

Progress of Solid-Phase Microextraction Coatings and Coating Techniques

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Abstract

Solid-phase microextraction (SPME) has been popular as an environmentally friendly sample pretreatment technique to extract a very wide range of analytes. This is partly owing to the development of SPME coatings. One of the key factors affecting the extraction performances, such as the sensitivity, selectivity, and reproducibility, is the properties of the coatings on SPME fibers. This paper classifies the materials used as SPME coatings and introduces some common preparation techniques of SPME coating in detail, such as sol-gel technique, electrochemical polymerization technique, particle direct pasting technique, restricted access matrix SPME technique, and molecularly imprinted SPME technique.

Introduction

Solid-phase microextraction (SPME) is a sample preparation technique developed by Pawliszyn et al. (1,2). The process of SPME includes two major operation steps: extraction and desorption. Because both extraction and desorption take place on the coatings, the properties of the coatings determine the performance of SPME. Based on this fact, the development of new coatings has been in great demand for a long time. In recent years, the quantity of papers discussing new coatings for SPME has increased rapidly. In this paper, many of the present coatings are classified, and the common preparation techniques are described in detail.

Discussion

The classifying of coatings

In the book *Applications of Solid-Phase Microextraction*, Górecki (3) sorted the coatings from Supelco (Bellefonte, PA) into two different categories: high-viscosity liquid coatings and solid coatings. He also described the extraction mechanism for both

kinds of coatings, respectively. For liquid coatings, the extraction of analytes is obtained by the absorption, in which the analytes can transfer from the surface of coatings to the inside. This kind of coating includes the common stationary phases polydimethylsiloxane (PDMS) and polyacrylate (PA). For solid coatings, the extraction of analytes is based on adsorption, in which the analytes may only stay on the surface of the coatings. Some composite coatings such as PDMS–divinylbenzene (DVB), carbowax–DVB, carbowax–temple resin, etc. from Supelco are solid coatings with porous surfaces. They can only extract analytes by adsorption. During the extraction process, the mechanism of adsorption is much more complex than absorption.

With the development of the SPME technique, more and more new materials are utilized in the preparation of coatings. More than half of currently available coatings are solid coatings. However, they are divided by the properties of the materials; the solid coatings are multifarious. Based on organic and inorganic types, there are two primary kinds of coatings: organic and inorganic.

Organic coating

Organic polymer materials are the first kind of material used as SPME coatings. Because traditional SPME fibers utilize fused-silica fiber as solid-phase carriers, compared with inorganic materials, organic polymer materials are easier to affix with fiber. In addition, at high temperature, the thermal coefficient of expansions for polymer materials and fused-silica fibers are similar, so it is not easy for the coating to flake off from fibers. Furthermore, a great diversity of structures is another important reason why polymers are very popular.

The analytes extracted on the fiber coating with SPME can be expressed by equation 1. Based on equation 1, for analytes with high K_{fs} values, the amount of extracted analytes (n) is greater than that for those analytes that have a low K_{fs} . In order to increase the K_{fs} value, some organic polymers containing particular functional groups were chosen to increase the interaction between polymers and coatings (4). For example, if the analytes contain $-OH$ or $-NH_2$, the polymer, which includes the groups (such as $-OH$ or $-NH_2$) that can interact with the group of analytes by hydrogen bond, can be selected.

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$$n = K_{fs} V_f V_s C_o / K_{fs} V_f + V_s \quad \text{Eq. 1}$$

where V_f is the volume of the fiber and V_s is the volume of the sample.

Therefore, several kinds of polymers with different functional groups have been synthesized and obtained. Descriptions of the categories of these organic coatings follow.

Coatings based on organosiloxane materials

Polysiloxane is a significant SPME coating material because of its high thermal stability, good film-forming performance, and extensive use as stationary phase for gas chromatography (GC). Also, it will be easier to introduce various functional groups to the side chains than other materials (5). Researchers in the department of Chemistry at Wuhan University have done plenty of work in this field. The group of Wu (6) had prepared a nonpolar coating, polymethylvinylsiloxane (PMVS), which has strong extraction capacity toward nonpolar organic contamination. In the application of extracting benzene derivatives, such as ethylbenzene, *o*-xylene, and *m*-xylene from an aqueous phase, PMVS coating showed better extraction capacity than 100 μm PDMS coating. By using the sol-gel technique, they bonded polyethylene glycols to the backbone of PDMS and successfully extracted benzene derivatives, phenols compounds, phthalate esters, polycyclic aromatic hydrocarbons, and organochloride pesticides by the coating. The results of the experiment proved that this new coating, with polar groups, can extract a number of polar and nonpolar analytes (7). The group of Zeng (8) prepared a polymethylphenylvinylsiloxane coating, which showed better extraction capacity than the commercial extraction fibers in the application of extracting benzene derivatives and polycyclic aromatic hydrocarbons. The group of Wu (9) bonded Fullerene (C60) to the side chain of polysiloxane and applied this coating in extracting benzene derivatives, phthalate esters, and polycyclic aromatic hydrocarbons in water. The result showed that the method had a wide linear range and good sensitivity. They also utilized this fiber in the determination of hydrocarbon compounds and aromatic compounds, though they found that this fiber had a good ability to extract polar compounds (10). In order to produce a more stable structure, they bonded hydroxyls of fullerenes into the skeleton of polysiloxane (Figure 1) by the sol-gel technique and tested the extraction ability of the new coating by extracting polychlorinated biphenyl, polycyclic aromatic hydrocarbon, and aromatic amine, by which they obtained very high sensitivity (11). Zeng et al. (12) also bonded crown ethers to the side chain of polysiloxane to obtain a new coating, which had a very high capacity in extracting phenols compounds. Some crown ethers with other substitutes were also bonded to the side chain of polysiloxane as SPME coatings (Figure 2) (13–18) to extract many kinds of organic compounds, such as organophosphorous pesticides, and showed excellent extraction characteristics for many organic compounds. Recently, the group of Zeng (19) also bonded calyx[4]arenes to the side chain of polysiloxane (Figure 3), which has a good ability to extract a supermolecule, and it also has good selectivity for polar aromatic amine compounds. In addition, they bonded calixarenes in order to extract polar compounds (20,21).

Gongke Li et al. (22) bonded the OH-group of γ -cyclodextrin to the terminal of polysiloxane, pasted it on the surface of a fused-

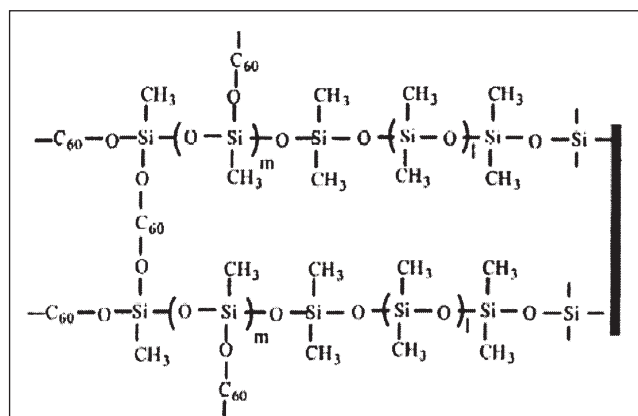


Figure 1. The structure of bonded fullerene polysiloxane stationary phase as an SPME coating.

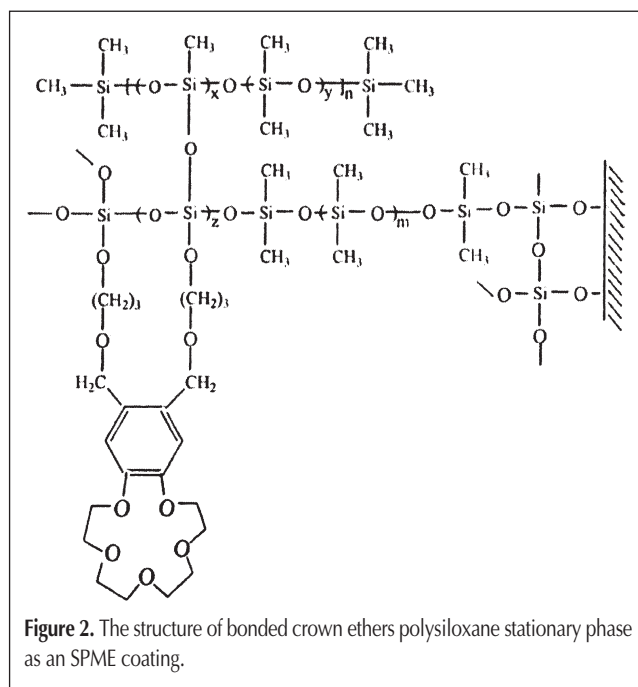


Figure 2. The structure of bonded crown ethers polysiloxane stationary phase as an SPME coating.

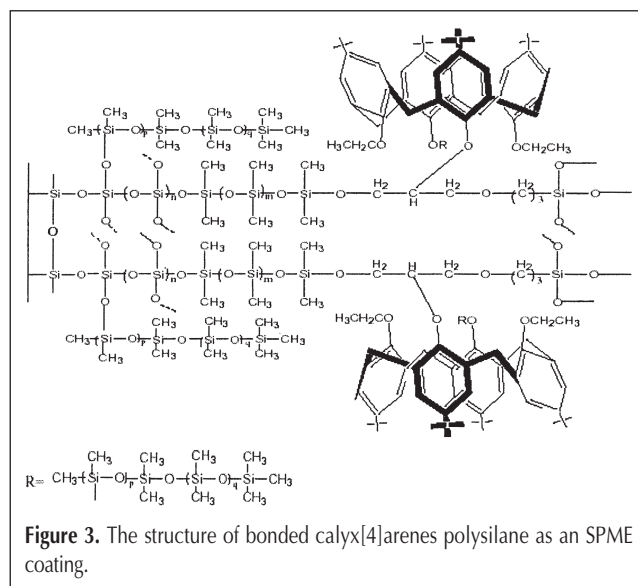


Figure 3. The structure of bonded calyx[4]arenes polysiloxane as an SPME coating.

silica fiber by high-temperature epoxy, and used it as an SPME coating. Then, they utilized microwave-assisted extraction and detected phenol compounds in water. Figure 4 is the schematic of the synthesizing process of this kind of cyclodextrin. They also prepared a poly(dimethylsiloxane)- β -cyclodextrin SPME membrane for the determination of polycyclic aromatic hydrocarbons and phenolic compounds in the water samples (23). The advantages of the method seemed to be high extraction effect and low cost.

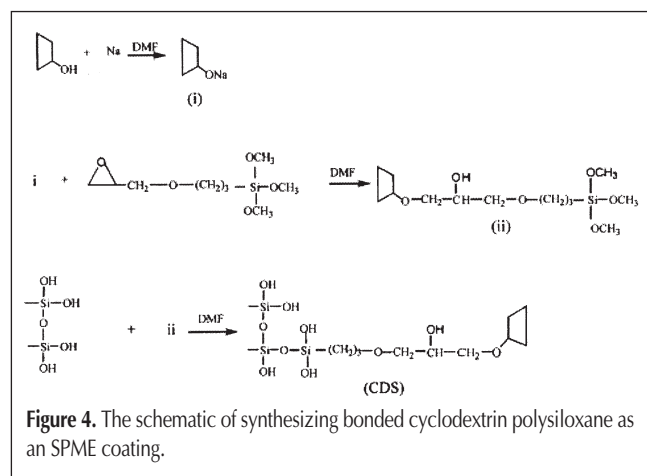
Bonded mesoporous silica material also have been applied in the SPME field. Recently, Du et al. (24) coated a stainless steel wire with phenyl-functionalized MCM-41-type mesoporous silica materials and used this wire as the SPME fiber for the extraction of aromatic compounds. The results showed that this novel coating exhibited many advantages, such as high sensitivity and selectivity, because of its large surface area and small mesopores, high mechanical strength, good thermal stability, easy preparation, and long lifetime. Fan et al. (25) introduced the ordered mesoporous silica modified with octadecyl groups into the capillary for in-tube SPME, used the in-tube SPME-high-performance liquid chromatography (HPLC) system, and determined bisphenol A in water samples.

Coatings based on polyamine materials (polyamide and polyimide)

The polyamine materials have strong polarity, high thermal stability, and good wetting ability on the surface of the silica fiber. Thus, they are often used as a protection coating for GC capillary columns. Whang et al. (26) detected Cr (III) in water using polyimide-coating-containing fibers as SPME fibers, and the result of their experiment exhibited very high sensitivity. Yang et al. (27) successfully extracted dichlorvos in blood sample and morphine and phenobarbital in urine samples by using polyamide SPME membranes containing Tenax and pyridine.

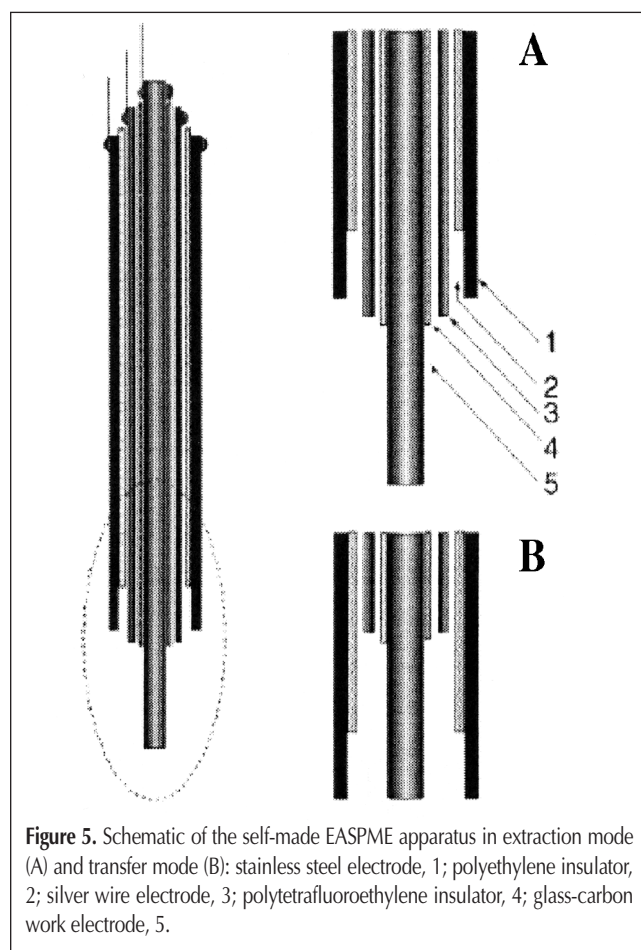
Coatings based on other polymeric materials

Farajzadeh et al. (28) coated both cellulose acetate and polyvinyl chloride (PVC) on silver wires and used this porous material as an SPME coating to extract alkanes in water samples, and they found that the coating has good selectivity for extracting alkanes with a carbon number higher than 10, especially for C_{12} - C_{15} .



Thompson et al. (29) coated poly-(3-methylthiophene) on the surface of platinum micro-fiber electrodes and utilized the electrodes to successfully extract arsenate ions from aqueous solutions by an electrochemical method without derivatization. This was the first time conductive polymers were used as SPME coating materials. Shortly after, they synthesized polythiophene, which was modified with longer alkyl groups and made for the speciation analysis of arsenic by using an electrochemically aided SPME (EASPME) method and HPLC-inductively coupled plasma-MS technique (30). Afterwards, other conductive polymers were used in SPME. Nyholm et al. (31) prepared two kinds of polypyrrole coatings, which were doped with perchlorate and *p*-toluenesulfonate, respectively, by an electrochemical method. They also designed a self-made EASPME apparatus (Figure 5). The results showed that under a constant potential of +1.0 V and -0.5 V, relative to the calomel electrodes, this apparatus is well-suited to extract parts per million level anions (like chloride, nitrite, bromide, sulfate, and phosphate) and cations (like calcium, cobalt, and zinc). Kadir et al. (32,33) found that SPME coatings based on overoxidized sulfonated polypyrrole (OSPPY) materials can be used to extract a great variety of cationic analytes, including metallic ions in electrochemically controlled SPME. Bagheri et al. (34) prepared an aniline-based coating to extract phenols from water by the electropolymerization method.

The research group of Pawliszyn (35) prepared three kinds of different doping polypyrroles: perchlorate, chloride, and poly(styrenesulfonate-pyrrole), and they concentrated sodium methy-



larsonates, glutamate, perchlorate, and dopamine by three different polypyrroles, respectively, then desorbed the compounds to water by electrolysis and injected them into the HPLC–MS directly by flow injection analysis. They also prepared one polypyrrole with the organic synthesis method and electrochemical polymerization method to extract several analytes. Most of their work was focused on coating polypyrrole inside of the capillaries and using the in-tube SPME method. Some of their work dealt with fiber SPME that extracted volatile organic compounds by fiber with a polypyrrole coating (36–44). In another paper, they coated polypyrrole on the surface of a fused-silica fiber and utilized surface-enhanced laser desorption/ionization, combined with MS, to analyze small-molecule peptides (45). Alizadeh et al. (46) used an electrochemical polymerization method to coat dodecylsulfate-doped polypyrrole on a platinum wire and extracted polycyclic aromatic hydrocarbons by a headspace (HS)–SPME method. Then, they used GC–flame ionization detection (FID) to analyze the compound with the sub-parts per billion detection limits. Tamer (33) synthesized overoxidized sulfonated polypyrrole using an electrochemical method and applied the polymer for the selective extraction of trace levels of nickel and cadmium ions.

In 2003, the research group of Pawliszyn (47) utilized polypyrrole fibers to study *in vivo* pharmacokinetics in dog blood. It was a great breakthrough for the application of *in vivo* SPME. They coated polypyrrole on the surface of metal wires by the electrochemical polymerization method. The excellent strength of the metal wires provided the possibility to do experiments *in vivo*. The polypyrrole SPME fibers were placed (through a catheter) into the cephalic vein of the lower front leg and then analyzed the samples by LC–MS–MS. The movement of the blood was expected to increase the extraction ability in a predetermined time.

In recent years, molecularly-imprinted polymers have been used in many analytical chemistry research fields, such as chromatographic stationary phases, selective materials for biosensors, and solid-phase adsorbents. Both Koster et al. (48) and Pawliszyn et al. (49) have done a lot work on the application of molecularly-imprinted polymers on SPME coating. They coated several methacrylate polymers, which had been synthesized with imprinted β -blockers, directly onto the surfaces of the silica fiber and used them as an SPME fiber for the extraction and determination of β -blockers in biological fluids. The molecularly-imprinted polymer selectivity simplified the sample preparation technique and chromatographic separation.

Inorganic coatings

For SPME coating materials, adsorptive capacity is an important factor. Although inorganic compounds are not as diversified as organic coatings as far as structures are concerned, some inorganic compounds with high adsorptive capacity are also popular as SPME coatings.

Coatings based on graphite materials

Activated carbon is a common kind of adsorbent because of its strong adsorptive capacity. Mangani et al. (50) coated graphitized carbon black on the surface of fused-silica fiber and used a self-modified SPME device to extract volatile organic compounds

from water and organochloride from blood and urine samples. The limit of detection of the method was at the approximately 1-pg/mL level. Djozan et al. (51) had affixed extra fine, porous-layer activated-charcoal powder to SPME fibers by PDMS as adherent and used it to extract benzene derivatives in water. They also inserted pencil lead into SPME fiber tubes and used them as coating directly (52). Jinping Jia et al. (53) explored the possibility of using activated carbon fiber as SPME fibers. Their experiment showed that, as an SPME fiber, the activated carbon fiber had many advantages, such as better resistance to organic solvents, better endurance to high temperature, longer lifetime, and a good extractability for chlorinated hydrocarbons.

Although graphite and activated carbon have strong adsorptive capacity, their selectivity for analytes is poor. However, being electrode material, glassy carbon is quite different from graphite because the arrays of carbon atoms in different layers are not accurately orientated, and the flat molecular surface provides special selectivity and retaining ability. Burk et al. (54) used polycrystalline graphite to extract nonionic surfactants, such as Triton X-100, and obtained the similar selectivity as commercial PDMS–DVB and carbowax–template resin. Olesik et al. (55) coated a low-temperature glassy carbon (LTGC) membrane, which can endure approximately 1000°C on stainless steel wires. The LTGC-coated silica particles were also immobilized onto stainless steel wire fibers and followed by GC–FID analysis. The result of experiments indicated that this membrane had good selectivity to the polar molecules or the molecules with the cross-sectional surface. They also detected three peculiar taste and odor compounds in aqueous samples by this method as. The same authors (56) had prepared the same coating on a 4-cm long fiber, and the extraction capability of the fiber was increased greatly. In 2004, they synthesized a fluorinated low-temperature glassy carbon film (57). Compared with many commercial fiber coatings, this kind of fluorinated LTGC membrane has better concentration capability in the application of extraction of the halogen-containing compounds (such as halogenated benzenes).

Coating materials based on metallic compounds

The solid supports of coating materials based on metallic compounds are mostly metal wires. Metal wires are dipped in solution, and metallic compounds are obtained by chemical or electrochemical methods during the preparation process. For example, Djozan et al. (58) dipped clean copper wire in a solution of CuCl_2 to produce a layer of CuCl microcrystals on the surface of copper wire. This kind of coating could be used to extract volatile amines, and the detection limit of the method was 0.1–0.3 ng/mL. Similar methods were used to prepare anodized aluminum wire (59), electrochemical anodized zinc wire (60), and copper sulfide wire (61). Farajzadeh et al. (62) had prepared three kinds of copper (I) compounds on the surface of copper wire, including copper (I) chloride, copper (I) oxide, and copper (I) sulfide by using the electrochemical method. The experiment result proved that copper (I) chloride exhibited the best extraction effect for amines among the three copper (I) compound coatings, and its detection limit was similar to that obtained with the CuCl_2 coating by Djozan et al. (58). They also utilized the special affinity between alumina and hydroxyl groups to extract alcohol compounds with the coating, which was made by the mixture coating of both alumina

powder and PVC (97:3) on the silver wire. The extraction effect was excellent, and the detection limit was 0.1 ng/mL (63). The group of Ou (64) also coated γ -Al₂O₃ on the surface of fused-silica fiber and successfully detected some volatile organic compounds in indoor air. Oliveira et al. (65) and Silveira et al. (66) coated Nb₂O₅ on fiberglass to extract phenols, and they also coated Nb₂O₅ on thin glass-ceramic rods to extract alcohols and phenols by HS-SPME. The result showed that the niobium (V) oxide coating had good extraction ability for phenols and alcohols.

Preparation technique of coatings

For different coating materials and different solid support phases, the preparation techniques are different. The following are some common coating methods.

Coating materials by direct-pasting technique

A simple device is enough for this technique. For a small amount of production, researchers only need a container and solution. They can dip one end of the silica fiber or metal fiber into the solution for a predetermined time and then cure the coating by UV light or heat. The group of Wu (41) had coated PMVS and 1% (m/m) photosensitizer onto silica fibers by the described method. Olesik et al. (55) designed a smart coating device (Figure 6) in order to obtain better reproducibility of preparation technique.

The described technique is not suitable for lot production. Mani (67) introduced the production process of commercial fibers by Supelco, in the book, *Applications of Solid Phase Microextraction*. After the silica fibers were drawn by machine, they were immediately cooled to the ambient temperature and drawn

through a container with the coating solution inside (for complex coating, multiple containers are necessary). After the fibers were drawn out of the container, the polymers were coated on the fibers. The fibers were then cured by heat or UV light and then coiled. Two centimeters of the fibers is always enough. It is then cut for the SPME device.

Sol-gel technique

In 1997, Chong et al. (68) were the first to apply the sol-gel immobilization method technology in the preparation of SPME coatings. The technique can not only make hydroxyl-terminate PDMS bond with the hydroxyls of the surface of silica fibers, but also make hydroxyl-terminate PDMSs bond with each other. Thus, the entire coating formed as net structures and was stabilized with the surface (see Figure 1 for the similar structure). The results of their experiments proved that the maximum temperature of this kind of coating was 100°C higher than the normal physical coatings. Both the groups of Wu and Zeng from Wuhan University had prepared many kinds of coating by the sol-gel technique and extracted several kinds of compounds, such as organophosphorus pesticides, organochlorine pesticides, aroma compounds in beer, phenolic compounds, 2-chloroethyl ethyl sulfide, and volatile compounds in red wine (16,69–73). Ligor et al. (74) prepared ethoxy-PDMS-coated fiber and polyurethaneacrylate coatings, which had high thermal stability (in the range of 300°C to 450°C). Caruso et al. (75) prepared new sol-gel coating, including the C8 group bonded on PDMS and applied in HPLC analysis, which had been used to detect organomercury, organoarsenic, organotin, etc., in water with the detection limits of 80–600 µg/L. Recently, Khalid et al. (76) developed a novel zirconia-based hybrid organic-inorganic sol-gel coating and used in-tube SPME to extract some polycyclic aromatic hydrocarbons, aldehydes, and ketones. The experiments showed that the novel sol-gel hybrid zirconia coating had excellent high pH stability and retained the extraction ability even after continuous rinsing with a 0.1M NaOH solution for 24 h. Basheer et al. (77) synthesized amphiphilic and hydrophilic oligomers and coated them on fused-silica fibers by a sol-gel technique; they used these fibers to extract many compounds, including organochlorine pesticides, triazine herbicides, estrogens, alkylphenols, and bisphenol-A. These fibers showed excellent SPME performance for the extraction of both polar and nonpolar organic compounds. The sol-gel coating demonstrated long lifetime and high thermal stability up to 280°C.

Besides the previously described research work using sol-gel synthesis technology, some researchers have developed poly(ethylene glycol)-modified ormosil coating (78,79), poly(ethylenepropyleneglycol) monobutyl ether coating (79), phenyl-functionalized coating (80), and modified ormosil coating fibers for the SPME of many kinds of compounds with very different polarity.

Using shaped materials directly as coatings

As described earlier, Djozan et al. (52) employed pencil lead as extraction fibers. The pencil lead does not need solid phase carrier support. The research group of Pawliszyn (81) enclosed silica fiber with a Nafion tube to extract polar compounds. Jinping Jia et al. (82) chose suitable reprocessed plant fibers as a matrix to

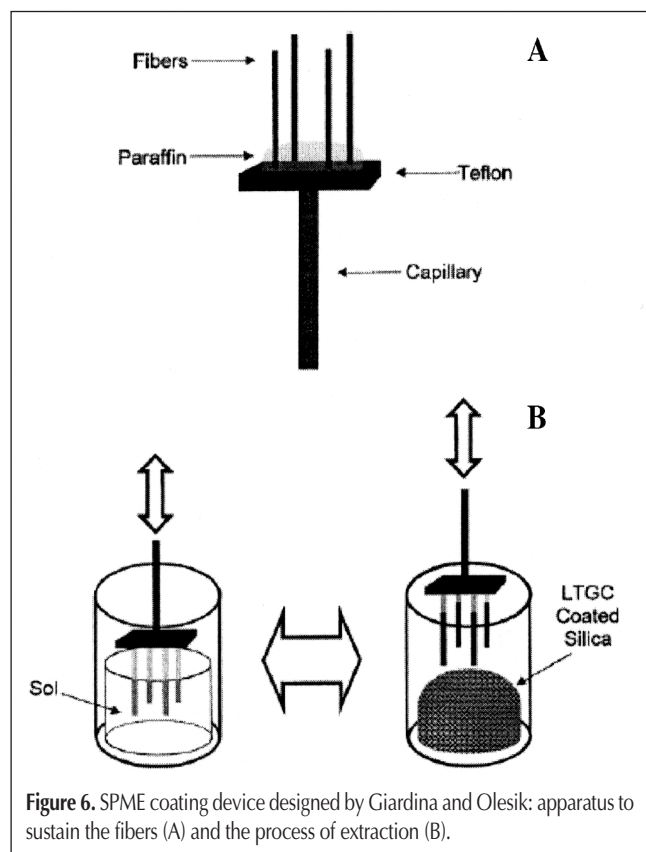


Figure 6. SPME coating device designed by Giardina and Olesik: apparatus to sustain the fibers (A) and the process of extraction (B).

obtain fibers in a self-made reactor and then put them in a self-made SPME holder to extract benzene. They also used activated carbon fiber for the determination of chlorinated hydrocarbons (53). He et al. (83) dipped the terminal of the silica fiber in hydrofluoric acid and found the eroded surface of the fiber had good selectivity for methylmercury. She also detected methylmercury in organisms and sediments by using this fiber combined with the hydride derivatization method. The coatings based on metal materials mentioned previously were all obtained by modifying the metal wires with the organic chemical or electrochemical method. Because of its simple operation, this kind of preparation technique is still popular.

Pasting coatings onto the carriers by adhesives

This coating technique is a little difficult to operate and it requires an adhesive of good quality. High-temperature epoxy glue was commonly used because of its high thermal stability. Liu et al. (84,85) had affixed C8 and C18 silica particles onto stainless steel wire with high-temperature epoxy glue to extract benzene derivatives, polycyclic aromatic hydrocarbons, and polychlorinated biphenyls. The silica gel particles increased the surface area of coating and, thus, increased the capability of the fiber coating, which is 500 times greater than PDMS coating when extracting the same concentration of benzene derivatives. Djozan et al. (51) prepared a new, porous-layer-activated charcoal coating with PDMS as the adhesive. The group of Pawliszyn (86) proposed a novel, restricted-access SPME method. First, they prepared the SPME fiber by pasting the alkyl diol-silica restricted-access materials onto the steel wire using an epoxy binding agent, and then they interfaced the SPME device with an LC-MS system and developed a method for the determination of some drugs and their metabolites in whole blood. This method exhibited excellent stability. The biggest advantage of this novel method was that there was no requirement to precipitate proteins from the biological sample prior to extraction. By using a similar method, they also prepared cation-exchange restricted-access SPME stainless fiber for the extraction and HPLC determination of angiotensin I in the whole blood sample (87). Hou et al. (88) pasted the inorganic-organic mesoporous silica C16-MCM-41 particle onto stainless steel wire by epoxy resin glue, and they used the fiber to determine trace anthracene in environmental samples. The results indicate that by using the fiber coating, the method would exhibit high extraction effect and good selectivity. It was reported that this new material had a very large surface area and high mechanical, chemical, and thermal stability.

Generally speaking, the coating prepared by the pasting technique has a large surface area, and this will result in good extraction capacity. But this technique has its own weakness (e.g., the interaction between coating particles and fiber is not strong enough to stand the solvent from the HPLC mobile phase), so any application of fibers prepared by this technique in HPLC fields should be performed cautiously. In addition, the interference from the adhesive impurities is also a problem to be overcome.

Electrochemical polymerization method

Some polymers prepared by this method have a good electrical conductivity property. Therefore, this kind of coating is sometimes called conductive polymer, even though in SPME the con-

ductivity of the coating sometimes did not matter. The technique has the advantages of easy operation. Moreover, in this method, the strength of metal wires is better than silica fibers; thus, this technique has a wider application range, like *in vivo* investigation. Besides, because of the great difference of the thermal expansion coefficient between polymer and metal, flaking of polymers may occur at high temperatures if the coatings were prepared with simple physical coating techniques. Polymers prepared by electrochemical polymerization are deposited, point by point, on the surface of the metal wire. They are too robust to flake off, even at high temperatures.

In the Coatings based on other polymer materials section, most of the polymers coated on metal wires were prepared by this technique. Besides polypyrrole and polythiophene, polyaniline is also a popular conducting polymer. According to Trojanowicz's paper (89), polyaniline had been the most popular conducting polymer in analytical chemistry. It has been used in SPME (90,91), LC (92,93), and ionic chromatography (94,95). Our group (96,97) had electroplated polyaniline onto metal wires by using electrochemical polymerization and detected aromatic amines (aniline, *N,N*-dimethylaniline, *m*-toluidine, 3,4-bichloroaniline, 2-chloroaniline, and 2,4-bimethylaniline) in water with HS-SPME-GC. The linear range was from 4.8 to 27.5×10^4 $\mu\text{g/L}$, the detection limits were from 0.019 to 1.06 $\mu\text{g/L}$, and the RSDs were 2.02–6.00% under optimizing condition. The self-made composite polyaniline coating was prepared and aimed at the commercial interface for HPLC and SPME. The fiber was applied to the concentration of three phenol compounds by using direct SPME with HPLC-fluorescence detector. The extraction fibers also showed better sensitivity than commercial CW-TPR coatings. Recently, Alireza et al. (98) developed a simple and sensitive method for determination of anatoxin-a in aqueous samples using SPME-GC-MS. In their method, they prepared the SPME fibers by precipitating polyaniline films directly onto the surface of gold wires using an electrochemical polymerization method. The experiments showed that these polyaniline coated fibers had a good extraction performance for anatoxin-a.

Conclusion

Generally speaking, more and more novel coatings have been developed, and they were suitable for the analysis of many kinds of compounds with very different properties, such as polarity and volatility. The SPME methods based on these new coating materials have been applied in many analytical fields. In the future, high selectivity, accuracy, sensitivity, long lifetime, and good compatibility with biological system of the SPME coating are still the goal for analysts. Based on a summary of a mass of literature, more efforts should be put on the following aspects in the research of SPME fiber coatings. First, the coating with high selectivity should be paid more attention. Because of their excellent selectivity, the fiber coating materials based on molecularly imprinted polymers and antibodies are absolutely a good choice. Many researchers, such as the group of Pawliszyn have done some excellent work on this aspect, but there is still a huge space in this field for researchers to study. Mullett et al. (99) wrote a review

paper in which he described some selective SPME coatings, including molecule imprinted polymer (50), bonding antibody technique (100), etc. Moreover, good biological compatibility and in vivo extraction, sampling, and determination by one step is another important trend in analytical chemistry. Thus, the SPME fiber coatings with such properties are definitely in demand; the efforts in this field should be further strengthened. The research on monolith materials is a hot topic in analytical chemistry in recent years, but their application in the SPME field is very limited (101,102). However, we believe that the SPME fiber coatings based on monolith materials should have a bright future because of their unique properties, such as very rapid extraction kinetics, high extraction effect, and good compatibility with biological samples.

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