercially available non-polar PDMS, the thermal stability,

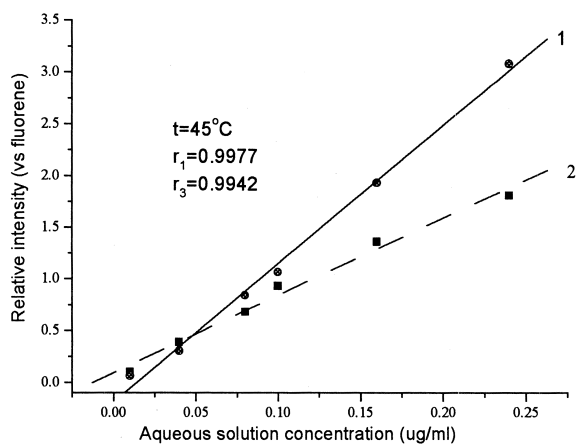


Fig. 7. Extraction-time profile of headspace SPME over aqueous solutions at 45°C. 1=Acenaphthylene, 2=phenanthrene. Extracted amount n is plotted against the initial concentration in aqueous solutions, C_0 . The sampling time was 10 min, which is shorter than the time required to reach partition equilibrium.

reproducibility and lifetime of the two coatings containing C_{60} are advantageous over the similar polarity of the commercially available PDMS. After use of the PF coatings for more than 150 times at 280°C it was still stable and reusable. The amount of analytes extracted on the fiber did not change apparently. The reproducibility is also good (RSD < 6.73% for the OV-1/PF coating, < 3.14% for PF coating, in the literature is RSD < 9% for the commercially available PDMS). The results clearly indicate that the coatings containing C_{60} have a unique molecular recognition capability for PAHs analyses. Once the extraction process is invariable and the extraction time held constant, including steady and

non-steady state under non-equilibrium conditions, the quantification method of HS-SPME is feasible.

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