RESEARCH REVIEW

Recent Development of Laboratory-made Solid-phase Microextraction Fibers on the Application of Food Safety Analysis

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Abstract Solid-phase microextraction (SPME) has gained widespread acceptance in sample pretreatment due to its solvent-free and easy-to-operate properties. SPME fibers are considered as a key part of SPME technique, since it primarily determines the extraction performance of the method including sensitivity, selectivity, and reproducibility. Generally speaking, target analyte with different chemical property requires fiber coating that has the best affinity towards it. Due to the lack of varieties of commercial fibers available currently, considerable efforts have been recently made to develop tailor-made fibers to fulfill increasing demands of different analysis. This paper concisely classify some SPME fiber preparation approaches such as sol-gel technology, physical deposition, molecularly imprinted technique, and their respective application in food safety analysis.

Keywords: laboratory-made fiber, food safety analysis, solid-phase microextraction

Introduction

As the increasing demand of foodstuff with high level of safety guarantee together with higher market competition, more sensitive, accurate monitoring, and determination methods of nocuous compounds in foodstuffs are considerably required. Taking into account that nocuous compounds are usually present at trace level in foodstuff, sample pre-concentration and clean-up are always needed to concentrate analytes and eliminate interferences from complex matrixes prior to measuring procedure. Based on this procedure, sample preparation approaches are considered to be the vital factors related to the overall performance of analytical methods for food safety analysis. Although the traditional sample preparation including liquid-liquid extraction (LLE), solid-phase extraction (SPE), microwave assisted extraction (MAE), and super fluid extraction (SFE) are easy to carry out and provide good recovery, they are tedious, labor consuming, and hazardous to operator health since the large volume of organic solvents are required. Solid-phase microextraction (SPME) is a solventless, time-efficient, and sensitive sample preparation technique, which was introduced by Authur and Pawliszyn (1). It combines pre-concentration, sampling, and injection [generally introduced to a gas chromatograph (GC) or high performance liquid chromatograph (HPLC) injection port] into one step. Last decades have seen continuously increasing application of SPME in the fields of environmental (2,3), pharmaceutical (4), biological (5), clinical, and forensic analysis (6). SPME is generally based on the partition of target analytes between the sample and the stationary phase deposited on

the solid support (typically silica fused fiber or metal wires). It is evident that the fiber coating plays an important role in SPME technology because it determines the sensitivity and selectivity of the method. Currently, several SPME coating materials, including non-polar polydimethylsiloxane (PDMS), carboxen/PDMS, semi-polar PDMS/divinylbenzene (DVB), polar polyacrylate (PA), carbowax/DVB, and carbowax/templated resin were commercially available (7). These commercial fibers, which possess high extraction capacity and provide good analytical precision, have been successfully applied in some cases of real sample analysis. In spite of cited advantages, some natural drawbacks such as limited range of polarity of fiber coating covered, fragility of the silica base, non-resistance to high temperature, and organic solvents have restricted the application of SPME for the analysis of nocuous compounds in food samples with complex matrixes. Recently, several fiber coating approaches including sol-gel technology, physical deposition, electrochemical procedure, vapor deposition, and molecularly imprinted technology (MIT) have been developed. The laboratory-made SPME fibers prepared by these approaches provide a wider range of SPME coatings alternative to commercial fibers with enhanced sensitivity and selectivity, high thermal, mechanical, and organic stability, which make them possible for the analysis of nocuous compounds at trace level in food samples with complex matrixes. Up to date, some cases of food safety analysis have been reported using these laboratory-made fibers. This paper summaries and reviews the approaches of laboratory-made fiber preparation and the applications of these fibers in food safety analysis.

Molecular Imprinted Technology (MIT)

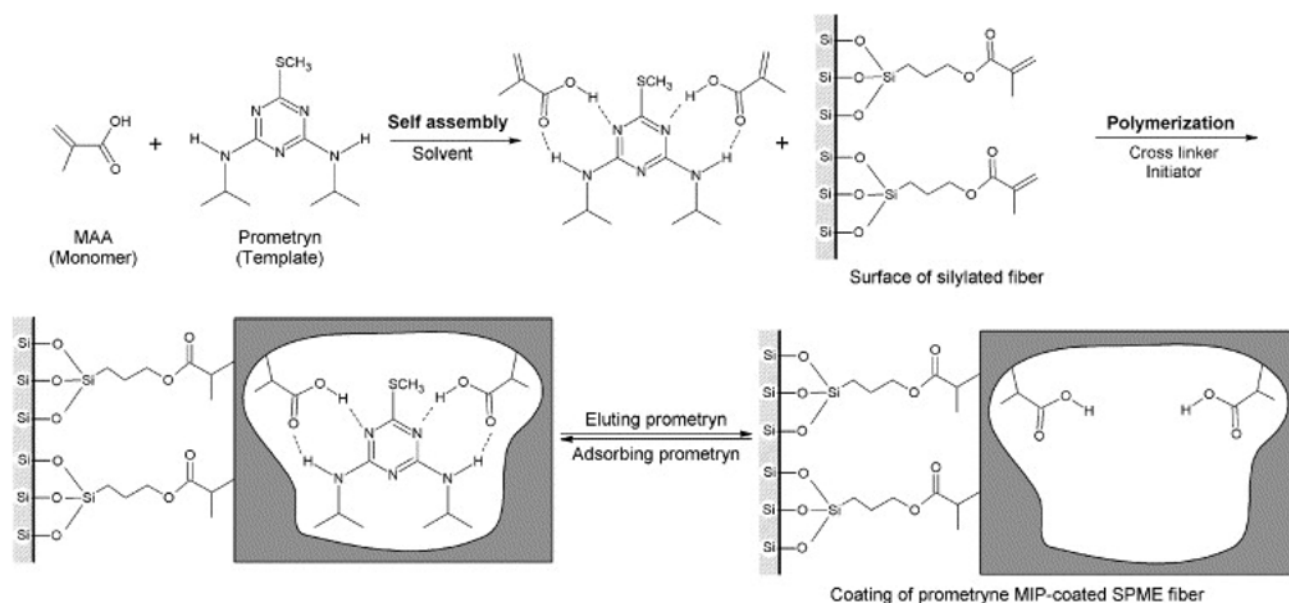Molecular imprinting is a technique involving the preorganization of the imprinted molecule with functional

Fig. 1. Schematic representation of prometryn MIP-SPME coating preparation. Adapted from reference (9).

monomers followed by a polymerization reaction fixing the monomers in the polymer network. After the removal of the imprinted molecule, the specific recognition sites are formed in the polymer with complementary structure and intermolecule interactions (8). Due to its chemical and physical robustness, easy preparation, and high selectivity, molecularly imprinted polymers (MIPs) have been widely applied in separation science such as materials for solid-phase extraction, chiral stationary phase for HPLC, and capillary electrochromatography. The inherent selectivity, chemical and physical robustness make the MIP materials ideally suited for SPME coating in the application of food safety analysis.

In 2007, Hu *et al.* (9) prepared a prometryn-imprinted SPME coating on the surface of silanized silica fibers (The schematic diagram of fiber preparation is shown in Fig. 1). The prometryn-imprinted fiber showed high selectivity and sensitivity towards prometryn (imprinted molecule) and its analogues with similar structure such as atrazine, simetryn, terbutylazin, ametryn, propazine, and terbutryn. The extraction yields of prometryn-imprinted fiber for the selected analytes were much higher than that of non-imprinted fiber, commercial PDMS, PDMS/DVB, and PA SPME fibers. In addition, the fiber showed good thermal stability (up to 260°C) and long service lifetime (more than 100 times). The prometryn-imprinted fiber was then used for the highly selective extraction of prometryn and its structural analogues in soybean, lettuce, and corn (Fig. 2). Subsequently, they prepared a tetracycline-imprinted fiber using similar method (10). The prepared fiber possessed homogeneous, highly crosslinked, and porous structure which could provide sufficient extraction efficiency of MIP coating with thin thickness (19.5 μm) for trace tetetracyclines. Under the optimized experimental conditions, the tetracycline-imprinted fiber was used for the selective extraction of tetracycline and other analogues in chicken feeds, milk, and chicken muscle. The detection limits of oxytetracycline, tetracycline, doxycycline, and chlortetracycline ranged

from 1.02 to 2.31 μg/L, which were much lower than the maximum allowed limits of the European Union (EU) and the US Food and Drug Administration (FDA) for tetracyclines. Turiel *et al.* (11) developed a strategy of MIP fiber preparation based on the direct synthesis of MIPs in the silica capillaries followed by etching away the silica after polymerizatiton. They used the propazine as the imprinted molecule to prepare propazine-imprinted polymeric fibers (monoliths). Using silica capillaries as molds, several fibers could be prepared with good reproducibility at one time. After optimizing several variables related to polymer morphology (i.e., polymerization time and fiber thickness) and binding-elution of target analytes (i.e., solvents, time, and temperature), the imprinted fiber showed good performance in terms of selectivity and sensitivity towards propazine and its structural analogues. The propazine-imprinted monoliths were successfully applied to the extraction of triazines in potato, pea, and soil. Djozan and Ebrahimi (12) also prepared a monolithic MIP SPME fiber on the basis of using glass capillaries as molds followed by fibers pulled out of the capillaries with mechanical strength. The prepared fiber is durable, inexpensive, chemically and thermally stable (up to 280°C) which makes it can be directly coupled to GC or GC/mass spectrometry (MS). The selectivity of prepared fiber for the target analytes was proved using 3 OPPs as reference compounds and non-imprinted polymers coated fiber (NIP) as reference fiber. The availability of prepared fiber for the extraction of atrazine and its analogues were verified by implementation of the fiber in real samples including tap water, onion, and rice. However, they did not mention how long this MIP-coated fiber can be used in the real samples. To date, MIP fibers designed for special analytes have proved to be the most effective ones for SPME in the extraction of analytes at trace level in food samples with complex matrix. Although MIP fibers have gained success in the SPME application of food samples, several aspects are needed to be considered for preparation of novel MIP fibers in the
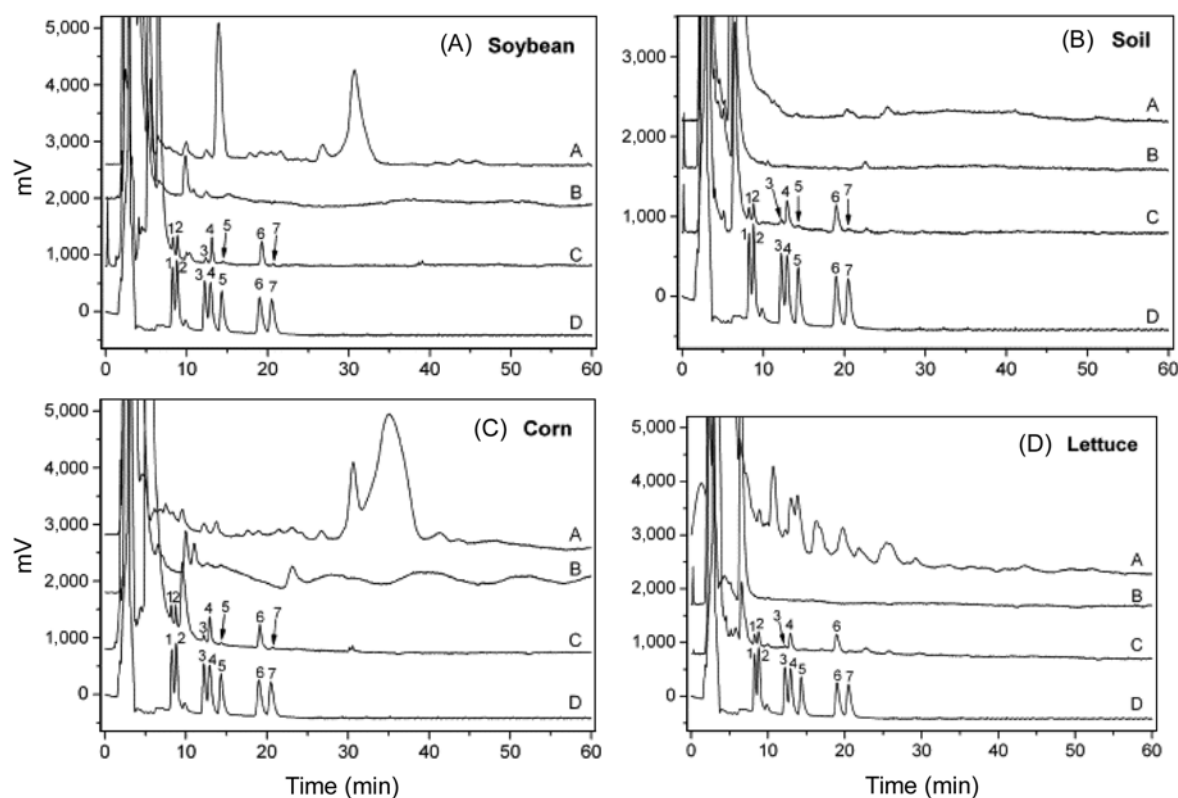
Fig. 2. Chromatograms of 0.500 mg/L triazines mixed standard solution, 0.500 µg/L triazines spiked microwave assisted extraction solutions of soybean, corn, lettuce, and soil samples and determination of triazines in spiked sample solutions with MIP- or NIP-coated fibers. (A) Triazines spiked microwave assisted extraction solutions of sample, (B) spiked sample solution extracted with NIP-coated fiber, (C) spiked sample solution extracted with MIP-coated fiber, (D) triazines mixed standard solution. (1) Simetryn, (2) atrazine, (3) ametryn, (4) terbutylazin, (5) propazine, (6) prometryn, and (7) terbutryn. Injection volume for A and D: 10 µL. Adapted from reference (9).

future: 1) the interaction mechanism and recognition ability of the MIPs towards target analytes at molecular level are needed to be further investigated and illuminated since they are currently not very clear; 2) the imprinted molecule in the MIP is difficult to completely remove and leakage of its residue will result in higher and irreproducible analytical results; 3) although the MIP SPME fiber has been reported successfully coupled to GC, the service time of the fiber in the application might be a problem since the high temperature in the GC injector will more or less lead to the distortion of the MIP microstructures and make them gradually lose their so-called 'memory effect'. Anyway, in the future, we believe that SPME fibers prepared by MIT will provide different MIP fibers with high selectivity for one specific analytes, and most of which are likely to be applied to the extraction of corresponding analytes in food samples.

Sol-Gel Technology

Recently, sol-gel technology has shown to be a good alternative to overcome the above-mentioned limitations related to commercial fibers. It enables good mixing of multi-components and provides efficient incorporation of organic components into inorganic polymeric structures under extraordinarily mild condition. Generally, the sol-gel process involves the evolution of inorganic networks through the formation of a colloidal suspension and gelation by the simultaneous hydrolysis and condensation of the precursor, followed by aging and drying under ambient atmosphere. The general process of sol-gel coating preparation was shown in Fig. 3 (13). The main advantages of sol-gel coating technology includes (1) possibility to fine-tune the extraction selectivity by controlling the pore size or morphology of the silica matrix or through the selection of precursor with specific functionality; (2) enhancing chemical and thermal stability of the fiber obtained due to the chemical bonding between the coating and the fused silica surface; (3) porous structures of sol-gel coating, which enlarges effective adsorption area and thus allow for higher extraction efficiency; and (4) relative ease of fiber coating preparation under thermal mild condition.

In 1997, a sol-gel method was firstly proposed as novel approach to prepare SPME coating. Chong *et al.* (14) prepared a chemically bonded PDMS on the surface of silica fused fiber. The sol-gel PDMS coated fiber exhibits high thermal stability (>320°C) and excellent extraction efficiencies towards polycyclic aromatic hydrocarbons, alkanes, aniline derivatives, alcohols, and phenolic compounds. Zeng *et al.* (15) prepared a sol-gel PDMS coated fiber and used it to extract dicofol in tea samples (green tea, *ulong* tea, and jasmine tea) associated with microwave-assisted extraction. Zhang *et al.* (16) used PDMS coated fiber for the extraction of organochlorines
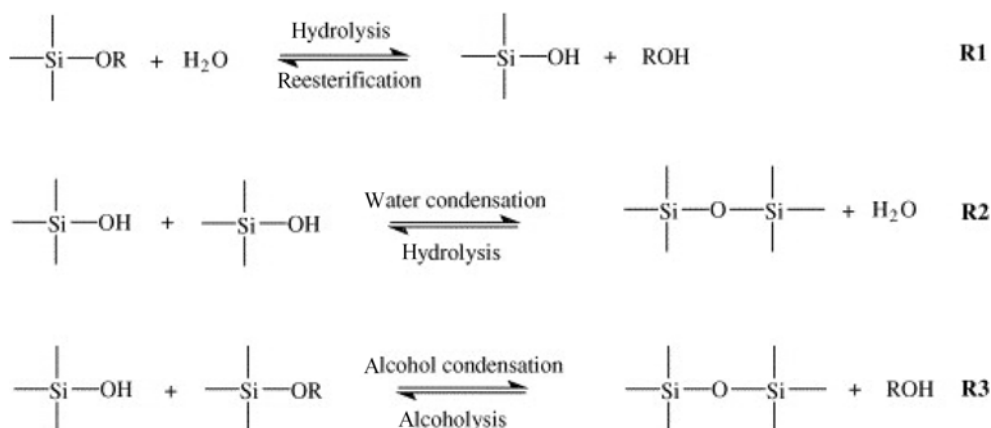
Fig. 3. Basic steps in sol-gel coating technology. Adapted from reference (13).

(OCPs) and pyrethroid pesticide residues in vegetables coupling with ultrasonic extraction. The proposed method shows satisfactory applicability for the selected light-color vegetables. Cai *et al.* (17) prepared a sol-gel polyphenyl-methylsiloxane (PPMS) coating through a light-induced radical procedure. The phenyl group which exhibited good affinity towards phenyl-contained compounds via π-π interaction was introduced into the coating matrix. Compared with 100 μm PDMS, the PPMS-coated fiber exhibited higher extraction sensitivity and selectivity towards organochlorine pesticides (OCPs), higher thermal stability (350°C), and longer lifetime (150 times). The PPMS-coated fiber was applied to the determination of 16 OCPs in Chinese teas including green tea and *ulong* tea, and the tested pesticides were at ng/g level. However, since many chain extenders was involved in the reaction and contained in the final product, relatively low content of PMPS in the coating would be obtained. The group of Chen (18,19) demonstrated an approach to the synthesis of PMPS-OH and successfully applied it as a precursor to prepare the PMPS-coated fiber, which was confirmed by Fourier transform infrared spectroscopy (FTIR) spectra. This PMPS-coated fiber was applied to the extraction of OCPs and pyrethroid pesticide residues in various tea and vegetable samples, respectively. Cai *et al.* (20) further developed radical crosslinked vinyl crown ether as a novel coating for SPME. The vinyl crown ether coated fiber possess cavity structure and the heteroatoms on the ring exhibit strong electronegative effect, which make the fiber coating selective for the polar compounds. In addition, the fiber with porous 3-dimensional network provided higher surface area for extraction. In the real sample analysis, samples were diluted at different ratio with water, which reduced the matrix effect and improved the recovery. The vinyl crown ether coated fiber was used for the analysis of organophosphorous pesticides in food samples including apple, apple juice, and tomato, and the detection limits were in the range 3 to 90 pg/g. A novel 3'-allylbenzo-15-crown-5 SPME fiber was prepared using radical cross-linked and sol-gel technique (21). The 3'-allylbenzo-15-crown-5 coated fiber was applied to extract volatile compounds in fenugreek concrete. Compared to commercial PA fiber, the proposed fiber was able to extract more volatile compounds due to the fact that the crown ether

group in the fiber coating has better affinity towards the aromatic compounds in fenugreek concrete. The group of Zeng (22) reported a calilx[4]arene fiber and applied it for the extraction of chloro-contained compounds in radish. The calilx[4]arene fiber showed good extraction efficiency towards these compounds due to the π-π interaction, hydrophobic interaction, and cavity-shaped cyclic molecular structure. Afterwards, they further introduced the polar open chain crown ether into calilx[4]arene molecule and developed the calilx[4]arene open chain crown ether fiber (23). Compared to calilx[4]arene fiber, commercial PDMS/DVB, and PA fiber, the proposed fiber showed much better sensitivity and selectivity towards polar compounds including volatile alcohol and fatty acids due to the strong hydrophobic and hydrogen bonding interaction. The fiber was applied to determine volatile alcohol and fatty acids in wine samples in conjunction with GC-flame ionization detector (FID), and the detection limits obtained for most analytes ranged from parts per billion to parts per trillion. A sol-gel derived co-poly (hydroxyl-terminated silicone divinylbenzene) (OH-TSO/DVB) fiber coated fiber was applied for headspace SPME coupled with GC-NPD to determine 5 OPPs in pakchoi samples (24). The OH-TSO/DVB coated fiber showed statistically better enrichment capability than commercial fibers for the selected OPPs, due to its 3-dimensional network and the polarizable phenyl group incorporated in the fiber coating. Recently, an alumina-based hybrid sol-gel coating (25) was prepared using a highly reactive alkoxide precursor, aluminum sec-butoxide, and a sol-gel-active organic polymer hydroxyl-terminated polydimethylsiloxane (OH-TSO). In comparison with the sol-gel silica-OH-TSO coated fiber, the alumina-OH-TSO coated fiber exhibit superior adsorption ability towards carboxylic acids. The special selectivity was mainly attributed to the strong ligand exchange interaction between the carboxylate group serving as an electron-pair donor and the cationic aluminum sites on the alumina-based coating surface serving as an electron-pair acceptor. Similar experiments showed that the fiber also exhibit good extraction efficiency towards phenolic compounds, alcohols, and aldehydes. The alumina-OH-TSO coated fiber proved to be suitable alternative for the analysis of alcohol and fatty acids in beer, and the recoveries obtained for all the analytes were in the range of 85.7 to 104%. Liu *et al.* (26)

proposed a novel sol-gel coating approach by physically incorporating PDMS containing vinyl group into network rather than chemically bonding. When the sol-gel reaction took place, the vinyl group was crosslinked to form long-branch chain polymers and the PDMS was wrapped in the 3 dimensional networks. The fiber prepared was used to extract the OPPs in orange juice and and red wines. To free the pesticide from matrix components and thus obtain higher recoveries, orange juice and red wine samples were diluted at 1:20 and 1:10, respectively. The relative recoveries obtained for orange juice and red wine samples were in the range of 50.3 to 100.2% and 47.7 to 116.2%, respectively. To simultaneously analyse polar and non-polar compounds, sol-gel derived 3-(trimethoxysilyl)propyl methacrylate-hydroxyl-terminated silicone oil (TMSPMA-OH-TSO) SPME fibers were prepared using TMSPMA as precursor (27). The TMSPMA-OH-TSO fiber coating possessed medium polarity and presented excellent extraction efficiency towards both polar alcohols and fatty acids and non-polar esters in beer. Using the 'volatile-free' beer as standard, the matrix effects from interfering substance were greatly avoided and the analytical precision was thus highly improved. The fiber was used to determine alcohols, fatty acids, and esters in 4 beer varieties, and the recoveries was so satisfactory ranged from 92.8 to 105.8%, with a mean value of 100.9%.

Although sol-gel coating techniques provided fibers with enhanced selectivity, chemical and thermal stability, some drawbacks are still remained to be solved. Firstly, the amount of functional molecules in fiber coatings is small, and the improved selectivity and sensitivity was usually insufficient. For example, the amount of crown ether in sol-gel-derived OH-DB14C4/OH-TSO fiber and in the sol-gel benzo-15-crown-5 coating is approximately 3.1 and 9.1%, respectively (28); secondly, the sol-gel process is inherently complex and often empirical since many ingredients were involved in the sol-gel solution; thirdly, relatively poor inter-laboratory fiber reproducibility was obtained due to the lack of standardized procedures. A review on development of SPME fibers by sol-gel methods and their application has been recently given by Kumara *et al.* (29).

Physical Deposition

A convenient and fast way to prepare SPME fiber is dipping the fiber support into adsorbent suspension, in which the stationary materials were dispersed in the solvent, followed by drying or thermal conditioning for immobility. This procedure can be repeated several times until desired thickness is obtained. The fibers prepared by this approach mostly suffer from chemical and thermal instability due to the lack of chemical bonding between coating and fiber support. However, one of the advantages is that different solid sorbents with special functionality can be easily incorporated on the fiber support as novel stationary phase for SPME. Farajzadeh and Rahmani (30) constructed a alumina-based SPME fiber using alumina powder and poly(vinyl chloride) (PVC) at the optimum ratio 97:3. The mechanical strength of the fiber was greatly improved using silver wire as fiber support. This alumina-based fiber showed high affinity towards hydroxyl

functional groups, and was applied to the determination of alcohol concentration in the fruit juices and vinegar coupled to capillary gas chromatography followed by flame ionization detection. Multiwalled carbon nanotubes (MWCNTs), possessing hexagonal arrays of carbon atoms in graphene sheets with large surface sorption area and internal tube cavity structure, are considered to have strong physical adsorption ability to hydrophobic organic pollutants (31). The group of Yan (32) firstly reported MWCNTs as SPME fiber coatings, by the approach of dispersing the MWCNTs (20-40 nm in diameter and 5-15 μm in length) in dimethylformamide (DMF) as suspension, and then dipping the fiber into the suspension followed by heating at 160°C to remove the solvent. Compared with other laboratory made SPME fibers with the same thickness and length, poly(dibenzene-dimethylsiloxane) and activated carbon coated fibers, MWCNTs coated fiber proved to give much higher enhancement factor for polybrominated diphenyl ethers (PBDEs). They used the MWCNTs coated fiber to extract 5 PBDEs from semi-skimmed, skimmed, and whole fat milk. Tian and Feng (33) reported a CNT-coated SPME fiber and used it to extract OCPs from yams. The extraction conditions including extraction temperature, time, ionic strength, and dilution ratio were optimized. The detection limits and recoveries were in the range of 1.98-12.4 ng/L and 70-120%, respectively. In recent years, ionic liquid (IL) has gained much attraction in the application of adsorbent coatings due to its unique properties including high thermal stability, excellent film stability, and reproducible extraction efficiencies. In addition, the extraction sensitivity and selectivity can be easily tuned by changes to the cation and/or the anion, polymerization or immobilization of the IL, and by involving different ILs with various compositions. Three homologous polymeric imidazolium-based ionic liquid coatings were synthesized and used as stationary phases for SPME (34). Three homologous polymeric ionic liquids (PILs) were prepared via a free radical reaction, and then dissolved in acetone at a ratio 1:9. Finally, the fused silica fiber supports was immersed into the PILs acetone solution for 20 sec, followed by drying in the air for 10 min to eliminate the residual solvent. These PIL coated fibers were applied to the extraction of esters and fatty acid methyl esters from synthetic wine (white wine and red wine), and showed comparable extraction performance to commercial fibers in terms of recovery, repeatability, sensitivity, and detection limits.

Conclusion and Outlook

Recently, more and more novel coatings with special functionality have been developed to fulfill the increasing demands of various kinds of analysis in different analytical fields. As is well-known, matrix compositions in food samples are extremely complicated. The matrix components in food such as protein, lipid, amylum, and pigment would strongly compete for the available adsorption sites of fiber coatings and thus severely affect the sensitivity and reproducibility of the method. In the future, more selective coatings with special affinity towards target analytes should be further considered. MIPs and antibodies would be excellent alternatives to prepare selective SPME coatings due to its specificity for the target analytes. This

kind of coatings will allow SPME for the direct analyis of food samples with complex matrixes. On the other hand, SPME coatings with more chemically, physically, and mechanically stable properties should be developed to fit for the extreme environment of food sample extraction (strong acidic, basic, or organic media). Recently, a relatively selective, chemically, and mechanically robust SPME coating based on methacrylic acid-trimethylolpropanetrimethacrylate (MAA/TRIM) monolithic polymers are developed using a glass capillary as a 'mold' (35). This MAA/TRIM polymeric coating shows excellent extraction efficiency in non-polar organic solvent for those highly functionalized molecules (typically containing multiple amino, hydroxy, carbonyl, and carboxy groups) via a hydrogen-bonding extraction mechanism. This MAA/TRIM coating showed good applicability in the direct extraction of triazines in food samples including ormosia and black rice. We believe that SPME coatings based on monolithic polymer materials will have huge potential for the application of food samples due to its chemical and physical stability, high extraction efficiency in non-polar organic solvent and simplicity for preparing different coatings with special functionalities.

Acknowledgments

References

1. Arthur CL, Pawliszyn J. Solid phase microextraction with thermal desorption using fused-silica optical fibers. Anal. Chem. 62: 2145-2148 (1990)
2. Ouyang GF, Pawliszyn J. SPME in environmental analysis. Anal. Bioanal. Chem. 386: 1059-1073 (2006)
3. Zeng JB, Yu BB, Chen WF, Lin ZJ, Zhang LM, Lin ZQ, Chen X, Wang XR. Application of ceramic/carbon composite as a novel coating for solid-phase microextraction. J. Chromatogr. A 1188: 26-33 (2008)
4. Hiroyuki K, Recent advances in solid-phase microextraction and related techniques for pharmaceutical and biomedical analysis. Curr. Pharm. Anal. 1: 65-84 (2005)
5. Theodoridis G, Koster EH, de Jong GJ. Solid-phase microextraction for the analysis of biological samples. J. Chromatogr. B 745: 49-82 (2000)
6. Pragst F. Application of solid-phase microextraction in analytical toxicology. Anal. Bioanal. Chem. 388: 1393-1414 (2007)
7. Manufacturer Data Sheet. Supelco Crop., Bellefonte, PA, USA (1999)
8. Mullett WM, Lai EPC. Determination of theophylline in serum by molecularly imprinted solid-phase extraction with pulsed elution. Anal. Chem. 70: 3636-3641 (1998)
9. Hu XG, Hu YL, Li GK. Development of novel molecularly imprinted solid-phase microextraction fiber and its application for the determination of triazines in complicated samples coupled with high-performance liquid chromatography. J. Chromatogr. A 1147: 1-9 (2007)
10. Hu XG, Pan JL, Hu YL, Huo Y, Li GK. Preparation and evaluation of solid-phase microextraction fiber based on molecularly imprinted polymers for trace analysis of tetracyclines in complicated samples. J. Chromatogr. A 1188: 97-107 (2008)
11. Turiel E, Tadeo JL, Esteban AM, Molecularly imprinted polymeric fibers for solid-phase microextraction. Anal. Chem. 79: 3099-3104 (2007)
12. Djozan D, Ebrahimi B. Preparation of new solid phase micro extraction fiber on the basis of atrazine-molecular imprinted polymer: Application for GC and GC/MS screening of triazine herbicides in water, rice, and onion. Anal. Chim. Acta 616: 152-159 (2008)
13. Dietz C, Sanz J, Carmar C. Recent developments in solid-phase microextraction coatings and related techniques. J. Chromatogr. A 1103: 183-192 (2006)
14. Chong SL, Wang DX, Hayes JD, Wilhite BW, Malik A. Sol-gel coating technology for the preparation of solid-phase microextraction fibers of enhanced thermal stability. Anal. Chem. 69: 3889-3898 (1997)
15. Zeng JB, Lin ZQ, Yu BB, Zhang MS, Chen X. Rapid determination of dicofol in Chinese teas by GC/ECD using microwave-assisted extraction associated with solid phase microextraction. Chinese J. Anal. Lab. 27: 77-80 (2008)
16. Zhang MS, Gong LF, Yu BB, Zeng JB, Yuan N, Chen X. Determination of organochlorine and pyrethroid pesticides in vegetable samples by ultrasonic extraction and SPME-GC method. Chinese J. Anal. Lab. 27: 25-28 (2008)
17. Cai LS, Jun X, Li D, Wu CY. Application of polyphenyl-methylsiloxane coated fiber for solid-phase microextraction combined with microwave-assisted extraction for the determination of Organochlorine pesticides in Chinese teas. J. Chromatogr. A 1015: 11-21 (2003)
18. Yuan N, Yu BB, Zhang MS, Zeng JB, Chen X. Simultaneous determination of residues of organochlorine and pyrethroid pesticides in tea by microwave assisted extraction solid phase microextraction-gas chromatography. Chinese J. Chromatogr. 24: 636-640 (2006)
19. Zeng JB, Chen JM, Lin ZQ, Chen WF, Chen X, Wang XR. Development of polymethylphenylsiloxane-coated fiber for solid-phase microextraction and its analytical application of qualitative and semi-quantitative of organochlorine and pyrethroid pesticides in vegetables. Anal. Chim. Acta 619: 59-66 (2008)
20. Cai LS, Gong SL, Chen M, Wu CY. Vinyl crown ether as a novel radical crosslinked sol–gel SPME fiber for determination of organophosphorus pesticides in food samples. Anal. Chim. Acta 559: 89-96 (2006)
21. Dong L, Cai LS, Zhu SK, Wu CY. Analysis of volatile components of fenugreek concrete by gas chromatography/mass spectrometry with solid-phase microextraction. J. Wuhan. Univ., China 50: 151-156 (2004)
22. Dong CZ, Zeng ZR, Li XJ. Determination of organochlorine pesticides and their metabolites in radish after headspace solid-phase microextraction using calix[4]arene fiber. Talanta 66: 721-727 (2005)
23. Liu MM, Zeng ZR, Lei Y, Li HB. High extraction efficiency fiber coated with calix[4]open-chain crown ether for solid-phase microextraction of polar aromatic and aliphatic compounds. J. Sep. Sci. 28: 2306-2318 (2005)
24. Wang YL, Zeng ZR, Liu MM, Yang M, Dong CZ. Determination of organophosphorus pesticides in pakchoi samples by headspace solid-phase microextraction coupled with gas chromatography using home-made fiber. Eur. Food Res. Technol. 226: 1091-1098 (2008)
25. Liu MM, Liu Y, Zeng ZR, Peng TY. Preparation and characteristics of high pH-resistant sol-gel alumina-based hybrid organic-inorganic coating for solid-phase microextraction of polar compounds. J. Chromatogr. A 1108: 149-157 (2006)
26. Liu WM, Hu Y, Zhao JH, Xu Y, Guan YF. Physically incorporated extraction phase of solid-phase microextraction by sol–gel technology. J. Chromatogr. A 1102: 37-43 (2006)
27. Liu MM, Zeng ZR, Xiong B. Preparation of novel solid-phase microextraction fibers by sol-gel technology for headspace solid-phase microextraction-gas chromatographic analysis of aroma compounds in beer. J. Chromatogr. A 1065: 287-299 (2005)
28. Li XJ, Gong SL, Zeng ZR. Development of a sol-gel procedure for preparation of a diglycidyloxycalix[4]arene solid-phase microextraction fiber with enhanced extraction efficiency. Chromatorgraphia 62: 519-525 (2005)
29. Kumar A, Gaurav, Malik AK, Tewary DK, Singh B. A review on development of solid phase microextraction fibers by sol-gel

methods and their applications. Anal. Chim. Acta 610: 1-14 (2008)

30. Farajzadeh M, Rahmani NA. Alumina-based fiber for solid phase microextraction of alcohols from gaseous samples. Anal. Sci. 20: 1359-1362 (2004)

31. Cai YQ, Jiang GB, Liu JF, Zhou QX. Multiwalled carbon nanotubes as a solid-phase extraction adsorbent for the determination of bisphenol A, 4-*n*-nonylphenol, and 4-*tert*-octylphenol. Anal. Chem. 75: 2517-2521 (2003)

32. Wang JX, Jiang DQ, Gu ZY, Yan XP. Multiwalled carbon nanotubes coated fibers for solid-phase microextraction of polybrominated diphenyl ethers in water and milk samples before gas chromatography with electron-capture detection. J. Chromatogr. A 1137: 8-14 (2006)

33. Tian MK, Feng XL. Analysis of organochlorine pesticides in yam samples by headspace solid phase microextraction with carbon nanotubes coated fibers and gas chromatography. J. Instru. Anal. 27: 825-829 (2008)

34. Zhao F, Meng YJ, Anderson JL. Polymeric ionic liquids as selective coatings for the extraction of esters using solid-phase microextraction. J. Chromatogr. A 1208: 1-9 (2008)

35. Zeng JB, Chen JM, Wang YR, Chen WF, Chen X, Wang XR. Development of relatively selective, chemically and mechanically robust solid-phase microextraction fibers based on methacrylic acid-trimethylolpropanetrimethacrylate co-polymers. J. Chromatogr. A 1208: 34-41 (2008)