Review

Development of new solid phase extraction techniques in the last ten years

Huixia Fan[1,2,3], Zhipeng Deng[1,3], Hao Zhong[1,3], Qingqiang Yao[1,3*]

1. Institute of Materia Medica, Shandong Academy of Medical Sciences, Jinan 250062, China
2. School of Medicine and Life Sciences, University of Jinan and Shandong Academy of Medical Sciences, Jinan 250022, China
3. Key Laboratory of Rare and Uncommon Diseases of Shandong Province, Jinan 250062, China

Abstract: Solid phase extraction (SPE) is a widely used sample pretreatment method for separation, purification and enrichment, which has been established due to its significant advantages of time-saving, low consumption of solvent, high enrichment factor, high accuracy, etc. In recent years, a variety of new SPE methods such as molecularly imprinted solid phase extraction (MISPE), magnetic solid phase extraction (MSPE), solid phase micro-extraction (SPME), etc., which are superior to the conventional SPE, have been developed and been widely applied to food, drugs, and environmental monitoring. In this paper, the basic principles and methods of SPE and its new applications in different areas are reviewed.

Keywords: Solid phase extraction; Molecularly imprinted solid phase extraction; Magnetic solid phase extraction; Solid phase micro-extraction

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1. Introduction

The analysis of trace substances including endogenous substances, drugs and their metabolites, food additives and environmentally hazardous substances is a very important task. Scientists engaging in the analytical work are continuously developing rapid, simple, efficient and accurate analytical methods. However, because of the diversity and complexity of the biological matrix and low concentration of the analytes, accurate analysis of the trace substances in complex samples becomes very difficult, there are no simple analytical methods which could solve all or most of the problems encountered in analytical process. Therefore sample pretreatment becomes a key factor in the analysis of trace substances[1,2]. The accuracy and precision of the analysis are significantly affected by the sample pretreatment.

Liquid-liquid extraction (LLE) and solid phase extraction (SPE) are the most commonly used sample pretreatment methods in routine analytical work[3]. Many analytical procedures are based on the usage of these two methods or combined usage of them followed by an analytical separation method, typically high performance liquid chromatography (HPLC), gas chromatography (GC) or capillary electrophoresis (CE)[4]. The analytes have different distribution ratios which are affected by the selected solvent, pH and volume of the aqueous phase and organic phase. The analytes are extracted and separated from the matrix by establishing an equilibrium distribution in two phases. Based on this principle, the LLE method was established. The analytes could be isolated by LLE on condition that the analytes have a higher distribution in the organic

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*Corresponding author. Tel.: 86-0531-82919960;
E-mail: yqingqiang@yahoo.com

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phase. If not, the sample should be extracted repeatedly to recover the analytes, which could be time-consuming and tedious. In fact, researchers usually employ excess organic solvent to extract the analytes for once in order to save time and achieve the same goals. Recently, SPE was developed as a new kind of sample pretreatment technology evolved from LLE and LC, mainly for sample separation, purification and enrichment. SPE gained its popularity owing to its superiority, e.g. less organic solvents, time-saving and high separation efficiency in comparison with LLE. Depending on the type of the adsorbent, SPE could be classified into normal phase SPE, reversed phase SPE and other types of SPE[5]. SPE embraces a liquid phase and a solid phase physical extraction processes. Firstly, the sample passes through the SPE column during which the analytes are adsorbed by the adsorbent, and then the washing solvent washes off the interfering compounds. Finally, appropriate elution solvent is used to elute the analytes off the adsorbent[6–8].

In order to meet the higher demand for analysis like wide application range, high selectivity and sensitivity, new SPE techniques are constantly developed and applied in different areas[9]. For example, matrix solid phase dispersion (MSPD) is a sample preparation method which is widely applied in conducting simultaneous distribution and extraction of target molecules from solid, semi-solid and viscous samples, such as animal tissues and food with a high lipidic content; ion-exchange solid phase extraction is mainly applicable for the analysis of compounds that could produce anions or cations in different matrix with high selectivity.

In this paper, the basic principles of several new SPE techniques commonly used such as molecularly imprinted solid phase extraction (MISPE), magnetic solid phase extraction (MSPE) and solid phase micro-extraction (SPME), and their applications in food, drugs, biological samples, environment-monitoring are reviewed.

2. Molecularly imprinted solid phase extraction

2.1. Basic principles of MISPE

Molecularly imprinted polymers (MIPs) are synthetic materials with artificially generated recognition sites that are able to specifically capture target molecules. Preparation process of MIPs is consisted of three steps: (1) specific functional monomers react with template molecules to form functional monomer, template molecular polymers; (2) the polymers are fixed to the chemical cross-linker; (3) the template molecules are removed. After removing the template molecules, there remains an "imprint" of the template molecules showing good selectivity, reversible binding to template molecules. The preparation process of MIPs and its application to extract target analytes can be simply represented in Figure 1. Ion imprinting polymers could also be prepared by the above procedures[10]. The principle of molecularly imprinted polymerization is similar to the theory of immunity when the antigen interacts with the antibody to form immunoadsorbent. In the above described reaction, the biological antibody is covalently conjugated with a suitable support, and then it could be used for separating specific drugs, pesticides and conducting other highly efficient separation. However, the application of the immunoadsorbent is limited due to the instability of antibody and high cost[8]. Thus, scientists use synthesis to prepare antibody analogues and further applied the method to obtain MIPs, which are applied to chromatography, sensors, immunoassay and other fields[11].

The imprinting techniques of MIPs are as follows: non-covalent cross-linking, functional monomers bind with template molecules by electrostatic, van der Waals forces, hydrogen bonds or other non-covalent bonding; covalent cross-linking, functional monomers and template molecules form covalent binding; semi-covalent cross-linking, functional monomers and template molecules partly form covalent binding. The preparation of MIPs is consisted of bulk polymerization, suspension polymerization, two- or multiple step swelling polymerization, dispersion polymerization, precipitation polymerization, etc.[12,13]. At present, a new polymerization method, surface polymerization, is developed and applied to prepare the diethylstilbestrol (DES)-imprinted silica adsorbent to determine DES in fish samples[14]. The result demonstrated that the prepared DES-imprinted silica sorbent showed high adsorption capacity, significant selectivity, good site accessibility and fast binding kinetics for DES.

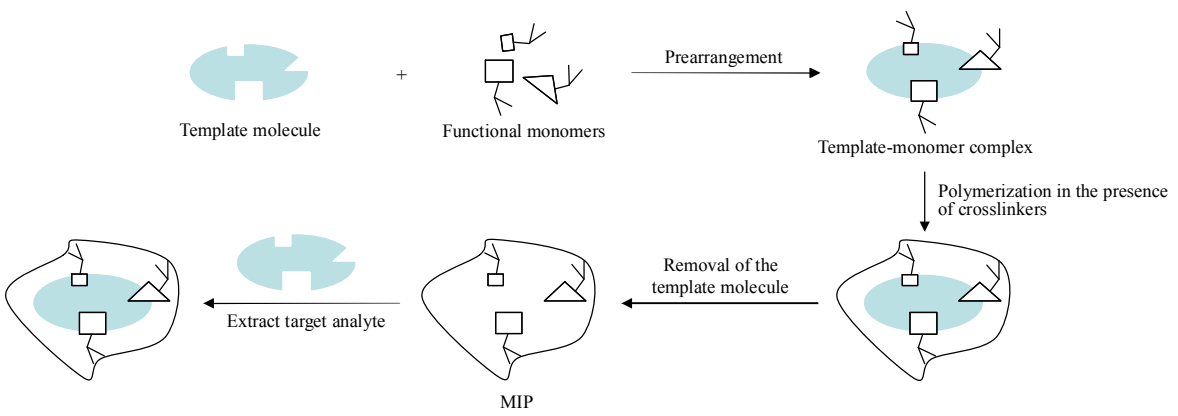

Figure 1. Preparation of MIPs and its application in extracting target analytes.

2.2. New applications of MISPE

In recent years, MISPE has been successfully applied to the extraction and determination of target molecules in different matrices.

Tributylammonium cefadroxil salt (TBA-CFD), methacrylic acid and ethylene glycol dimethacrylate were used by Carolina as template molecules, functional monomers and cross-linkers for the synthesis of cephalosporin-imprinted polymers, respectively[15]. In acetone–methanol (92:8, v/v) mixture, the polymers were synthesized by non-covalent polymerization and used as SPE adsorbents to determine the cephalosporins by HPLC in milk samples. Whether in a simple or complex matrix, the MIPs showed high selectivity and quantitative extraction for cephalexin, cephapirin and cefadroxil. Milk samples originated from different sources could be used for antibiotic analysis with high sensitivity, accuracy and good recovery by the simple and rapid method. The tetracyclines and oxytetracyclines imprinted polymers were synthesized by non-covalent procedures and showed cross-reactivity for certain other tetracycline analytes[16]. The feasibility of the use of MIPs to extract tetracycline antibiotics in pig kidney tissues was demonstrated with the oxytetracycline MIPs. Oxytetracycline and tetracycline were selectively extracted from pig kidney tissues with good recoveries, respectively. A surface polymerization method was used to synthesize 2,4-dinitrophenol (2,4-DNP)-coated SiO_2 micro-particles in aqueous solutions. Then the MIPs were successfully used as SPE adsorbent to enrich and determine 2,4-DNP in water samples by HPLC method[17]. The experimental results indicated that the MISPE column yielded recoveries higher than 92% with RSD<2.8%, much better than the commercial C_{18}-SPE column. MIPs, owing to their simple synthesis, stable property and good adsorption for target molecules, were widely used in SPE for enrichment and analysis in different matrices. New applications of MISPE in analysis of biological samples[18–25], environment monitoring[21,26–30], food[31–36], and drug analysis[37–45] are listed in Table 1.

Table 1. New applications of MISPE in different areas

Template	Polymerization method	Sample	Analytes	Analytical system	Ref.
7-Hydroxycoumarin	Precipitation	Urine	7-Hydroxycoumarin	CZE	[18]
Amiodarone	Bulk	Serum	Amiodarone	HPLC	[19]
Bromhexine	Bulk	Serum Urine	Bromhexine	HPLC	[20]
Carbamazepine	Bulk	Urine Waste water	Carbamazepine	LC LC-MS	[21]
Cephalexin	Bulk	Serum	Cephalexin	MS	[22]
Nicotine	In situ	Hair	Nicotine	HPLC	[23]
Ofloxacin	Precipitation	Urine	Quinolones	HPLC	[24]
Tramadol	Bulk	Plasma Urine	Tramadol	HPLC	[25]
Alkyl methylphosphonic acids	Bulk	Soil	Alkyl methylphosphonic acids	LC-MS	[26]
Catechol	Bulk	Waste water	Catechol	DPV	[27]
Pirimicarb	Bulk	Waste water	Carbamate pirimicarb	DPV	[28]
Polycyclic aromatic hydrocarbons	Sol-gel/surface	Sea water	Polycyclicaromatic hydrocarbons	GC-MS	[29]
Diphenolic acid Bisphenol A	Sol/gel	Waste water	Tetrabromobisphenol A	RRLC	[30]
Metolachlor deschloro	Suspension	Cabbage Tea Sunflower seed Tangerines	Chloroacetamide herbicides	LC/MS/MS	[31]
Dibutyl phthalate	Bulk	Soybean milk	Dibuthyl phthalate	GC-MS	[32]
Hydrochloride	Sol/gel	Milk	Oxytetracycline	HPLC	[33]
Bensulfuron-methyl	Precipitation	Soybean	Sulfonylurea herbicides	HPLC	[34]
17β-Estradiol	Precipitation	Milk powder	17β-Estradiol	HPLC GC-MS	[35]
Sulfamethazine	Bulk	Milk	Sulfamethazine	SWV	[36]
Matrine	In situ.	*Sophorae flavescentis* Ait	Matrine	HPLC	[37]
Puerarin	Bulk	Radix puerarine	Puerarin	HPLC	[38]
Rutin	Solution	*Saururus chinensis* (Lour.) Bail flos sophorae	Rutin	HPLC	[39]
Oleanolic acid	Solution	Roots of kiwi fruit	Oleanolic acid	HPLC	[40]
Andrographolide	Precipitation	*Andrographis paniculata* (Burm.f.) Nees	Andrographolide Dehydroandrographolide	HPLC	[41]
Quercetin	Bulk	Cacumen platycladi	Quercetin	HPLC-UV	[42]
Kirenol	Thermal	*Siegesbeckia pubescens*	Kirenol	HPLC	[43]
Metformin	Solution	Mixed solution	Metformin	HPLC	[44]
Esculetin	Bulk	Ash bark of Chinese traditional medicine	Esculetin	HPLC	[45]

Notes: CZE, capillary zone electrophoresis; DPV, different pulse voltammetry; SWV, square wave voltammetry; RRLC, rapid resolution liquid chromatography; SWV, square wave voltammetry.

As shown in Table 1, MISPE coupled with different analytical methods has been widely employed in biological analysis, and environmental monitoring especially in water quality monitoring and analysis of harmful substances in food. Bulk polymerization was the most commonly used method in the preparation of MIPs while other polymerization methods such as suspension polymerization and precipitation polymerization were used relatively less frequently. In addition, there are increasing reports on MISPE in the analysis of chemical composition of natural product pharmaceuticals, which provided a fast, simple and efficient analytical method for determining the active chemical ingredients or harmful substances in natural product medicines. Furthermore, MISPE is commonly used in sample pretreatment for analyzing many pharmaceutical molecules with different chemical structures such as coumarins, benzofurans, benzodiazepines and so on. This also could provide an effective method for the metabolite enrichment in drug metabolism study.

3. Magnetic solid phase extraction

3.1. Basic principles of MSPE

Magnetic solid phase extraction (MSPE) is another kind of sample pretreatment method which has drawn much attention recently. In MSPE, a magnet is introduced as an adsorbent in SPE to isolate magnetic extraction particles from sample matrix[46]. Unlike the traditional SPE technology, magnetic adsorbents need not to be directly filled in the SPE cartridge, but dispersed in the sample solution or suspension. Then the target analytes are adsorbed by the magnetic adsorbent, separated from the matrix by using external magnetic field instead of filtration or centrifugation, and eluted by a small volume of appropriate eluent from the adsorbent[47]. The process of MSPE is represented in Figure 2.

It is critical to select appropriate adsorbent to achieve efficient and accurate extraction in SPE, so is the magnetic adsorbent to the MSPE. It is very important to prepare the magnetic adsorbent with high adsorption capacity for the target analytes. Iron minerals and magnetic iron oxides including magnetite (Fe_3O_4) and maghemite (Fe_2O_3) are the most commonly used magnetic adsorbents[48]. However, the pure inorganic magnetic particles are easily gathered because of the presence of residual magnet after the removal of external magnetic field, so it is difficult to operate with high selectivity and separate target analytes in the complex matrix.

Superparamagnetic nanoparticles are one of the most promising new adsorbents in analytical nanotechnology compared with conventional ones. Superparamagnetic nanoparticles have many advantages including large surface area, high adsorption capacity and less usage of organic solvents. Under the external magnetic field the analytes are easily separated from the matrix without retaining residual magnetization. Besides, we could improve the selectivity of the adsorbent and facilitate the separation of target molecules in complex matrices by the magnetic particle surface modification with specific functional groups[49].

3.2. Applications of MSPE

Because of the advantages of easy operation and high-adsorption capacity, MSPE has been increasingly used for sample separation and concentration in the field of food, biology and environmental sciences. Superparamagnetic Fe_3O_4 diphenyl nanoparticles with the average particle size of 200 nm were successfully prepared by solvothermal procedure and applied as a new SPE adsorbent for the analysis of 16 polycyclic aromatic hydrocarbon compounds (PAHs) in urine. Compared with the commercial devices, the magnetic nanoparticles synthesized using a rapid and low-cost procedure can achieve superior extraction performances with good precision in the detection of PAHs from biological samples[49]. The lower limit of quantitation (LLOQ) was within the ng/L range. Hydrophilic carbon-functionalized magnetic Fe_3O_4 microspheres coated with chitosan (Fe_3O_4@C@CHI) were initially synthesized by Geng[50]. The nanoparticles with particle size of 400 nm were successfully applied for the determination of bisphenol A in aqueous samples with good recovery and low RSD, which indicated the nanoparticles were good MSPE materials for the extraction of the analytes. New applications of MSPE in different areas are listed in Table 2.

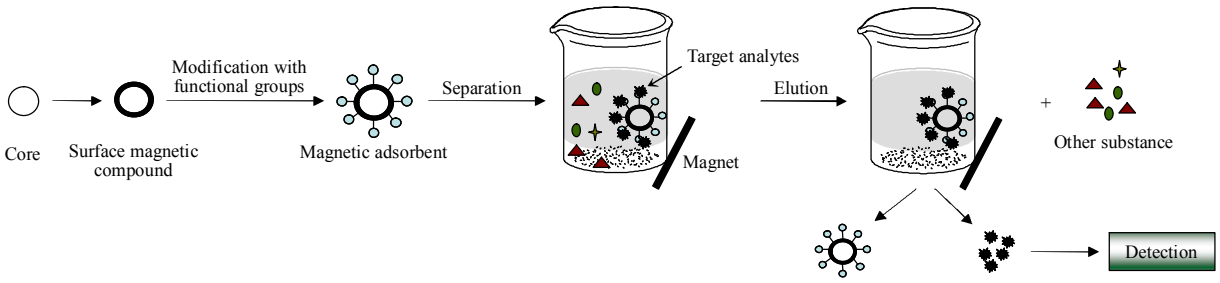

Figure 2. Process of magnetic solid phase extraction.

Table 2. New applications of MSPE in different areas

Surface modification materials	Sample	Analyte	Analytical system	Region	Ref
Zincon	Natural water Drinking water	Lead	GFAAS	Environment Environment	[51]
Poly (divinylbenzene-co-methacrylic acid)	Natural water	Endocrine	HPLC-MS/MS	Environment	[52]
2-Acrylamido-2-methyl-1-propanesulfonic acid-co-ethylene glycol dimethacrylate	*Oryza sativa* roots	Cytokinins	HILIC-MS/MS	Natural pharmceutical	[53]
Carbon	River water	Organophosphorus pesticides	HPLC-UV	Environment	[54]
Dodecyltriethoxysilane	River water Tap water Urine	Steroid hormones	HPLC-UV	Environment Environment Bio-sample	[55]
γ-Ercaptopropyltrimethoxysilane	Lake sediment Milk powder Sea water	Cd Cu Hg Pb	ICP-MS	Environment Food Environment	[56]
Oleic acid	Tap water River water Sea water	Cosmetic products	GC-MS	Environment Environment Environment	[57]
Organic modified montmorillonite	River water Waste water	4-Chlorophenol 2-Chlorophenol	HPLC-MS	Environment Environment	[58]
Polyanilines	Honey samples	Fluoroquinolones	HPLC-FLD	Food	[59]
Aptamer for ochratoxin A	Wheat Cereal Coffee	Ochratoxin A	HPLC-FLD	Food Food Food	[60]
Phenyl silica	Milk	Tetracylines	CE	Food	[61]
Al_2O_3	Water sample	Surfactants	UV	Environment	[62]
Bismuthiol-II	River water Lake water	Cr Cu Pb	ICP-OES	Environment Environment	[63]
Octadecyltrimethylammonium bromide	Tap water Sewage	Sulfonamides	HPLC-UV	Environment Environment	[64]
Cetyltrimethylammonium bromide	Tap water Groundwater Jingmi canal water Xiaoqing water Gaobeidian water	2-Chlorophenol 2,4-Dichlorophenol 2,4,6-Trichlorophenol Pentachlorophenol	HPLC	Environment Environment Environment Environment Environment	[65]
Gatifloxacin MIPs	Human serum samples	Gatifloxacin	HPLC	Pharmaceutical	[66]
C_{18}	Rat plasma	Puerarin	HPLC	Pharmaceutical	[67]
Iron oxide	Human blood serum	Salicylic acid	HPLC-UV	Pharmaceutical	[68]
Diol groups	Human serum	Methotrexate (MTX) Leucovorin (LV) Folic acid (FA)	HPLC	Pharmaceutical Pharmaceutical Pharmaceutical	[69]
Ionic liquid	*Salvia miltiorrhiza* Bunge	Cryptotanshinone Tanshinone I Tanshinone IIA	HPLC	Pharmaceutical Pharmaceutical Pharmaceutical	[70]
Cetyltrimethyl ammonium bromide	Urine Serum	Rhein Emodin	HPLC-FLD	Pharmaceutical	[71]

Notes: FAAS, Flame atomic absorption spectrometry; GFAAS, Graphite furnace atomic absorption spectrometry; HILIC-MS/MS, Hydrophilic interaction chromatography-tandem mass spectrometry; ICP-MS, Inductively coupled plasma mass spectrometry; HPLC-FLD, High performance liquid chromatography with fluorescence; CE, Capillary electrophoresis; ICP-OES, Inductively coupled plasma optical emission spectrometer.

MSPE is mainly used in environmental monitoring[50–52,54–58,62–65] and pharmaceutical analysis[66–71], while the applications in food science are relatively less[56,59–61]. This technique as well as MISPE is mainly applied in the analysis of various drugs in biological samples. The coupled analytical methods are mainly restricted to HPLC system. Selecting new adsorbent with superior properties is the key for MSPE in future development, toward broadening the sample range, improving the recoveries, detection limit and the accuracy of target analytes. In the future, MSPE will take an increasingly more important role in sample pretreatment.

4. Solid phase micro-extraction

4.1. Basic principles of SPME

Solid phase micro-extraction (SPME) is another kind of sample pretreatment method combining the four steps of sampling, extraction, preconcentration and matrix removal into one. The technology was first introduced and further developed by Prof. Pawliszyn and his colleagues in 1990s, which was a soventless extraction. The fiber immerses into the sample solution or the headspace for

a period of time, while the solution is stirred to accelerate the equilibrium between the two phases. After the equilibrium, the fiber is removed from the matrix and the analytes are introduced into the analytical instruments after desorption.

SPME is composed of the adsorption and desorption processes. Based on the chemical structure of the analyte, selecting appropriate materials as SPME coating for the fiber is the key to SPME. Traditional coating materials are high polymers such as polydimethylsiloxane (PDMS), polydimethylsiloxane/divinylbenzene (PDMS/DVB), polydimethylsiloxane/carboxen (PDMS/CAR), polyacrylonitrile (PAN) etc[72]. To overcome the shortcomings like poor thermal stability, low selectivity, low sensitivity and narrow application scope of the high polymer coating materials, new coating materials are gradually developed and gained wide application. The new coating materials including carbon nanotubes (CNTs)[73], molecularly imprinted polymers[74,75], and sol-gel coating materials[76] have been successfully applied in different aspects. The most common method coupled with SPME for quantitative analysis includes GC and HPLC. When GC is used for the quantitative analysis of the volatile compounds, the fiber is directly inserted into the vaporization chamber of gas chromatography system to undergo thermal desorption for target analytes separating from the adsorbent. Due to the superiority of non-solvent use in SPME, the analytes adsorbed on the stationary phase are introduced directly into the gas chromatography system without any complicated volume reduction/splitting technologies. When SPME is connected with HPLC systems, liquid desorption is the common desorption method. Moreover, laser desorption is another method for the disassociation of the analytes from the fiber with high intensity laser[72]. SPME coupled with GC is mainly used for the analysis of volatile or semi-volatile organic compounds, but the metal ions and organometallic compounds could still be analyzed using SPME with derivatization to enhance the detection intensity[77]. Compared with the traditional SPE methods, SPME is simple, solventless, selective and flexible[78].

There are two basic extraction modes of SPME: direct solid phase micro-extraction (DI-SPME)[79,80] and headspace solid phase micro-extraction (HS-SPME)[76,81]. The choice of extraction mode is dependent on the composition of sample matrix and volatility of the analyte. In direct extraction, the fiber coated with stationary phase is directly inserted into the sample matrix and the target analytes are adsorbed from the matrix onto the fiber under the principle of partitioning. Direct SPME is applicable for the analysis of non-volatile compounds in the clean matrix. When the sample components are complex or contain many biological macromolecules, the direct extraction is not available because of the matrix impurities adsorbed on the SPME fiber could exhibit interference for the chromatographic analysis and even reduce the working life of the extraction fiber. In headspace extraction, the easily volatile analytes in the sample could be adsorbed in the top of the vial as a consequence of volatility, removing the impurity interference and matrix effects. Therefore, this mode is suitable for volatile analytes in complex matrix. To achieve a wider range of analytes and more high capacity, new extraction modes are constantly developed, e.g. membrane protect extraction. The schematic illustration of SPME is shown in Figure 3.

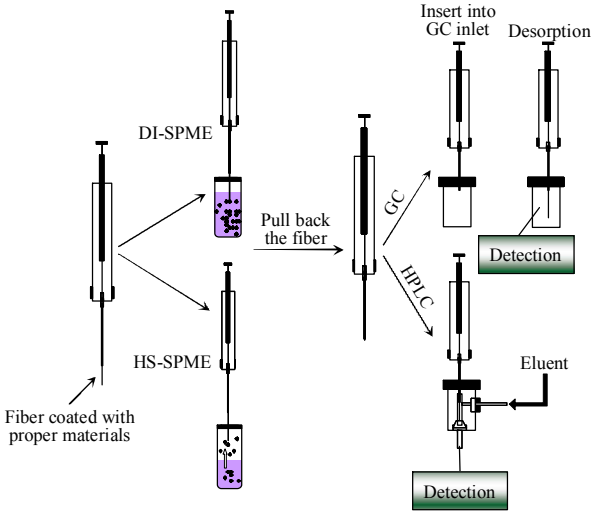

Figure 3. Schematic illustration of solid phase micro-extraction.

4.2. Applications of SPME

With the development of SPME technology, SPME has been widely used in different fields. A type of sol-gel/graphite coating material on a silica rod was prepared by Farhadi and applied as the micro-extraction fiber for headspace sampling and determination of benzene, toluene, ethylbenzene and xylene (BTEX) by GC in indoor air and outdoor soil samples[76]. The fiber coating was thermally stable and demonstrated high sensitivity for BTEX. The limit of detection using this method for BTEX in indoor air and soil samples were 0.2–0.7 ng/mL and 8–20 ng/mL with the RSD of 5.0% and 7.9%, respectively. A method for the determination of trace Cr (III) in an aqueous solution by SPME coupled with gas chromatography-flame photometric detection (GC-FPD) was established[77]. Aqueous Cr (III) was converted to the volatile $Cr(TFA)_3$ isomers by the derivatization with 1,1,1-trifluoroacetylacetone and then extracted by SPME using a polyimide-coated silica fiber. The isomers can be efficiently separated by a DB-210 GC column within 9 min. The limit of detection was 2.00 ng/mL and the RSD was 7% at 10 ng/mL (n = 5). The method was successfully applied to the analysis of Cr (III) in industrial effluent. A SPME probe with antibodies specific for benzodiazepines covalently immobilized on the surface was prepared and evaluated for analyzing 7-aminoflunitrazepam of sub ng/mL concentrations in urine with SPME-LC-MS/MS[82]. The developed method showed a limit of detection of 0.02 ng/mL, with the accuracy ranging from 1% to 27% and the precision (RSD) ranging from 2% to 10% between the lower and upper

limits of quantitation. This method has the advantage of simple sample preparation over other methods and can be used effectively in drug monitoring. New applications of SPME in different areas are listed in Table 3.

As shown in Table 3, the extraction, enrichment and detection of different volatile, semi-volatile and non-volatile compounds after derivatization by HS-SPME coupled with GC and HPLC in different areas have been extensively studied[73,81,83,85,86,88–95], while the DI-SPME mode[80,84,87,96–98] was studied relatively less. This technique is seldom used in analyzing pharmaceuticals in biological samples or other complex matrix, which may be affected by the impurities. Nowadays, new coating materials with good selectivity, high sensitivity and practicality are continually developed and the SPME is being coupled with more analytical technologies.

5. Conclusion

The principles and usages of MISPE, MSPE, and SPME are reviewed. MISPE is a type of SPE technique using MIPs with specific recognition for target molecules to extract the target compound from different sample matrix. This technique has the advantages of specificity, high selectivity and good stability because of the properties of MIPs and can extract target molecules from complex sample matrix, while the SPME cannot be applied in this case. But the use of MISPE is restricted to the specific structures of the target analytes. MSPE can simplify the operation process with high efficiency as well as reproducibility comparing with the traditional SPE technique. However, the specificity of this technique is restricted to the magnetic adsorbents, and its selectivity is relatively lower than MISPE. There are two main extraction approaches including HS-SPME and DI-SPME for SPME, and HS-SPME is more often used in daily research work. But the main disadvantage of this extraction approach is that only volatile analytes or their derivatives can be extracted with this method. DI-SPME is suitable for the extraction of analytes that are not easily volatile, but its sensitivity could be affected by the complexity of the biological matrix. In general, the technique is easy to operate and flexible, and no solvent is used in spite of the drawbacks.

Table 3. New applications of SPME in different areas

Fiber coating	Analyte	Sample	Extraction mode	Analytical system	Ref.
PAN/MWCNTs	BTEX, 2-Octanone Benzaldehyde Acetophenone 2,6-Dimethylphenol	Water solution	HS-SPME	GC	[73]
PDMS	Triazine Chloroacetamide herbicides	Tile-fed ditch Water	DI-SPME	GC-MS	[80]
DVB/CAR/PDMS	Acromatic fraction	Wine	HS-SPME	GC-MS GC-FID	[81]
PDMS/DVB	Volatile composition	*Passiflora* fruits	HS-SPME	GC-qMS	[83]
CW/TPR	Chlorhexidine	Saliva	DI-SPME	HPLC-MS	[84]
DVB/CAR/PDMS	Short-chain fatty acids	Faecal	HS-SPME	GC-MS	[85]
DVB/CAR/PDMS	Methyl tert-butyl ether	Surface water Tap water Mineral water Snow samples	HS-SPME	GC-MS	[86]
Sol-gel-TMSPA/PDMS	Organophosphorous pesticides	River water	DI-SPME	GC-MS	[87]
Sol-gel-DDP	Polycyclic aromatic hydrocarbons	Ground water Drinking water	HS-SPME	GC-MS	[88]
PA nanofibers	Phenol Chlorophenls	River water Tap water	HS-SPME	GC-MS	[89]
PDMS	Organochlorine residue	River sediment	HS-SPME	GC	[90]
DS-doped PPY	Methyl tert-butyl ether	Ground water Unsealed gasoline	HS-SPME	IMS	[91]
DVB/CAR/PDMS	Volatile compounds	Jackfruit cultivars	HS-SPME	GC-TOFMS	[92]
SWCNTs	Benzene Toluene Ethylbenzene Xylenes	Sea water Tap water Waste water	HS-SPME	GC-FID	[93]
DVB/CAR/PDMS	Volatile and Semi-volatile compounds	*Eupatorium odoratum* extract	HS-SPME	GC-MS	[94]
PA	Alky phenols	Water	HS-SPME	GC-MS	[95]
Polyacrylate	Tetramine	Human urine	DI-SPME	GC-FTD	[96]
Berberine-imprinted polymer	Berberine	Human plasma Urine	DI-SPME	HPLC-UV	[97]
Polypyrrole	Linezolid	Human plasma	DI-SPME	HPLC-MS	[98]

Notes: MWCNTs/SWCNTs, Multi/single-walled carbon nanotubes; GC-FID, gas chromatography-flame ionization detection; CW/TPR, carbowax/templated Resin; GC-qMS, gas chromatography-quadrupole mass spectrometric; TMSPA/PDMS, 3-(trimethoxysilylpropyl)amine/polydimethylsiloxane; DDP, diethoxydiphenylsiliane; PA, polyamide; DS-doped PPY, dodecylsulfate-doped polypyrrole; IMS, ion mobility spectrometry; GC-TOFMS, gas chromatography-time-of flight mass spectrometry; GC-FTD, gas chromatography-flame thermionic detection.

Since the discovery of the SPE technique, it has been successfully applied in cleaning up and selectively enriching the target analytes from different types of samples owing to its significant advantages including high selectivity, high efficiency and less organic solvents. However, there are still some limitations such as the narrow scope of application, specific target analytes, limited coupling technologies and high cost. Therefore, the development of new SPE techniques with wider applications, lower cost, higher precision and accuracy in sample pretreatment has been a great challenge for researchers. Firstly, developing new adsorbents with high selectivity, stable properties and high reproducibility is crucial to broaden the applications of SPE. Secondly, advancement of different instrument technologies like GC, HPLC, HPLC-MS/MS will promote the applications of SPE in sample pretreatment. Finally, developing new SPE methods for the sample analysis should be focused. In the foreseeable future, new applications of SPE will continue to emerge.

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几种固相萃取新技术近十年的研究进展

范惠霞[1,2,3], 邓志鹏[1,3], 仲浩[1,3], 姚庆强[1,3*]

1. 山东省医学科学院 药物研究所, 山东 济南 250062
2. 济南大学 山东省医学科学院 医学与生命科学学院, 山东 济南 250022
3. 山东省罕少见病重点实验室, 山东 济南 250062

摘要: 固相萃取技术是近年来发展较快并得到广泛应用的一种样品前处理方法 (分离、纯化、富集), 具有节省时间、溶剂消耗少, 富集倍数高, 准确度高等优点。随着科学技术的不断发展及研究的不断深入, 多种优于传统固相萃取技术的新型固相萃取新技术如分子印迹固相萃取、磁性固相萃取、固相微萃取等不断出现并广泛应用到食品、药品、生物及环境监测等领域。本文对几种固相萃取新技术的基本原理、方法及近十年来在不同研究领域的研究应用进行综述。

关键词: 固相萃取; 分子印迹固相萃取; 磁性固相萃取; 基质分散固相萃取

Dr. Yao graduated from the School of Pharmaceutical Sciences, Shandong Medical University in 1987 with the Bachelor degree. He obtained his PhD degree in science at Peking Union Medical College in 1988. In 2001, he joined the University of Sydney in Australia as a visiting scholar. In 2003, he engaged in the research on the plant metabolomics at the University of Leiden in Netherlands. Currently Dr. Yao is the director of Institute of Materia Medica, Shandong Academy of Medical Sciences, and the editor of *Chin. Trad. Herb. Drugs*. Besides, he is also the executive director of Pharmaceutical Society of Shandong Province, and deputy director of Professional Committee of Chinese Natural Medicine. He won the second National Scientific and Technological Progress Award, and the second Shandong Province Scientific and Technological Progress Award in twice. His team was repeatedly funded by National Natural Science Foundation of China and the National Science and Technology Major Projects.

姚庆强博士, 1987年7月毕业于山东医科大学(现山东大学)药学院; 1998年7月获中国协和医科大学理学博士学位。2001年在澳大利亚悉尼大学任访问学者, 2003年在荷兰莱顿大学从事植物代谢组学的研究。现任山东省医学科学院药物研究所所长, 《中草药》杂志编委, 山东省药学会常务理事, 中药与天然药物专业委员会副主任委员。先后获国家科技进步二等奖一项, 山东省科技进步二等奖两项。他领导的团队多次承担国家自然基金, 国家重大科技专项。