Use of Polymeric Fullerene as a New Coating for Solid-Phase Microextraction

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Key Words

Gas chromatography
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Summary

The use of polymeric fullerene to coat the fiber used in solid-phase microextraction (SPME) is described. The efficiency, sensitivity, and reliability of the new coated fibers have been investigated for the extraction of three kinds of sample, BTEX, naphthalene congeners, and phthalic acid diesters, from the headspace of water samples. Detection limits at the ng L^{-1} to µg L^{-1} level were achieved by use of GC–FID. A wide linear range was obtained with precision typically below 12% relative standard deviation for phthalic acid diesters. The effects on extraction efficiency of factors such as addition of salt, stirring, and exposure time were also studied.

Introduction

Solid-phase microextraction (SPME) is a relatively new technique that has recently been developing rapidly. It is a convenient and efficient method of extraction compared with more complex sample-preparation techniques. It has become increasingly popular for the analysis of volatile and semivolatile compounds. The analytes are adsorbed on a fused silica fiber coated with stationary phase. The fiber is then introduced into the injector of a gas chromatograph and the analytes are desorbed thermally and analyzed by a suitable GC method. It is inexpensive, solvent-free, simple, rapid, easily automated and reliable. This technique has been used for chemical analysis in fields as diverse as forensic and biomedical analysis, environmental monitoring, and flavour, fragrance, and food chemistry. The strength of the technique is its simplicity, as a result of integrating sampling, extraction, concentration, and sample introduction. The development of this technique has, however, been hindered by the limited variety of SPME coatings in practical application [1–5].

Since two physicists, Huffman and Krätscher, devised a method for producing macroscopic amounts of fullerenes in 1990, the number of publications on this class of material has increased every year. The discovery of the material properties of the fullerenes and their derivatives, and the development of efficient processes for separating fullerene mixtures, have increasingly attracted the interest of scientists. The results obtained can be summarized: (i) C_{60} is an exceptionally stable molecule that adds most reaction partners reversibly only; (ii) fullerene and most fullerene derivatives are only slightly soluble [6]; (iii) fullerene and its derivatives can be used as novel chromatographic materials.

Surface-linked $C_{60/70}$-polystyrene divinylbenzene beads have been investigated by Stalling et al. as a new chromatographic material for enrichment of coplanar PCBs [7]. They confirmed the affinity of this stationary phase for coplanar PCB constituents and the analytical potential of C_{60} fullerene as an adsorbent. Bianco et al. have shown that silica-bonded fullerene derivatives enable molecular recognition [8]. This prompted us to investigate the interaction between fullerene and coplanar compounds. Fullerene and its derivatives used as chromatographic materials result in high column efficiency, wide operating temperature range (80–360 °C), good thermal stability, and excellent selectivity. As stationary phases they have unique separation selectivity for high boiling, low volatility aromatic compounds that degrade slowly in the environment.

In this study we have synthesized a polymeric fullerene and used it as a coating for solid-phase microextraction. Fibers coated with this material result in higher extraction efficiency and greater sensitivity for aromatic compounds and phthalic acid diesters than commercially available PDMS and home-made OV-1 fibers.

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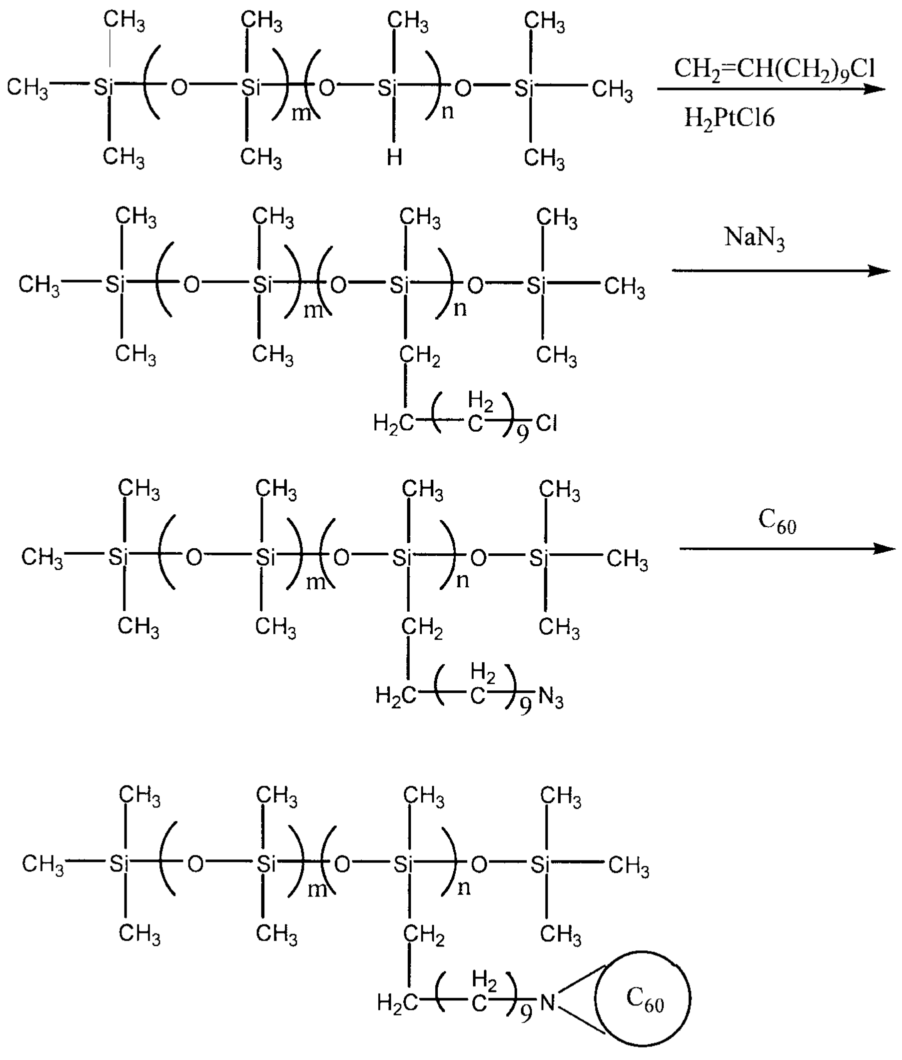

Figure 1. Steps in the synthesis of polymeric fullerenes.

Table I. The types of fiber used.

Fiber	Coating	Film thickness (μm)
PDMS	Commercially available PDMS	100
OV-1	Polysiloxane	74
OV-1/PF	Mixture of polysiloxane and polymeric fullerene (ratio 4:1)	40
PF	Polymeric fullerene	33

Experimental

Chemicals

All solvents used in this study were analytical-reagent grade. Three stock solutions – BTEX (benzene, toluene, ethylbenzene, *o*-xylene, and *p*-xylene), naphthalene congeners (naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, 2,3- dimethylnaphthalene, and 2,6-dimethylnaphthalene), and phthalic acid diesters (dibutyl phthalate, dipentyl phthalate, dihexyl phthalate, dioctyl phthalate, and dinonyl phthalate) were prepared by dissolving each compound (10 mg) in methanol (10 mL) in a volumetric flask. These standard solutions were diluted with deionized water to give a $10\,\mathrm{mg\,L^{-1}}$ BTEX solution, a $1\,\mathrm{mg\,L^{-1}}$ solution of naphthalene congeners, and a $4\,\mathrm{mg\,L^{-1}}$ solution of phthalic acid diesters. A PVC plastic product containing DEHP was provided by Import & Export Commodity Inspection Bureau.

Synthesis of Polymeric Fullerene

Polymeric fullerene was synthesized according to a procedure described elsewhere [9, 10] as indicated in Figure 1.

Instruments and Apparatus

SPME devices were obtained from Supelco (Bellefonte, PA, USA) and were also prepared by modification of a commercial SPME fiber holder and assembly.

Gas chromatography was performed with a GC-900 gas chromatograph (Shanghai Ke Chuang, China) with a capillary split injection system and flame ionization detector. The equipment also included a Shimadzu Chromatopac model CR3A data processor. Nitrogen was the carrier gas at a linear velocity of 13–14 cm s^{-1}. The injection split ratio was 17:1 and the injector and detector temperatures were maintained at 250–320 and 250 °C, respectively. BTEX analysis was performed with a 25 m × 0.32 mm i. d. capillary column coated with an open-ring crown ether. Columns (15 m × 0.25 mm) coated with OV-1 and OV-1701, respectively, were employed for analysis of phthalic acid diesters and naphthalene congeners including biphenyl.

Preparation of Fiber

Four fibers were used in this study (Table I): a commercially available fiber coated with a 100-μm film of polydimethylsiloxane (PDMS), a home-made fiber coated with a 74-μm film of OV-1, a fiber coated with a 40-μm film of a 4:1 mixture of polysiloxane (OV-1) and polymeric fullerene, and a fiber coated with a 33 μm film of polymeric fullerene. The OV-1 coating was prepared to enable characterization of the performance of the fiber coated with a mixture of polymeric fullerene and polysiloxane.

Extraction Procedure

The SPME unit consists of a length of fused silica fiber coated with one or more of a several different phases and attached to a stainless steel plunger and holder. The depth of penetration of the coated wire in the GC injector can be adjusted directly by using the scale near the barrel window. The SPME process involves two steps, partitioning of analytes between the coating and the sample matrix and desorption of the analytes from the coating into an analytical instrument. The technique involves immersing the fiber in either the liquid sample or the gas headspace above it. The rate of mass transfer is faster in the

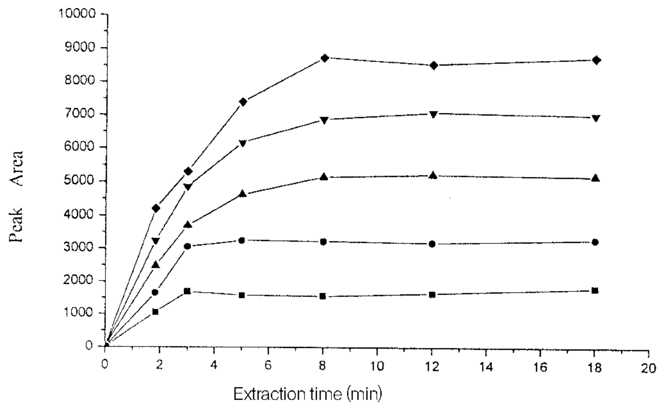

Figure 2. Response–extraction time profile of BTEX for the mixed OV-1/ polymeric fullerene coating under agitation conditions: ■, benzene; ●, toluene; ▲, ethylbenzene; ▼, *p*-xylene; ◆, *o*-xylene. Concentration of each compound, 10 mg L^{-1}, exposure temperature, 30 °C.

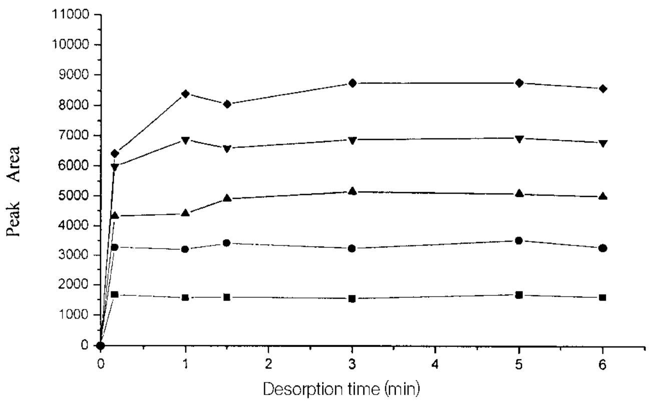

Figure 3. Response–desorption time profile of BTEX for the mixed OV-1/ polymeric fullerene coating: ■, benzene; ●, toluene; ▲, ethylbenzene; ▼, *p*-xylene; ◆, *o*-xylene.

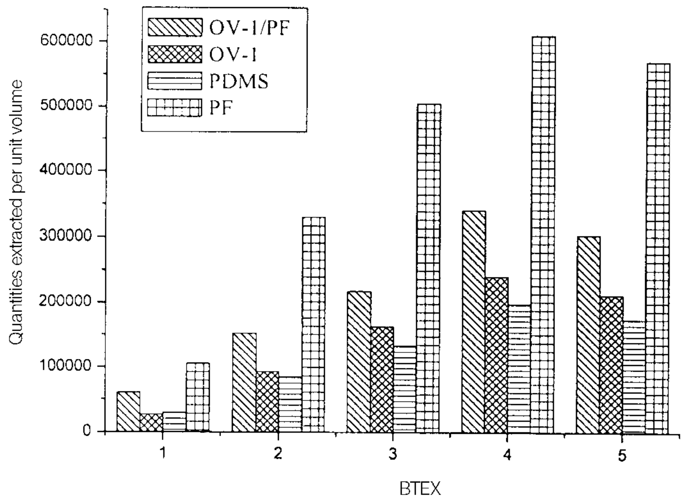

Figure 4. Comparison of the quantities of BTEX extracted per unit volume by the four different coatings: **1** = benzene, **2** = toluene, **3** = ethylbenzene, **4** = *p*-xylene, **5** = *o*-xylene. Concentration of each compound, 10 mg L^{-1}; exposure time, 15 min; exposure temperature, 30 °C.

gas phase than in the liquid, and headspace sampling eliminates complex matrix effects because the fiber is not in contact with the sample matrix. Headspace sampling also prolongs the useful life of the fiber. In this work headspace SPME was used in combination with GC. Before extraction, the SPME fibers were conditioned at 250 °C 1 h by insertion into the GC injection port.

After establishment of the equilibrium between the headspace and aqueous solution, the gaseous headspace was sampled by means of different SPME fibers. Before sampling the fiber was drawn back into the syringe needle. When the needle had penetrated the septum of the sample vial the fiber was pushed out of the needle and exposed for a fixed time and at a fixed temperature to the headspace generated in the sample vial. After extraction, the fiber was withdrawn into the needle and the needle was removed from the sample vial. The fiber was then ready for thermal desorption in a GC injector at given temperature; here the analytes were desorbed from the coating and entered the GC column for separation and analysis. The completeness of desorption was checked by blank runs performed on the fiber after previous desorption.

Results and Discussion

Generally speaking, diffusion of the analyte into the air is the limiting factor in mass transfer into air and thus on to the fiber. Although heating the sample increases diffusion into the air, if the fiber is exposed to higher temperatures, the mass loading decreases, which results in lower sensitivity, because the partition coefficient decreases as the temperature of the fiber increases. To avoid this the temperature of water bath was held at 30 °C during extraction of BTEX and the naphthalene congeners.

Profiles of detector response against extraction time for the benzene congeners are shown in Figure 2. The mixed OV-1/ polymeric fullerene coating was used to obtain the results in Figure 2. In the extraction of BTEX equilibrium is reached after approximately 10 min in the absence of mixing. (Equilibrium is reached when a further increase in extraction time does not result in a significant increase in the detector response.) The desorption process took much less time than this (Figure 3).

As is apparent from Figure 4, the use of the mixed coating to extract nonpolar BTEX gave results superior to those from the home-made fiber coated with OV-1 or from the commercial PDMS-coated fiber. The selectivity of the PDMS and home-made OV-1 coatings for BTEX were similar although greater quantities were extracted by use of the home-made OV-1 coating.

Response–extraction time profiles for a standard solution of an homologous series of naphthalenes were obtained under different sampling conditions. Under static sampling conditions the analytes are adsorbed by the coating and eventually equilibrium is reached. The time to reach equilibrium depends on the kinetics of the overall process of uptake of analytes by the fiber, which is based in part on the rate of diffusion of the analyte in the air and the distribution coefficient of the analyte between the air and the coating. Vigorous

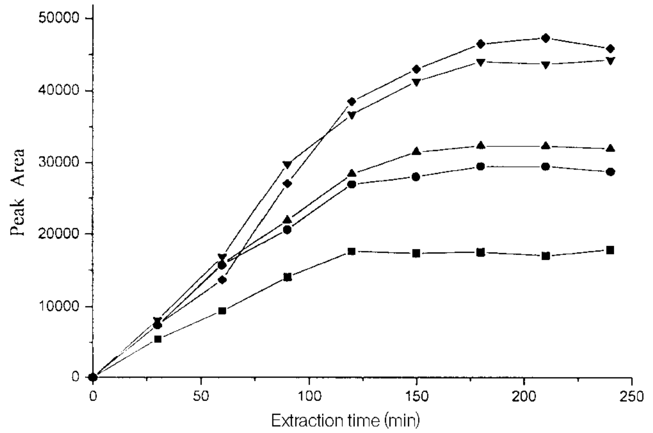

Figure 5. Response–extraction time profiles of the naphthalene congeners for the mixed OV-1/polymeric fullerene coating with no agitation: ■, naphthalene; ●, 2-methylnaphthalene; ▲, 1-methylnaphthalene; ▼, 2,6-dimethylnaphthalene; ◆, 2,3-dimethylnaphthalene. Concentration of each compound, 1 mg L^{-1}, exposure temperature, 30 °C.

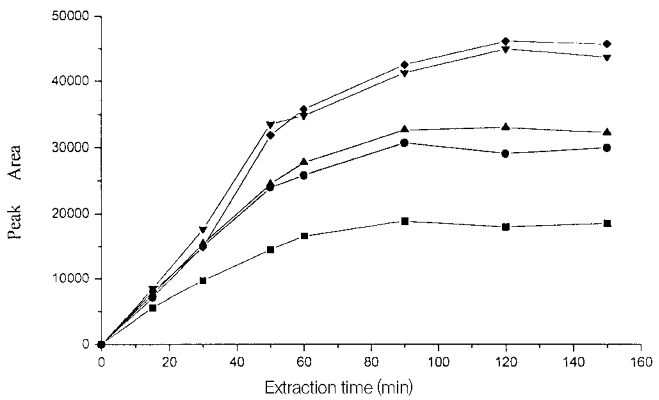

Figure 6. Response–extraction time profiles of the naphthalene congeners for the mixed OV-1/polymeric fullerene coating under agitation conditions: ■, naphthalene; ●, 2-methylnaphthalene; ▲, 1-methylnaphthalene; ▼, 2,6-dimethylnaphthalene; ◆, 2,3-dimethylnaphthalene. Concentration of each compound, 1 mg L^{-1}, exposure temperature, 30 °C.

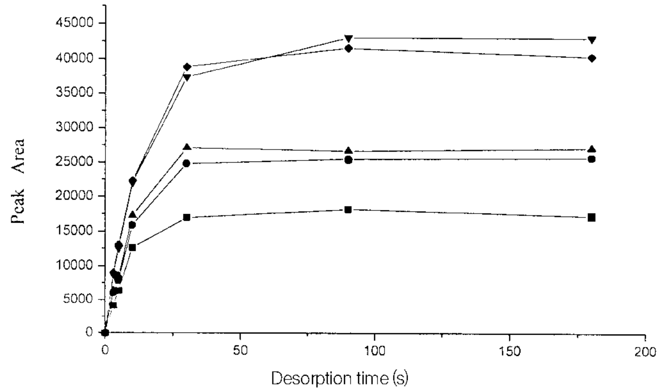

Figure 7. Response–desorption time profiles of the naphthalene congeners from the mixed OV-1/polymeric fullerene coating: ■, naphthalene; ●, 2-methylnaphthalene; ▲, 1-methylnaphthalene; ▼, 2,6-dimethylnaphthalene; ◆, 2,3-dimethylnaphthalene.

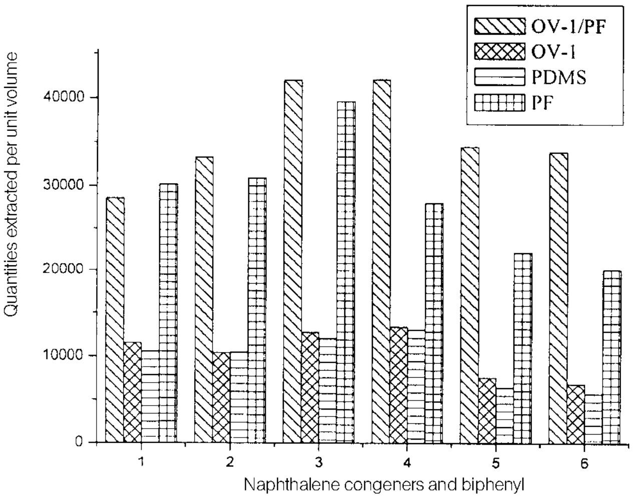

Figure 8. Comparison of the quantities of naphthalene congeners and biphenyl extracted per unit volume by use of four different coatings: **1** = naphthalene, **2** = 2-methylnaphthalene, **3** = 1-methylnaphthalene, **4** = biphenyl, **5** = 2,6-dimethylnaphthalene, **6** = 2,3-dimethylnaphthalene. Concentration of each compound, 1 mg L^{-1}; exposure time, 30 min; exposure temperature, 30 °C.

agitation of the analyte mixture and matrix has been shown to be ideal for studying analyte concentrations in aqueous systems, both by direct extraction and by extraction from the headspace. In headspace SPME stirring might be beneficial because it facilitates mass transfer from the liquid to the gaseous phase.

Figures 5 and 6 show that agitation significantly reduced the time required to reach equilibrium. Figure 5 shows the response–extraction time profile obtained for the naphthalene congeners by use of the polymeric fullerene coating under static sampling conditions. A better response was obtained for mono- and disubstituted homologs, for which longer extraction times were required than for nonsubstituted naphthalene – as is apparent from Figure 5, the time to reach equilibrium, without stirring, was approximately 120 min for naphthalene and 180–200 min for disubstituted congeners. Displacement of small molecules by larger might occur as extraction time is increased. The naphthalene congeners with side chains were more soluble in the hydrophobic stationary phase and extracted more completely. According to the literature [11–13], the time to reach the extraction equilibrium is not long compared with other fiber coatings.

The response–desorption time profile is illustrated in Figure 7. Thermal desorption of the analytes in the GC injector is the reverse of the adsorption process. Analytes adsorbed by the coating diffuse from the coating into the carrier gas. Because mass transfer of analytes into the carrier gas is very rapid, it should not influence the desorption kinetics. The desorption procedure is, therefore, so rapid it can be completed within 1 min at 280 °C.

The mass adsorbed by the fiber depends on the surface of the coating and on the distribution coefficient K. Analyte distribution coefficients are determined by intermolecular interactions between the solute and the coating; these include hydrocarbon-bonding, acid–base, dipole–dipole, and dipole–induced-dipole interac-

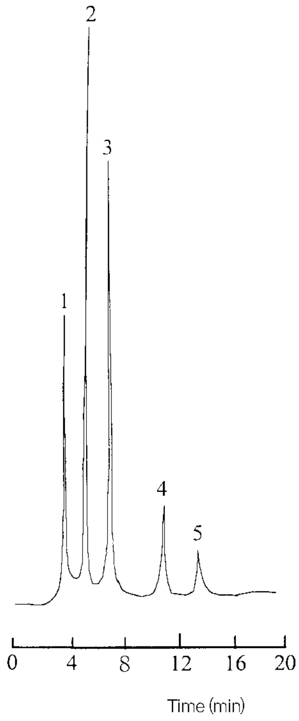

Figure 9. Chromatogram of phthalic acid diesters after desorption at 280 °C from the mixed OV-1/polymeric fullerene coating. The oven and detector temperatures were 250 °C and 280 °C, respectively.

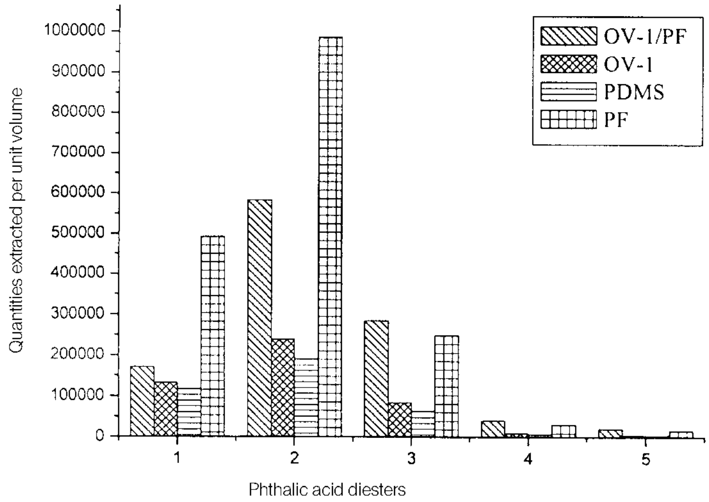

Figure 10. Comparison of the quantities of phthalic acid diesters extracted per unit volume by use of four different coatings: **1** = dibutyl phthalate, **2** = dipentyl phthalate, **3** = dihexyl phthalate, **4** = dioctyl phthalate, **5** = dinonyl phthalate. Concentration of each compound 1 mg L^{-1}; exposure time, 60 min; exposure temperature, 90 °C

tions, and dispersion forces. Dispersion forces are very important for hydrophobic coatings. Polymeric fullerene coatings can participate in π–π interactions with aromatic compounds, including polarizable phenyl groups, because fullerenes can serve as relatively strong electron donors, as a result of the large number of C = C double bonds and aromatic rings.

Equilibrium extraction conditions were not established for the coatings; the conditions used were a compromise between extraction time and extraction efficiency. As expected, greater responses were obtained for non- or monosubstituted naphthalene than for disubstituted naphthalene, owing to their higher vapor pressures (Figure 8). Compared with the results depicted in Figure 4, the polymeric fullerene coating adsorbs naphthalene congeners more strongly than BTEX, possibly because of the strong affinity of the fullerene for aromatic rings. The interaction becomes stronger as the number of aromatic rings increases. Polymeric fullerene fibers were more sensitive and selective than OV-1 for naphthalene congeners. The structures of naphthalene congeners and biphenyl differ because the two aromatic rings of biphenyl are not coplanar. Under nonequilibrium conditions the affinity of the polymeric fullerene coating for biphenyl was less than that for naphthalene and monosubstituted naphthalene; the affinity difference was not as large for the OV-1 coating or for the mixed OV-1/polymeric fullerene coating.

It should be pointed out that experiments used to furnish the results depicted in Figures 9 and 10 were not performed under equilibrium conditions. Increasing the temperature provides the system with more kinetic energy, speeding up mass transfer, so response increases. Use of higher temperatures would not give higher responses under equilibrium conditions, because adsorption is an exothermic process. Thus higher temperatures increase response only under nonequilibrium conditions.

The quantities of phthalic acid diesters extracted by the different coatings are summarized in Figure 10. Phthalic acid diesters are high boiling-point compounds differing only in alkyl chain length. Although the greatest response was obtained from the polymeric fullerene fiber, with these analytes the results obtained from the different coatings did not vary substantially. The behavior of the polymeric fullerene fiber suggests that it could be used for the analysis of aromatic compounds in environmental water samples.

The effect of adding sodium chloride to the sample was also investigated. Saturation of the aqueous solution with NaCl before extraction did not significantly change the response obtained in headspace SPME.

A series of six consecutive extractions was performed on different aliquots of the same sample to evaluate the repeatability of the method. The precision of the method was good – the relative standard deviation was < 12% for all the compounds except dinonyl phthalate. Another series of six extractions of the same sample was performed on different days to evaluate the reproducibility of the method. The precision was also good (relative standard deviation <5%).

To evaluate the linearity of adsorption by the mixed OV-1/polymeric fullerene fiber, calibration plots were constructed after extraction of demineralized water spiked with standard solutions to give samples of different concentration. For naphthalene congeners the plot was linear for concentrations between 0.1 and 200 µg L^{-1}; the correlation coefficient was 0.999. The five-point calibration curve obtained for dipentyl phthalate was linear in the range 0.01 to 500 µg L^{-1} (correlation coefficient 0.998). Limits of detection (Tables II–IV) were calculated from procedural blanks as the concentration corresponding to three times the signal-to-noise ratio.

The thermal stability of the mixed OV-1/polymeric fullerene coating was also evaluated. After use of the coating more than 150 times at 280 °C it was still stable and reusable, as is apparent from Table V. The coating can be used at 300 °C. The amount of coating on the fiber decreased slightly when the coating was conditioned at 320 °C in the GC injection port.

Table II. Limits of detection and linear range for BTEX.

Compound	Linear range (μg L^{-1})	Detection limit (ng L^{-1})	*RSD* (%; *n* = 6)	Correlation coefficient
Benzene	5–1000	2.5	7.30	1
Toluene	5–1000	2.0	3.50	0.9997
Ethyl benzene	5–1000	2.0	5.40	0.9998
p-Xylene	5–1000	1.4	8.54	0.9995
o-Xylene	5–1000	1.7	8.83	0.9997

Table III. Limits of detection and linear range for naphthalene congeners and biphenyl.

Compound	Linear range (μg L^{-1})	Detection limit (μg L^{-1})	*RSD* (%; *n* = 6)	Correlation coefficient
Naphthalene	0.1–200	0.034	4.40	0.9992
2-Methylnaphthalene	0.1–100	0.020	4.36	0.9986
1-Methylnaphthalene	0.1–100	0.018	3.24	0.9998
Biphenyl	0.5–100	0.018	8.54	0.9969
2,6-Dimethylnaphthalene	0.5–100	0.014	8.83	0.9974
2,3-Dimethylnaphthalene	0.5–100	0.013	9.61	0.9983

Table IV. Limits of detection and linear range for analysis of phthalic acid diesters by headspace SPME at 90 °C.

Compound	Linear range (ng L^{-1})	Detection limit (μg L^{-1})	*RSD* (%; *n* = 6)	Correlation coefficient
Dibutyl phthalate	$1-10^6$	0.00033	4.90	0.9948
Dipentyl phthalate	$10-5\times10^5$	0.0005	3.26	0.9999
Dihexyl phthalate	$10-10^5$	0.002	12.10	0.9991
Dioctyl phthalate	10^4-10^7	3.75	7.18	0.8847
Dinonyl phthalate	10^5-10^7	12.5	24.34	0.9812

Table V. Amounts (peak area) of naphthalene congeners desorbed at 280 °C by the mixed OV-1/polymeric fullerene coating.

Compound	Number of extractions				
	20	50	100	150	162
Naphthalene	8736	9586	9693	9458	8168
2-methylnaphthalene	14408	15004	14957	15678	9264
1-methylnaphthalene	14651	15762	15366	15401	9748
2,6-dimethylnaphthalene	15632	18325	17621	17453	10972
2,3-dimethylnaphthalene	13621	15024	14879	14762	10297

Table VI. The amounts (ng mL^{-1}) of DEHP extracted from the headspace by use of different coatings.

Plastic product	Type of fiber used			
	OV-1	OV-1/PF*	PF	PDMS
1	278.23	335.64	379.72	233.91
2	68.28	83.74	90.46	54.49

* Polymeric fullerene.

Headspace Extraction of a PVC Plastic Product

Phthalate esters, synthetic organic chemicals produced and used on a large scale, especially as additives in the manufacture of plastics, have been become global environmental organic pollutants – concentrations in the aquatic environment are approximately 0.1–1000 ppb. They might be harmful to health because they can be gradually accumulated in the human body. Because the longer the chain of the phthalate ester, the lower is the toxicity of this kind of compound, di-(*iso*-ethyl)hexyl phthalate (DEHP) is used widely as an additive in plastic products instead of dibutyl phthalate. It is difficult to determine the concentration of phthalate esters in an aqueous sample, because of low aqueous solubility and low volatility. It is also urgent to overcome the problem of effective and accurate measurement of the concentrations of phthalate diesters in aqueous solutions. SPME has been used for the extractive concentrate of numerous compounds from different matrixes.

A new method, GC–FID combined with headspace SPME, is presented for determination of DEHP in water or in PVC plastics. Two types of PVC (0.2 g) were cut into small pieces and immersed separately in water. The method devised eliminated the disadvantage of the use of trichloromethane, and was not labor-intensive, time consuming, or incompatible with the sample. The fiber coated with the mixture of polymeric fullerene and OV-1 was more efficient than that coated with PDMS – the ratio of detector responses were approximately 1.53 (OV-1/polymeric fullerene:PDMS) and 1.63 (polymeric fullerene:PDMS). The results are summarized in Table VI.

Conclusions

Fibers coated with a mixture of polysiloxane and polymeric fullerene were more long-lived than those coated with other adsorbents and had unique extraction efficiency and sensitivity for aromatic compounds. Initial work using this polymeric fullerene coating has shown the high potential of the material, suggesting that further studies would be valuable.

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