

# RECENT DEVELOPMENT AND APPLICATION OF SOLID PHASE EXTRACTION MATERIALS

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**Abstract.** Recently, the solid phase extraction technology has received considerable attention considering serious environmental problems and much more contaminants present in the samples at trace level that is different to be analyzed. During the whole process of analyzing sample, the preconcentration of sample is the most complicated and significant step, which typically spend much time, affecting the analysis efficiency and accuracy of results to a large extent. Obviously, the sample pretreatment has become an obstacle that prevents us from improving analysis efficiency. If this problem cannot be resolved, the overall efficiency of analytical work will not be enhanced, even using the advanced analysis devices. As a result, increasing the success rate of sample pretreatment is especially necessary. Now, this review mainly represents the current development of solid phase extraction from the following aspects: (1) the type of adsorbent, including organic, polymer materials; (2) the different mode of separation, such as solid phase extraction, molecule imprinting solid phase extraction, solid phase microextraction, dispersive solid phase extraction, matrix solid phase dispersion, magnetic solid phase extraction, microchip solid phase extraction, stir bar sorptive extraction, immunoaffinity solid phase extraction, monolith solid phase extraction; (3) the practical applications of various solid phase extraction methods are also have been described in this article.

## 1. INTRODUCTION

To date, a collection of the detrimental pollutant has been released before disposed. As a result, the water and environment have been polluted seriously, for example pesticides, antibiotics as well as food additives and other harmful substances. Taking the human health and environment safety into consideration, it is urgent to reduce and even to eliminate the discharge of organic contaminant, heavy metal ions and so on. Generally, a complete process

of sample processing contains four steps, i.e. the sample collection, the preconcentration of sample, sample analysis and the data processing. In consideration of the complexity of sample matrices and these objectives present in sample at trace level (mg/L) and even lower, the preconcentration of sample become a key step in SPE technique. At the same time, this step has a significant impact on eliminating chaff interferent as well as enhancing the analysis sensitivity.

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The conditionally disposed methods of preconcentration of sample include liquid-liquid extraction (LLE), natural subsidence, centrifugal separation and filtration etc., have some disadvantages: lower accuracy and precision, difficult to automate, waste of time, high limitation. These traditional techniques cannot well meet with the requirements of sample analysis with the detection condition has been becoming more and more rigor. Especially, it is possible to result in secondary pollution when a great number of the organic solvents are used in the experiments. Therefore, it is necessary to seek and employ selective, rapid, handy and accurate analysis methods for preconcentration of the trace level of the substance.

To settle this problem, many investigators have made great efforts. Solid phase extraction (SPE) based on LLE procedure is a technique that can separate and enrich the target analytes from complicated matrix successfully. There are many outstanding advantages about SPE technology, such as high safety, low consumption of organic solvents, simple and rapid phase extraction, high efficiency, great repeatability and reproducibility, and good capability of combination with distinct detection devices in different forms, and so on [1].

A key point in SPE is the choice of adsorbent. During a routine SPE process, the objectives can be adsorbed onto the external or internal surface of selected adsorbents and then they will be collected and detected via different advanced technologies after carrying out elution procedure. Hence, an appropriate adsorbent used can shorten the analysis time, improve the precision of results, save organic solvents, etc. To date, various adsorbents were used in SPE, such as carbon material, silica, titanium dioxide, ion exchange resins etc. Each of them has its own special advantages and different experimental purposes can be come true with them.

In recent years, so many researchers focus their attentions on the preconcentration of samples that several new separation modes have been developed constantly, e.g. solid phase micro-extraction (SPME), molecularly imprinted solid-phase extraction (MISPE), dispersive solid-phase extraction (DSPE), magnetic solid phase extraction (MSPE), microfluidic solid phase extraction (uchipSPE), etc. Although all of methods have something in common, each has its distinct characteristics and scope of application as well as different limitations sometimes. In order to get more accurate results and higher stability, generally, some detecting instruments must be utilized with SPE technology together. Among them, high performance liquid chro-

matography (HPLC), ultra performance liquid chromatography (UPLC), inductively coupled plasma (ICP), gas chromatography (GC), mass spectrometry (MS), liquid chromatography–tandem mass spectrometry (LC-MS), gas chromatography–mass spectrometry (GC–MS) etc. are the usual apparatus for determination and analysis of the samples. For example, selective extraction of 2-,3-,4-methyltaoic and cyclohexanecarboxylic acids in wine via GC-MS was realized successfully by Elisa Gracia-Moreno group [2]. And Borrull et al. determined musk fragrances from waste water based on GC-MS [3]. Ballesteros et al. successfully separated endocrine disrupting compounds (EDCs) in environmental water using SPE system in combination with GC-MS [4]. And then, Noventa et al. succeeded in concentrating the organotin compounds in biota samples via HS-SPME–GC–MS/MS [5]. Huang et al. isolated five benzoylurea insecticides (BUs) in water and juice samples using environmentally friendly method of multiple monolithic fiber SPME and LC analysis, the relative standard deviations (RSD) of all BUs are less than 10% [6]. Fiorini et al. successfully analyzed and quantified 22 main volatile compounds by a head space SPE coupled to gas chromatography with mass spectrometry and flame ionization detection (HS-SPME-GC-MS/FID) method [7]. Wang et al. developed a novel MIP-SPE method via a covalent imprinting interaction for selective and effective enrichment of ractopamine by hydrogen bonding [8]. Javier Hernández-Borges et al. employed multi-walled carbon nanotubes as the adsorbent for the simultaneous determination of 15 pesticides in cereal-based baby foods by DSPE method coupled with GC-nitrogen phosphorus detection (GC-NPD) analysis [9].

It is proved that SPE technology show excellent performances in isolating and enriching the various analytes such as pharmaceuticals, heavy metal ions, protein, organic contaminants, pesticide, hormone compounds from food, water, oil, soil, human urine, human blood, raw bovine milk, as well as vegetable samples.

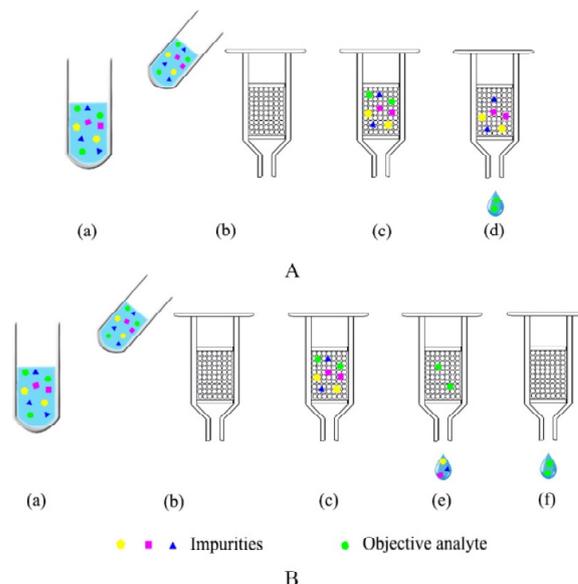
All these characters make it possible that the procedure could be applied comprehensively in different fields, including examination of medicines, analysis of the food, detection of the environment and other fields. There is no doubt that, equipped with these advantages, solid phase extraction has gradually substituted the traditional liquid phase extraction as the effective method for the concentration and enrichment of complicated samples to a certain extent.

The purpose of this review reported is to describe the present development of the sample preparation in solid phase extraction techniques, i.e. the importance of choice of adsorbent materials as well as the mode of separating analytes free from complicated matrices in sample. Furthermore, to have a good understanding of SPE, several practical applications associated with these technologies are also discussed.

## 2. BASIC OPERATION PROCESS OF SOLID PHASE EXTRACTION

When applying the SPE, the sorbents are served as the stationary phase and simultaneously the liquid phase is the aqueous samples during the extraction. As shown in Fig. 1, when the liquid phase flows through the columns, the analytes are able to be enriched and adsorbed due to their high affinity for the sorbent, including ion exchange interaction forces, hydrophobic force adsorption and physical adsorption. According to the distinct distribution coefficient between the analytes and impurities with the solid phase extraction cartridges, the impurities matrices are able to be eluted through the certain polar solvent for some time. Then it is time to utilize the appropriate solvent to elute the analytes adsorbed onto the solid phase so that the aim of purification, concentration as well as separation could be realized successfully. There is another way to achieve the same goals. Briefly, fixing the impurities onto the solid phase, and then eluting the analytes through applying applicable polar dissolvent, accordingly.

In simple words, there are several steps need to be considered when the solid phase extraction procedure is executed, such as the appropriate selection and activation of the cartridge, upper sample, leaching and elution. All these steps need be controlled very well. Activation: using certain polar solvent flow through the column to wipe off the impurities and create an ideal solvent condition. Upper sample: after dissolving the samples, the analytes and impurities could be loaded onto the adsorbents. It would be better to select the low polar solution so as to the analytes are able to be retained on the sorbents. If the polarity of the solution is higher, it is possible that some analytes will be wasted and lost. Leaching: the purpose of the step is to wipe off the almost impurity components, thus the influence of the interfering components could be decreased to maximum extent. During this procedure, the polarity of the solution could be increased to some degree to dislodge the impurities loaded on the ex-



**Fig. 1** The modes of adsorbing the impurities (A) and the target analytes (B): (a) the sample solution, (b) and (c) upper sample, (d) the separation of analytes from impurities, (e) adsorption of analytes with extractant, (f) elution of the analytes from extractant.

tractant. However, there is a tip that needed to have second thoughts, that is the polar solution cannot leach the target analytes from the adsorbents. Elution: it is essential to elute the analytes in order to achieve the goal of concentration. The polarity of the solvent must be controlled properly. Once the polarity is higher, some impurities maybe flowed into the analytes solution. Reversely, if the polarity is lower, it is possible that some analytes are still left on the adsorbents and the recoveries will be decreased. In addition, it is necessary to make sure that the order of the solvents used in the extraction is correct. Furthermore, to acquire the ideal value, the optimum conditions of preconcentration and enrichment, for example pH of aqueous phase, amount of the sorbent, potential interfering ions, volume of the solutions, flow variables and rate are needed to be investigated carefully. By and large, if every factor could be conditioned to the best value, the optimum results will be obtained, accurately.

## 3. ADSORBENTS USED IN SOLID PHASE EXTRACTION

In the preconcentration of samples, adsorbent is the core, and the selectivity of an adsorbent has a significant influence on the accuracy of results. As

a consequence, an appropriate and ideal adsorbent will not only reduce the time consumption, simplify protocol, save solvents, but enhance adsorption efficiency and improve reliability of conclusions. Apart from the use of adsorbent, applying different SPE technologies coupled with advanced analytical instruments, including HPLC, UPLC, GC, MS, ICP, etc., in on-line or off-line modes, the qualitative and quantitative detection of analytes can be realized successfully.

A variety of adsorbents are explored and used in SPE, such as activated carbon [10], graphene [11], carbon nanotubes [12], silica [13,14], alumina [15], polystyrene [16], chitosan [17], polysulfone/montmorillonite composites [18], activated carbon/polymer hybrids [19], etc., these adsorbents can be mainly divided into three fields, i.e. inorganic material, polymer material and inorganic/polymer material briefly. Given the inorganic/polymer composite hybrids usually are based on these two types of materials and combined with the advantages of them, here we mainly introduce the first two materials.

### 3.1. Inorganic adsorbent

A collection of inorganic materials are applied as adsorbents with the aim of extraction, for instance, carbon material, silica, titanium dioxide and other materials. Herein, these three ones are widely used. Inorganic adsorbents play the critical role in SPE system, massive reported literatures have affirmed its extraordinary influence, just like for enrichment of metal ions [20,21], heterocyclic amines [22], pesticides [23], etc. All these literatures have affirmed the importance of the inorganic adsorbent.

#### 3.1.1. Carbon material

In adsorption applications, carbon material is an important member of inorganic adsorbents. There are many adsorbents belonging to carbon material. Activated carbon, carbon nanotubes and graphene are the most commonly used adsorbents for isolating analytes resulting from high extraction capability and removal efficiency.

##### 3.1.1.1. Activated carbon

Activated carbon, as traditional adsorbent, is the most important one due to its large surface area, low cost, high chemical and physical adsorption capacity, porous structure and selective adsorption ability as well [24]. For instance, Msagati et al. has carried out many researches about this material.

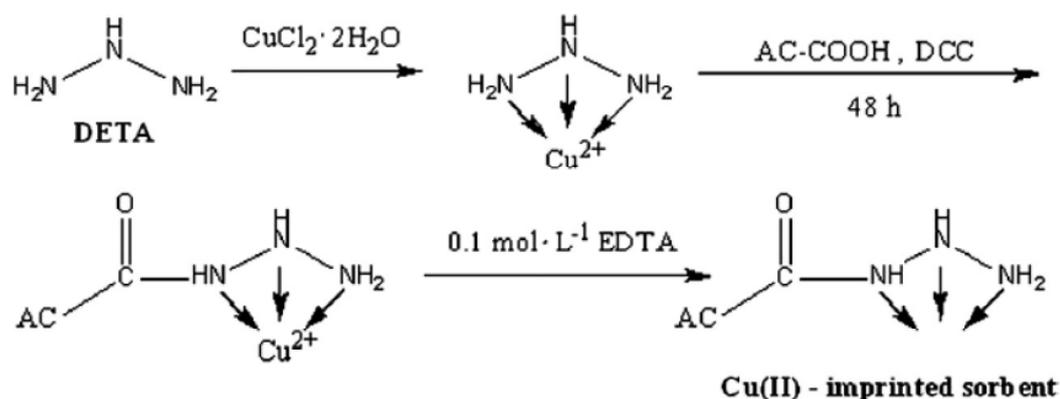
They have employed the maize tassels activated carbon as adsorbents prepared from maize tassels, a natural materials, and effectively eliminated three phenolic compounds in the waste water [25].

Activated carbon decorated with different functional groups is equipped with higher selectivity and adsorption ability. Ensafi et al. used the activated carbon modified with xylenol orange (XO) as sorbent for separation and enrichment of trace Pb (II), the highly selective separation of the Pb(II) then was presented and the detection limit was reached to level of ng/L [26]. Khodadoust et al. utilized the activated carbon loaded with methylene blue as the extractant for highly selective adsorption and preconcentration of trace Sn(II) ion [27]. All of them indicate that the activated carbon is a kind of excellent adsorbent which can absorb target components from different samples, for instance, rivers, waste water, soil. Some people devote themselves to modify the activated carbon in order to improve adsorption capability. Li et al. prepared amino-modified activated carbon (AC-ZCN) by using the molecular imprinting technique as a solid-phase extractant for selectively pretreatment of trace level of Cr(II). In the experiment, the adsorption capability had been compared between many other ions (i.e. Zn(II), Ni(II), Co(II), Pb(II)) and Cu(II) by using Cu(II)-imprinted and non-imprinted sorbent. After a collection of trials, the amazing results indicate that Cu(II)-imprinted amino-functionalized activated carbon sorbent presents strikingly higher selectivity and sorption capacity for Cu (II) than other interfering ions. Here, the preparation process of the target adsorbents of Cu(II)-imprinted sorbent is illustrated in Fig. 2 [24]. This modification with molecular imprinting technology on the activated carbon can effectively enhance the efficiency.

##### 3.1.1.2. Graphene

To date, graphene, a promising carbon material, has been drawn increasing number researchers' attentions. High surface area, extraordinary electronic property, high adsorption capability, and mechanical strength, which make this material, become an ideal adsorbent in preconcentration of samples [28-30]. Graphene oxide, a material prepared via graphene, also applied as extractant in SPE technology resulting from substantial reactive sites, e.g. hydroxyl, epoxy, and carboxylic groups [31].

Chen et al. prepared the graphene-based magnetic nanoparticles (G-MNPs) via a one-step method for adsorbents in MSPE. After pretreatment, the sample was mixed fully with the adsorbent for a



**Fig. 2.** Schematic plot for preparation of Cu (II)-imprinted sorbent with activated carbon as the material, reprinted with permission from Z.H. Li, J.W. Li, Y.B. Wang and Y.J. Wei // *Spectrochim. Acta, Part A* **117** (2014) 422, (c) 2014 Elsevier.

period of time. The adsorbent that adsorbed with the targets was separated from the solution via an external magnet. Following that, the targets were separated from the magnetic adsorbent, and were injected into HPLC system. Using the proposed method, five carbamate pesticides were isolated and analyzed successfully [32].

Wang et al. introduced a new way to apply graphene oxide in SPE. They synthesized an adsorbent by dispersing the carbon nanotubes into the GO colloids before modified with diethylenetriamine (DETA). They used two methods to operate the experiment. One method is that adding the adsorbents into the solution that containing different heavy metal ions in direct extraction mode; another method, packing the adsorbents into a column, then flowing the sample solution through the column. After adsorption of the targets, the metal ions were eluted with HCl from adsorbents. And then, the inductively coupled plasma optical emission spectrometry (ICP-OES) was executed for determination [21]. The magnetic graphene oxide (MGO) was prepared via using chemical coprecipitation of Fe(III) and Fe(II) ions with GO by Dadfarnia team. In the experiment, extraction performance of this material was evaluated by using gold ions as the target analyte. To obtain the optimum extraction conditions, several parameters were invested, such as pH, desorbing solution, sorbent amount, the sample volume. In the extraction process, after pre-treatment of MGO and the sample solutions, the extractant was introduced into the solution for a while to adsorb the analyte. Subsequently, the extract was eluted and applied for quantification via flow injection

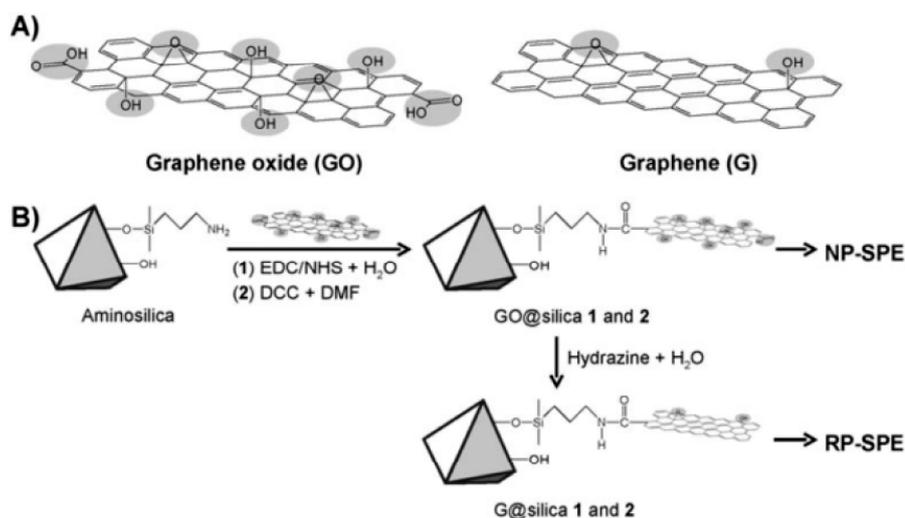
flame atomic absorption spectrometry (FI-FAAS). Using this method, the analysis of the gold ions from waste water sample were executed [33].

### 3.1.1.3. Carbon nanotubes

In the family of adsorbents, carbon nanotubes are utilized in SPE for separation and enrichment of bismuth [34], crystal-violet dye [35], bisphenol F [36], organophosphate esters [37] etc. from a collection of complex matrix samples resulting from large surface area, high mechanical strength [38, 39]. Moreover, carbon nanotubes grafted with different functional groups will improve its excellent adsorption properties [40,41].

Gouda team utilized carbon nanotubes impregnated with 2-(2-benzothiazolylazo)orcinol (BTAO), metal chelating agent, as adsorbents for selective separation of different metal ions, e.g. Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) in aqueous solution. The influence factors of extraction efficiency were investigated, including interfering ions and eluent. The results find that matrix ions do not have a significant influence on the extraction of target ions. When it comes to eluent, three eluents, CH<sub>3</sub>COOH, HCl and HNO<sub>3</sub>, were compared. The best recoveries were obtained by using HNO<sub>3</sub> as the elution solvent. As a consequence, this material has good adsorption capability for metal ions in solution [42].

Applying carbon nanotubes (CNTs) into SPME can effectively utilize the advantages of CNTs, e.g. high flux, it is beneficial for enrichment of analytes. Chen team used SPME method by filling CNTs in the wall pores of hollow fiber with the assist of surfactant for extraction of strychnine and brucine. They



**Fig. 3.** Structures of GO and G sheets (A). Synthesis illustration of GO@silica and G@silica (B), reprinted with permission from Q. Liu, J.B. Shi, J.T. Sun, T. Wang, L.X. Zeng and G.B. Jiang // *Angew. Chem. Int. Ed.* **123** (2011) 6035, (c) 2011 Wiley online library.

studied the parameters that affect extraction experiments and under the optimal conditions, the best separation efficiency was obtained. The limits of detection of two analytes were below 0.9  $\mu\text{g/L}$ , at the same time, this method shows good reproducibility and high recoveries [43]. Moreover, using the similar method, they again successfully applied CNTs in SPME. After functionalizing CNTs with  $\beta$ -cyclodextrin, CNTs were filled into the pores of hollow fiber. The good results indicate this simple method can effective extraction of 1-naphthaleneacetic acid (NAA) and 2-naphthoxyacetic acid in samples [44]. Han et al. used multi-walled carbon nanotubes as sorbents in SPE for selective and simultaneous extraction of four type A trichothecenes prior to quantification the analytes using UHPLC-MS/MS. The accuracy of results indicate this method proposed is in accordance with Commission Decision 2002/657/EC [45]. Many successful studies confirm that carbon nanotubes can be regarded as promising materials for preconcentration of pollutants in various samples.

### 3.1.2. Silica

Porous silica has already become the most popular sorbent in various fields. There are abundant with the silanols on the silica surface, and the hydroxyl groups are the most reactive functional groups. By grafting distinct functional groups to silanols, many great and functional applications could be realized.

Among all the modifications about the silica, C8/C18 reversed-phase silica is the most important and used intensively. Song et al. had successfully removed the Sudan dyes from water using C18-functional magnetic silica nanoparticles [46]. Wang and co-workers utilized C18-functionalized silica as adsorbent for preconcentration of methylprednisolone [47]. Jiang et al. prepared reversed-phase (RP) and irreversible-phase (NP) SPE by covalently binding Graphene (G) and Graphene Oxide (GO) sheets to the silica, and then the analysis performance of them were compared with other commercial adsorbents, for instance C18, carbon nanotubes. The results suggest the adsorption efficiency of these two adsorbents are higher than commercial materials. Here, the schematic procedure of the sorbents is shown in Fig. 3 [48].

Additionally, several other alkylating agents are also frequently used for modification of the silica in order to get different functions. He et al. firstly used the micro-sized silica loaded with a 30-membered macrocyclic polyamine, (1,4,11,14,21,21-hexaaza-(2,3:12,13:22,23)-tributano-(6,9:16,19:26,29)-trietheno(1H,2H,3H,4H,5H,10H,11H,12H,13H,14H,15H,20H,21H,22H,23H,24H,25H,30H)octadecahydro-(30)-annulene), as the extractant material in SPE for preconcentration of five polycyclic aromatic hydrocarbons (naphthalene, acenaphthene, anthracene, chrysene, perylene) in four real water samples. Using this adsorbent, the authors could achieve higher extraction and separation efficiency [49]. Ye

et al. firstly employed silica loaded with amino-bearing calixcrown receptor as the adsorbent material in SPE for pretreatment and separation of Pd(II) in HNO<sub>3</sub> solution, the recovery value of palladium are almost 99.3% [50].

These evidences are enough to demonstrate that the silica modified by the alkylating agents has great adsorption ability and acceptable sensitivity for the target components. Furtherly, tetramethoxysilane (TMOS) and tetraethylorthosilicate (TEOS) [50,51] are used as the alkylating agents widely in the process of preparation or modification.

Although the alkylating agents are intensively employed for modification of the silica for a variety of the aims, for example isolation, preconcentration, enrichment of the objective, it also has many disadvantages, such as these reagents are subjected to be hydrolyzed, having toxicity and high price. As a consequence, other materials have been used in place of these alkylating agents for modification of the silica particles. Zhu et al. used GO as the adsorbents for concentration of the 14 polycyclic aromatic hydrocarbons (PAHs) in cigarette smoke. The result is satisfactory and the LOD and LOQ are very low [52]. Additionally, in order to obtain great extraction efficiency, the traditional silica column must be activated by polar solvents before using.

### 3.1.3. Titanium dioxide

Titanium dioxide (TiO<sub>2</sub>), a metal oxide, is regarded as a promising material used in preconcentration and enrichment of metal ions, organic pollutants, etc. due to its large surface area, ease of preparation, low cost, high selectivity and good adsorption ability [53-55]. These outstanding advantages make it widely used not only in spherical particles formation, but also nanotubes. Elongated titanium dioxide nanotubes (TDNTs) remain the features mentioned above, and are good for enlarging its application fields [56,57].

An adsorbent that titanium dioxide nanotubes coated with carbon was first synthesized by Valcárcel team. After that, this adsorbent was successfully utilized for isolation and preconcentration of naproxen and ketoprofen, and good extraction performance was obtained, in contrast with other nanoparticles. High recovery values suggest this adsorbent can be as an alternative used for preconcentration of biological samples [58]. Jiang et al. packaged nanotitanium dioxide into microcolumn as adsorption device for on-line simultaneous enrichment of trace levels metal ions from aqueous solutions combined with inductively

coupled plasma atomic emission spectrometry (ICP-AES). Different concentrations of Cu(II), Mn(II), Cr(III) and Ni(II) were as template analytes to evaluate the extraction efficiency of this adsorbent. The precision of consequences was verified through a confrontation between the experimental and theoretical values [59]. Pourreza group also successfully extracted trace metal ions via titanium dioxide. Following, these analytes were quantitated via flame atomic absorption spectrometry. Different from Jiang team, this group used titanium dioxide grafted with 2-mercaptobenzothiazole, a metal chelating ligand, as extractants. In addition, the adsorption isotherm was studied as well in detail [60].

## 3.2. Polymer material

In the fields of polymer material, a great deal of materials are used as adsorbents in preconcentration of samples. These polymer adsorbents are capable of special functional groups or molecules, so that equipped with adsorption capabilities. Polymer adsorbents can adsorb or extract some substances from different matrices owing to large surface area, high adsorption capability, good mechanical strength as well as thermodynamic stability, etc. On the basis of sources of materials, polymer adsorbents are able to be divided into two categories: natural polymer adsorbents and artificial synthetic adsorbents. Reasonable use of these materials, different experimental purposes can be achieved.

### 3.2.1. Natural polymer adsorbent

Natural polymer adsorbents like as cellulose, starch, chitin, chitosan, etc. are widely utilized in environmental protection, food and drug testing, medicine and other fields in consideration of safety, low cost, environmental friendly. Furthermore, these materials are widely existed in nature.

Shi et al. established a SPE mode that using chitosan as adsorbents directly extract flavonoids, and then using Fe<sub>3</sub>O<sub>4</sub> as a magnetic carrier for isolation of chitosan adsorbed analytes from samples prior to detection using high-performance liquid chromatography-diode array detection (HPLC-DAD). High recovery values and low LODs certificate the reliability and effectiveness of this method. At the same time, this mode conquers the problem that difficult separation of chitosan from solution and composite of Fe<sub>3</sub>O<sub>4</sub> and chitosan cannot used in acidic solution [61]. Juang et al. used chitosan beads that swollen with acetic acid to extract three dyes

in solutions, compared with the common chitosan flasks. The results reveal that the swollen chitosan beads have enhance the adsorption efficiency for five times than chitosan flasks [62].

As one of natural polymer adsorbents, lignin, an aromatic polymer that abounds in ligneous tissue, has drawn researchers' attentions. Zhang team extracted lignin from a paper mill with the aim of enrichment of Cr(III) in aqueous solution. Through experiments, they found that pH value of solution and amount of extractants play critical roles in the adsorption capability of lignin, but is not affected by ionic strength as well as other interfering ions [63].

All through these natural polymers are regarded as adsorbents for preconcentration of heavy metal ions or contaminants, they are not capable of pretty outstanding adsorption efficiency in consideration of the nature of themselves. Hence, a great number of hybrids and functional of natural polymers are studied widely due to various functional groups (hydroxy, carboxyl, amino) grafted onto them can enhance chemical and physical properties, adsorption performance, etc.

Nanohybrid that growing  $Mn_3O_4$  on the surface of cellulose was prepared and used in SPE for isolation of Cu(II), Cd(II), Co(II), Cr(III), Fe(III), Ni(II), Zn(II) and Zr(IV). In all metal ions, this adsorbents present best adsorption ability for Cr(III) [64]. Using similar method, Khan et al. synthesized cellulose/ $ZrO_2$  nanohybrid with the aim of extracting different metal ions from aqueous solution prior to quantitation using inductively coupled plasma-optical emission spectrometry. The nanohybrid has best extraction efficiency and excellent selectivity for Ni(II) [65]. Chitosan modified silica was applied and packaged in micro-column as adsorbents for preconcentration of heavy metal ions. Afterwards, the extracts were eluted using HCl and analyzed via inductively coupled plasma optical emission spectrometry (ICP-OES) determination. The results show that this material has higher adsorption capability in contrast with other extractants. Furthermore, the calibration experiments also reveal this method is reliable potential to be used in SPE technic [66]. All these successful applications demonstrate the modification of natural polymers can improve materials' adsorption performance and decrease the economic costs.

### 3.2.2. Artificial synthetic adsorbent

More and more researchers have been trying to explore a variety of polymer adsorbents in consideration of ease of preparation without need of spe-

cial devices, low prices of raw materials, but high effectivity, widespread applications, convenience of modification and other excellent features. When it comes to use of synthetic materials, ion exchange resin and adsorption resin are crucial extractants used in SPE. These two resins has been frequently used in a variety of complex water samples, where metal ions, basic compounds in pharmaceutical analysis and other toxic pollutants can also be detected effectively due to its high sensitivity and selectivity for the analysts.

Many studies about ion exchange resin-based SPE technology were published in literatures. Fontanals and co-workers prepared eight different strong cation-exchange (SCX) resins by utilizing the mode of precipitation polymerisation or non-aqueous dispersion polymerization. Simultaneously, these SCX resins considered as the adsorption extractants, are used in the SPE to monitor the pharmaceuticals from the waste water samples. The results indicate that these kinds of SCX adsorbents are equipped with higher icon-exchange abilities and particular surface area [67]. Furthermore, Fontanals et al. synthesized two distinct icon exchange reagents by two methods. One is by the way of copolymerization and the other is modified with sulfonic groups after synthesis. The two materials are used as adsorbents for chemical drugs from the waste water in SPE. The main process of the experiment is as same as the literature [67], and the good consequence was obtained with the second adsorbent [68]. Dmitrienko et al. synthesized a novel magnetic resin through adsorbing  $Fe_3O_4$  with hypercrosslinked polystyrene. Using this material, four sulfonamides were successfully extracted from aqueous samples and detected HPLC. The impactors of extraction were investigated systematically. High recoveries and low LODs mean this adsorbent is reliable used in SPE [69]. Noble metals of Pt(IV), Ru(III) and Ru(IV) were isolated from HCl solution by Holdt group using polystyrene resins grafted with sulphoxide as extractant. Three parameters that affect adsorption were studied, e.g. substitution of sulphoxide. After a series of experiments, the separation and determination of three metal ions were realized [70]. Typically, polymer adsorbent possesses high adsorption capability, when appropriate one is selected, the good results will be acquired.

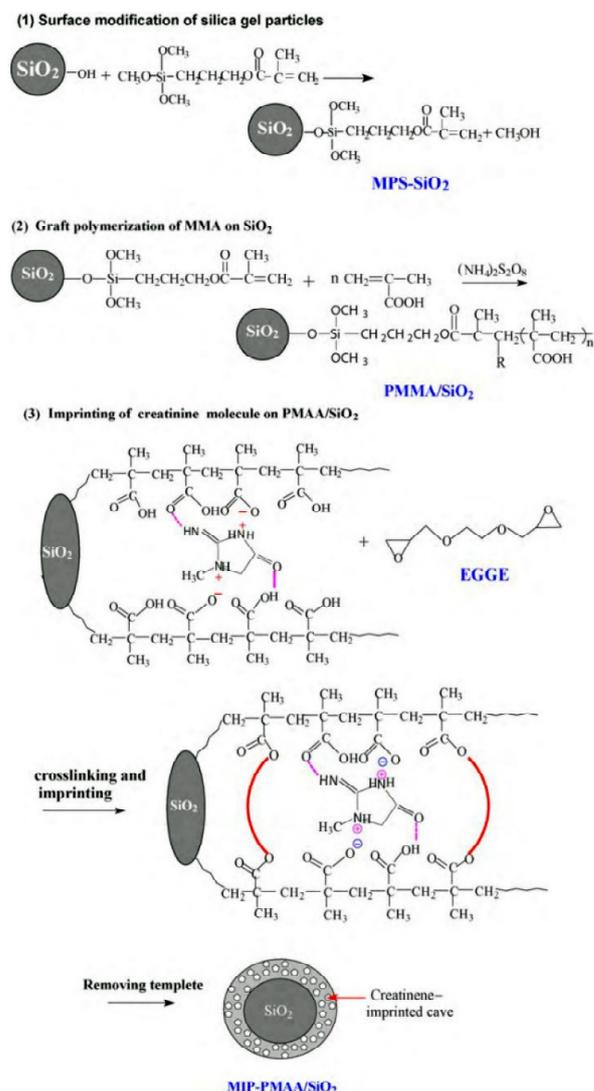
## 4. SEPARATION MODES OF SOLID PHASE EXTRACTION

### 4.1. Molecularly imprinted solid phase extraction

Molecular imprinting (MIP) technique is a portion of the field of biological imitation, which is comprehensively employed in the solid phase extraction areas currently. Molecularly imprinted solid-phase extraction (MISPE) possesses lower cost, high stability and good applicability to selectively separate and enrich trace level of the analytes from complex samples [71]. Coupled with SPE technology, the selectivity and recovery of the enrichment could be increased to a great extent. Molecularly imprinted polymers (MIPs) are highly cross-linked synthetic polymers [72]. In general, the template molecule used in the synthesis of the MIPs is the target analytes. After forming the polymers, the template molecule will be removed by washing, the special recognition cavities and binding sites are created, which is complementary to the template in size, shape, and molecular interactions or functionality. To have an apparent understanding of the theory of the MIPs technology, the preparation of an adsorbent (MIP-PMAA/SiO<sub>2</sub>) of molecularly imprinted polymer was presented in Fig. 4 [73].

Maybe there are still a few of template molecules left that will have an important influence on the results eventually, even though the template is washed sufficiently. In order to avoid this unsatisfactory interference, it would be good to employ the analogue of the target analytes as the template during the preparation procedure of the polymers [74,75].

According to the interaction type between the template molecule and the appropriate functional monomer, there are three the synthetic approaches of MIP, i.e. the non-covalent imprinting, the covalent imprinting, and the semi-covalent imprinting [76,77]. In general, covalent approach possess higher affinity than non-covalent [76]. Nevertheless, the non-covalent self-assembly formation is the used most intensively in the MIP [71]. For example, Rossi et al. had employed fluconazole as the template molecule to prepare the MIP with non-covalent formation in SPE, then the separation of fluconazole achieved successfully from pharmaceutical formulations [78]. He et al. synthesized molecularly imprinted mesoporous silica polymer (SBA-15@MIP) using covalent formation for baicalein (BAI) extraction [72]. On the other hand non-covalent imprinting protocol is still used intensively because of its diversity of interaction, accessibility of removing the

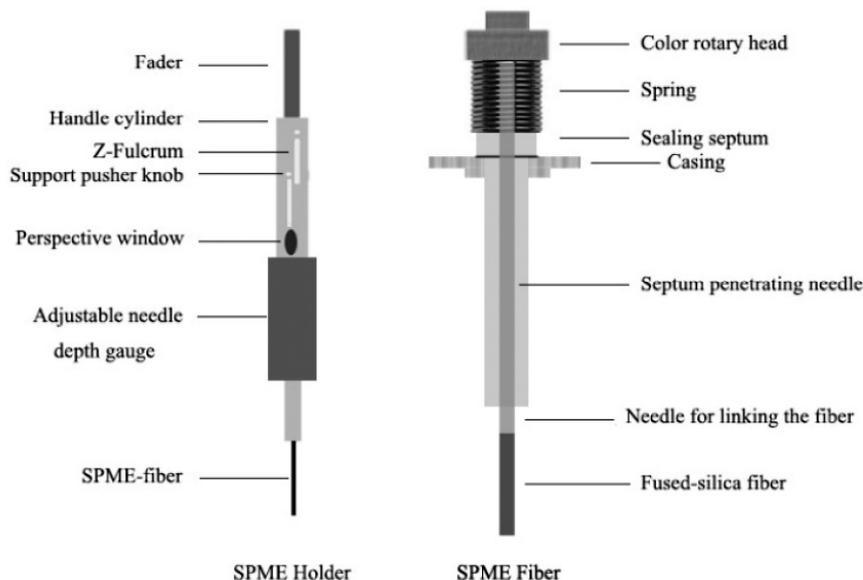


**Fig. 4.** A synthesis scheme of MIP-PMAA/SiO<sub>2</sub>, reprinted with permission from B.J. Gao, Y.B. Li and Z.G. Zhang // *J. Chromatogr. B* **878** (2010) 2077, (c) 2010 Elsevier.

template molecule, etc. Here, a novel MIPS was prepared utilizing coenzyme Q0 (CoQ0) as the template in non-covalent manner. And then Tripodi et al. used this MIP as the sorbent for enrichment of the CoQ0 from biological matrices [75]. Refer to concrete detection of target analytes from real environmental samples, numerous documents about the applications of MISPE are published as shown in Table 1 [75,79-89].

### 4.2. Solid phase microextraction

Solid phase microextraction (SPME) is applied to the enrichment and assay detection of the volatile substance owing to low consumption of the solvent,



**Fig. 5.** Schematic diagram of the SPME device.

simple, rapid and portability both in laboratory and outdoor where the target sample is located [90]. The core component of the SPME is the fused fiber, which can adsorb the analytes. Once the distribution equilibrium is reached, the target analytes will be adsorbed from the complex matrix components quickly. After the analytes be decomposed and vaporized, the gas will be detected and analyzed by the GC. SPE is used widely with HPLC, but SPME is generally combined with GC and other analytical instruments.

Due to only a few of the samples using fiber to be injected into the instrument such as GC or HPLC initially, the good performance and reliable results could be guaranteed at the most extent. In order to satisfy the more and more complicated sample systems, the device of the SPME is developed gradually. The basic schematic diagram of the solid phase microextraction device is shown in Fig. 5.

SPME mainly possesses two ways for separation and enrichment of samples: direct solid phase microextraction (DI-SPME), headspace solid phase extraction (HS-SPME). The fiber is immersed directly in the sample solution with the analytes in DI-SPME. After the distribution equilibrium between the analytes and the solid phase is reached, the analytes adsorbed on the fiber could be analyzed. Indeed, many operations about the separation and preconcentration of the objective components had been done in this way have obtained good effects. For instance, Luan et al. enriched the target analytes

(tetramethylenedisulfotetramine) using the solid-phase microextraction (SPME) by infiltrating directly a SPME fiber into the standard solutions and samples [91]. Likewise, Luan et al. also enriched and isolated the trans-resveratrol in wine using the SPME by inserting a fiber into the samples [92]. Using direct injection mode, Brodbelt et al. successfully realize the extraction of target barbiturates from sample solution [93]. Huang et al. had gained satisfactory effects by using polymeric ionic liquid-based multiple monolithic fiber (MMF) with direct extraction mode for estrogen mimics [94]. Cardeal team applied cold fiber (CF) SPME coupled with GC/MS to enrich and identify 16 polycyclic aromatic hydrocarbons (PAHs) in 24 spring water samples. The lower limits of detection and higher recoveries were achieved with direct extraction [95].

In HS-SPME, the solid fused-silica fiber coated stationary phase is not immersed directly into the sample solution, but suspending the fiber in the gas. Once the equilibrium between the gas phase and fiber coating is reached, the analytes will be isolated at certain temperature. Subsequently the gas will be adsorbed onto the stationary phase for analysis and detection, such as immediately transferred the fiber into the GC or HPLC injector [96]. And using rapid method of HS-SPME with GC-MS/MS, the enrichment as well as detection of several biota samples were realized successfully.

HS-SPME is mainly used for detection of the high volatility gases, for instance, organotin com-

pounds (OTCs) in their alkylated forms. However, generally, the organotin compounds have low volatility, it is necessary to carry out derivatization procedure before injecting the gas into GC [97]. In addition, the results will be better using headspace mode than direct injection when the analytes and the high molecule mass or/and non-volatile components are presented at the same time in matrix [90]. Once the samples are isolated, the fiber will be desorbed by a sort of process.

### 4.3. Dispersive solid phase extraction

Compared with the method that fill the adsorbents into the solid phase column, the dispersive solid phase extraction (DSPE) is a simple way because it can save time for settlement of the samples. The main operating procedure of DSPE is presented briefly. Firstly, adding the polymer microspheres, such as silica, that loaded available functional groups into the standard solution or the sample solution, and then the sonication is needed to make the sorbents and the analytes dispersion totally. Secondly, it is necessary for the extractant adsorbing analytes to execute the centrifugation and filtration. And then the analytes are eluted from the adsorbents by using appropriate polar solvent. Finally, the detection and analysis are conducted via HPLC, GC-MS.

Many studies about DSPE for preparation of samples have been published. Plossl et al., for example, separated and enriched eight drugs in whole blood using DSPE method. Simply, the process is executed by adding the acetonitrile, magnesium sulfate and sodium chloride into the whole blood, then the solution is shaken intensively and centrifuged. Then the extract was mixed with abundant adsorbents (Bondesil NH<sub>2</sub> and PSA) and magnesium sulfate. After centrifuging, almost of the impurities in the blood matrix are removed, the suspension cleaned by the way of DSPE was transferred to auto sampler vials for analysis with GC/MS. Using this method, eight distinct target pharmaceuticals in the whole blood were enriched and separated successively as well. The mean recoveries of the analytes are above 80%, the limits of detection are below 20 ng/ml [98]. Furthermore, Posyniak et al. utilized DSPE method for preconcentration of six sulfonamide (SA) residues from chicken that are not injected veterinary drugs. The determinations of the pharmaceuticals are executed subsequently via LC, where a fluorescence detector FR-10AXL was utilized for study of the target solution. In the experiment, a non-polar octadecyl sorbent had been

used and testified that was available for the preconcentration of the sulfonamides, meanwhile the satisfactory results revealed that this method is suitable for the removal of almost endogenous matrix components. The basic process is described briefly. Firstly, 5 g chicken muscle was solved through moderate amount of acetonitrile, then the octadecyl sorbent was added into the solution. After ultrasonic dispersion and centrifugation, the objective solution was mixed with acetate buffer and was ready for pre-column derivatization. Since all these six SAs have weaker absorption in the ultraviolet region, it is necessary to take actions to increase in the fluorescence intensity by derivatization with fluorescamine reagent to introduce chromophore or auxochrome groups to enhance the detection. Actually, the authors have obtained ideal results. In general, pre-column derivatization has several advantages, for instance, enhancing the detection sensitive, increasing the accuracy and precision, decreasing the limits of the detection and simplifying the procedure, [99,100]. Furthermore, Fagerquist et al. utilized a novel, rapid, sensitive DSPE coupled with LC/MS/MS to achieve their goals. Using the advanced method, 10  $\beta$ -lactam antibiotics are detected in Bovine Kidney Tissue. All the recoveries of antibiotics are above 70% (apart from DCCD with recovery of 58%). The proposed method could handle 3-4 times amount of samples in one day, and it is able to be used for pretreatment of samples in shorter time as well [101]. Compared to conventional SPE approaches, DSPE is a more sufficiently rapid and effective method for concentration of the samples [102].

### 4.4. Matrix solid phase dispersion

Matrix solid phase dispersion is a technique for preconcentration of the sample, and usually used to extract different drugs, contaminants in environmental, food and pharmaceutical fields whether solid or semi-solid state, due to its effective selectivity, low organic solvent consumption, inexpensive in term of time.

Although MSPD is similar to DSPE, the difference in the pretreatment of sample is also existent. In MSPD method, the extractant is dispersed with the original sample, after reaching the homogenization of semi-dry state; the mixture will be loaded into the solid phase column. Then the different polar solvents are used to leach the mixture so that different analytes can be isolated following certain order. Instead, in the DSPE, the adsorbent is mixed fully with an aliquot of extract [102]. The amount of

**Table 1.** MISPE for real samples with different analytical methods.

Target Analytes	Template	Matrices	Monomer/CL/ solvent	Sample pretreatment	Analytical methods	Ref.
Coenzyme Q10	Coenzyme Q0	Bovine liver extract	MAA/EGDMA/ acetonitrile	Ice bath	HPLC	[75]
Bisphenols	BPA	Humaurine	4-VP/EGDMA/ methanol	Dilution with water	HPLC-DCL detection	[79]
Dibutyl phthalate	Dibutyl phthalate	Soybean milk and milk samples	MAA/EGDMA/ (methanol/acetic acid)	Elution with methanol/acetic acid	CV and DPV	[80]
Triazines	Atrazine	Tap water and river water	HEMA/EGDMA/ (methanol and water)	Filtration and concentration	HPLC	[81]
Bisphenols	Bisphenols	Tap water and river water	4-VP/EGDMA/ acetonitrile	Elution with methanol-trifluoroacetic acid	HPLC	[82]
Dicofol	a-chloro-DDT	Celery samples	Acrylamide/ acrylamide/1-allyl-3-methylimidazolium bromide	Washed by ACN-H <sub>2</sub> O	GC	[83]
Clenbuterol and clorprenaline	Phenylephrine	Human urine	1-allyl-3-ethylimidazolium bromide/ EGDMA/chloroform	Filtration	HPLC	[84]
Glyphosate	Phenylphosphonic acid	Mineral water and ground water	1-allyl-2-thiourea/ 2-EGDMA/ acetonitrile	Acidified with HCl	CE and UPLC-MS/MS	[85]
Ginkgolic acids	MOSA and HOSA	Ginkgo bilobaL. leaves extracts	4-VP/EGDMA/ cyclohexane	Addition of EtOH-H <sub>2</sub> O	HPLC	[86]
Fluoroquinolone antimicrobials	MAA and TFMAA	Chicken meat	MAA and TFMAA/ EDMA/Acetonitrile	Outgassed at 50°C for 2h	HPLC	[87]
Bisphenol A	Lecithin/ dodecylamine mixed-micelles	Sediment extracts	BPA/TEOS/ (water and methanol)	Filtration	HPLC-DAD	[88]
Acidic pharmaceuticals	Mixture of IBP,NPX, KEP,DFC and CA	Real water and sediment samples	2-VP/EGDMA/ Toluene	Elution with methanol/acetic acid	LC/MS/MS	[89]

Note (abbreviations in the table): MOSA: 6-methoxysalicylic acid. HOSA: 6-hexadecyloxysalicylic acid. a-chloro-DDT: á-chloro-dichlorodiphenyltrichloroethane. IBP: ibuprofen. NPX: naproxen. KEP: ketoprofen. DFC: diclofenac. CA: clofibrac acid. BPA: bisphenol A. BCA: biochanin A. 2-VP: 2-vinylpyridine. 4-VP: 4-vinylpyridine. HEMA: 2-hydroxyethyl methacrylate. APTES: 3-aminopropyltriethoxysilane. TEOS: tetraethoxysilane. EDMA: Ethylene glycol dimethacrylate. MAA: methacrylic acid. DEAEMA: 2-diethylaminoethyl methacrylate. EGDMA: ethylene glycoldimethacrylate. TFMAA: trifluoromethacrylic acid. Gen: genistein. Da: daidzein. THF: Tetrahydrofuran. ACN: acetonitrile. EtOH: ethyl alcohol. CL: crosslinker. CV: cyclic voltammetry. DPV: differential pulse voltammetry. CE: capillary electrophoresis. LC/MS/MS: liquid chromatography–mass spectrometry. GC: gas chromatography.

bulk adsorbent material is larger in MSPD than that in DSPE.

Based on MSPD, Singh et al. utilized an ingenious method for concentration and isolation of the combined residues of lindane pesticide and other HCH isomers in vegetables, fruits, wheat, pulses and medicinal plants prior to the determinant of gas chromatography combined with electron capture detection (GC–ECD). The satisfactory results present the recoveries of the samples ranging from 93% to 103%, and the limits of detection of the HCH are below 6 ng/g. Compared to the traditional MSPD, the proposed method is inexpensive and the time of the performance is minimized. In addition to these advantages, this approach is suitable for abundant of the samples in one test cycle [103]. Dai et al. applied a rapid, simple, effective method for preconcentration of the samples. The on-line MSPD-LC–MS/MS method is evaluated by using chloramphenicol (CAP) from soft-shelled turtle tissues as the suitable analytes. By adjusting the different parameters, the ideal consequence is obtained from the operation, such as the recoveries of the chloramphenicol are varying from 92.05% to 98.07% in different levels, and the RSDs are below 4.20%. Meanwhile, the proposed method is justified as appropriate for the detection of the trace level of the chloramphenicol in soft-shelled turtle tissues. Compared with the conventional MSPD, the on-line MSPD-LC–MS/MS procedure could save more time, and it is environmental friendly since the consumption of the poisoned organic solvents is decreased to the maximum extent. Even though the consumption of the solvent is decreased, the yield of the product is not reduced [104]. Navickiene et al. used MSPD coupled with GC/MS for simultaneous detection of eight pesticide residues in coconut. To acquire the perfect results, several factors are conditioned carefully, such as types and dosages of the adsorbents and eluents. Although the recoveries of the lufenuron and difenoconazole are 47.2% and 48.2%, the mean recoveries of the other six pesticides ranged from 70.1% to 98.7%, respectively. The limits of detection of 0.02 to 0.17 mg/kg are achieved. It is important that the detection limits are consistent with the value of limit confirmed by Brazilian legislation [105].

Compared to the traditional SPE, MSPD and DSPE do not need to load many adsorbents into columns for many time, these two technologies simplify the concentration procedures and save lots of time accordingly.

## 4.5. Magnetic solid phase extraction

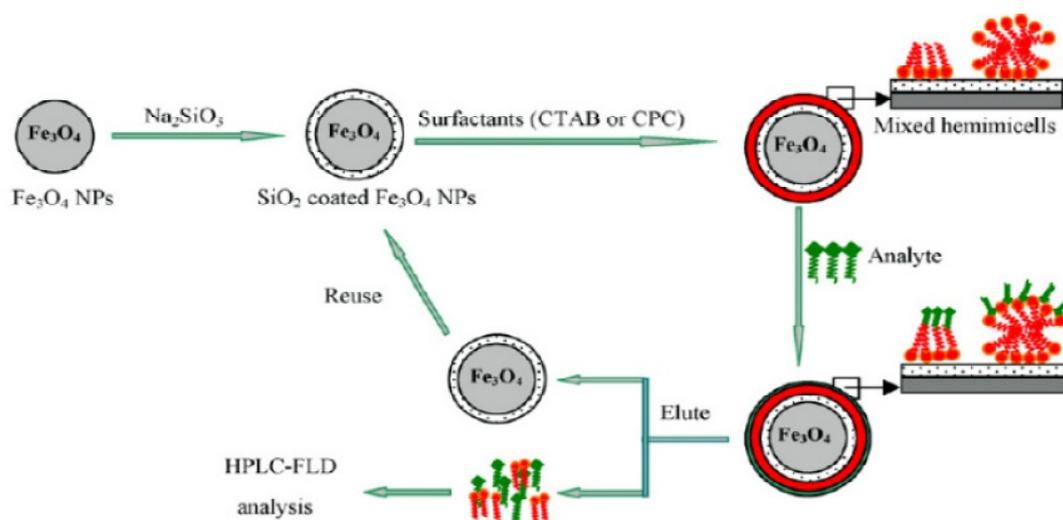
Magnetic solid phase extraction (MSPE) technology has received growing interest on the green chemistry in recent years arising from its special character that easily separate the sorbents from the solution by using an external magnetic field, once the analytes are attached successfully to the adsorbents. There is a simple example about using  $\text{Fe}_3\text{O}_4$  particles as the magnetic cores for preparation of the extractant material. The schematic illustration of surfactants (CTAB or CPC) coated  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs and its application in SPE is shown in Fig. 6 [106]. Furthermore, using this interesting procedure, the time consumption will be decreased.

When using the MSPE as the technology for preconcentration of the target samples,  $\text{Fe}_3\text{O}_4$  particles are usually considered as the magnetic cores in the magnetic material of adsorbent. Nevertheless, these magnetic materials have some limits. It is prone to be oxidized when the pH is below 4.0, thus it is vulnerable to the acidity of the solution. As a consequence, silica generally is used as the shell to protect  $\text{Fe}_3\text{O}_4$  from other materials as well as property of concentration [107].

Shi et al. first fabricated a novel adsorbents of magnetic reduced graphene oxide via in situ polymerization, and then the composite was grafted with  $\beta$ -cyclodextrin, ( $\beta$ -CD), and also first applied this adsorbent for highly effective separation, enrichment and analysis of two naphthalene-derived phytohormones in tomatoes coupled with HPLC. They investigated the optimum experimental parameters that affect the extraction of analytes, for instance, amount of adsorbents, initial pH value as well as adsorption time. Under the optimal conditions, comparing with SPE, HF-SPME, MISPE and other techniques, this sorbents presented good extraction performance due to size complementarity of  $\beta$ -CD. The facts suggest that this simple method is appropriate for extraction of phytohormones in tomatoes [108].

## 4.6. Microchip solid phase extraction

To date, the microchip device is an advanced technique [109]. To expand its application scope, SPE is one of the most extraction methods to apply this device. In current years, the microchip solid phase extraction ( $\mu$ chipSPE) are employed pervasively in various areas, for example, the environmental protection and food hygiene, especially in biological analysis, since its advantages including high throughput, miniaturization, multifunction, small vol-



**Fig. 6.** Schematic illustration of the preparation of surfactants coated  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs and its application for enrich analytes as SPE sorbents, reprinted with permission from X.L. Zhao, Y. Shi, T. Wang, Y.Q. Cai and G.B. Jiang // *J. Chromatogr. A* **1188** (2008) 140, (c) 2008 Elsevier.

ume of solvent, low cost, conveniences for carrying and other striking advantages.

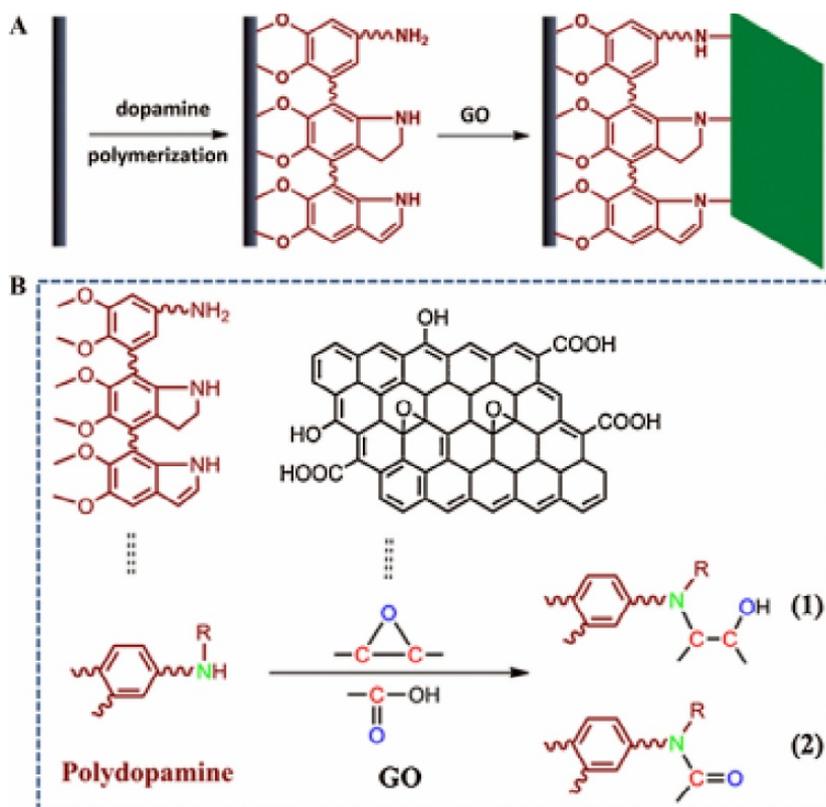
Taking the glass microfluidic chip as an example, the preparation method can be described here. There are several steps will be acquired in the whole fabrication. Firstly, a mask is prepared via laser printing technology. Then the channel pattern is transferred onto the photoresist by photolithography, and handled with a developer solution. Now, it is time to remove chromium using chrometch solution. After the channel pattern can be seen clearly, the substance need to be backed for a sufficient period of time. Once the substance is backed enough, the channel on the surface of the substance will be etched using hydrofluoric acid (HF) buffered with solution of ammonium fluoride via wet etching method. After these processes are finished, the glass is washed with water and chrometch solution to remove the residue and a small of chromium [110].

To employ this  $\mu$ chipSPE method, however, two decisive factors need to be considered. First, it is a need to restrict part of the reaction area within single channel of the microchip platform. Second, the solid phase material must prepare just in microchip devices. It is a trend that all the operations including the synthesis, extraction and analysis are integrated into a set of process, especially in analysis for DNA [109,111]. A microchip device was constructed using polymer material by Kim team, replacing the

traditional inorganic-based material with polymethylmethacrylate (PMMA) as substrate, such as glass and Si. With this device, the author achieved the extraction and purification of bacterial DNA [112]. Mitra et al. manufactured two microchip devices by packing 3 or 5  $\mu\text{m}$  ODS particles and nano-scale silica particles into the PDMS microchannels as the sorbents. Afterward, the  $\mu$ -SPE procedure with micro and nanoscale silica as the extraction materials was applied for extraction of DNA [113]. In the conventional SPE, the sample solution is passed through the cartridge prior to the elution, then the target analytes will be obtained. However, in the  $\mu$ chipSPE, the preconcentration of the analytes from the complex matrix become suitable and simple.

#### 4.7. Stir bar sorptive extraction

Stir bar sorptive extraction (SBSE) is an environmental friendly method for preconcentration of samples. Similar to SPME, The basic principle of this method is based on the equilibrium distribution of objective between an extraction medium i.e. a stir bar and sample matrices [114]. The SBSE has two extraction modes. One mode is dispersing a bar into the liquid sample, during is stirred in the liquid sample, the target analytes will be enriched on the surface of the bar, which is applied to semivolatile analytes in aqueous samples. Another



**Fig. 7.** Schematic of modification of stainless steel wire (A) and reaction process (B), reprinted with permission from W.P. Zhang, Z.X. Zhang, J. Zhang, J.W. Meng, T. Bao and Z.L. Chen // *J. Chromatogr. A* 1351 (2014) 12, (c) 2014 Elsevier.

is headspace extraction, placing the bar above the liquid solution, the volatile organic compounds will be volatilized and extracted on the bar in the stirring process. After extraction, the target analytes need to be eluted from stir bar using small amount of organic liquid solvents or thermal desorption for HPLC or GC system for detection. Compared with SPME, however, the extraction efficiency of SBSE is much higher, considering much bigger solid phase volume is available to contact with analytes in the aqueous solution. Furthermore, applicability and high preconcentration ability at ultra-trace level also enforce its applications.

The core technique of SBSE is the coating of magnetic stir bar. In general, bars are coated with liquid polydimethylsiloxane (PDMS) sorbent phase. During the extraction, the analytes will be adsorbed on this material [115]. However, this nonpolar PDMS phase makes it difficult to be applied to the separation and analysis of polar compounds [116]. As a result, there is a huge demand to deplore many novel coating materials to conquer the problem.

Chen et al. first fabricated adsorbent on the surface of stainless steel wire as stir bar for extraction of polyaromatic hydrocarbons (PAHs), using covalent bonding method. After immobilizing polydopamine on the stir bar, graphene oxide (GO) was then reacted with polydopamine to form a layer of graphene-based sorbent. Using layer-by-layer method, they can control the thickness of layer of graphene in order to improve the extraction capability of adsorbents. The good linearity with the correlation coefficient ( $R^2$ )  $\geq 0.9950$  and good reproducibility demonstrate this method presents high efficiency and good removal capability of toxic pollutants in food and soil samples. The whole fabrication process of the adsorption on stainless steel wire was presented in Fig. 7 [117]. What's more, this team also modified graphene on the surface of stainless steel wire. They have immobilized cross-linked organic polymer (poly(EGDMA-AA)) onto stir bars with stainless steel wire but glass jacket for extraction of three protoberberines, the results indicate that this novel polymer coating presents excellent ex-

traction and enrichment efficiency for alkaloids, the good reproducibility and linearity were also obtained. At the same time, this material are stability and cannot be degraded under acidic and alkaline solutions and ultrasonication [118].

Gan team functionalized poly(diallyldimethylammonium chloride) (PDDA), a polycation, on stainless steel wire for specially recognize two polychlorinated biphenyls (PCBs) from fish samples. Contrast with Chen team, they pretreated stir bar by modifying MOF-5 ( $Zn_4O(BDC)_3$ ) utilizing potential-controlled cathodic electrodeposition on stainless steel. The results suggest this method can be used for analysis of polychlorinated biphenyls from fish samples [119].

In addition, many other materials were studied to be used for SBSE, for instance, polyurethane [120] presents good thermal stability and long lifetime, poly(acrylate) [121] and polypyrrole [122] are ideal materials due to high thermal stability and good extraction efficiency. Ethylene glycol-silicone (EG-Silicone) copolymer and polyacrylate [123] can bind with polar compounds and show remarkable enrichment ability for objective than PDMS. However, EG material possess weak mechanical stability and always degraded quickly, hence, this coating cannot be used for much times. Usually, new coating materials are manufactured via Molecular Imprinting Technology (MIT) and sol-gel techniques. The MIPs fabricated through MIT are equipped with the ability to specifically recognize. This characteristic makes these materials have high efficiency and selectivity for target analytes, especially in complex samples. The coatings prepared via sol-gel technology possess high thermal and solvent stability. Using this method, many different functional groups are bale to be introduced on stir bar to achieve different applications in a wide of areas [124,125].

#### 4.8. Immunoaffinity solid phase extraction

Immunoaffinity solid phase extraction (IASPE), also known as Immunoaffinity extraction (IAC), is a simple and effective sample preconcentration method, it is based on the antigen-antibody interactions [126]. Immunosorbents are prepared by immobilizing special antibody on the solid supports via physical or chemical means. On the basis of particular reversible interactions between antigen and antibody, target antigen can be easily enriched and separated from complicated matrices, and then the extracts were desorpted using organic solvents. Coupled with

HPLC, GC and MS, the qualitative and quantitative detection of analytes will be come true. Contrast to other extraction methods, high specificity and high affinity make IAC technic can shorten the analysis time to avoid further detection for distinguishing probe analytes from analogues, and simplify the operation process [127,128]. Given these advantages, IAC is usually regard as a highly effective method for extraction of analytes from various samples.

Abad-Fuentes team established IAC-HPLC-UV method and investigated affinity efficacy of three monoclonal antibodies to pyraclostrobin (PY) from fruit juices. The results indicate that the amount and type of immunosorbents have a significant influence on the binding capacity of between antigen and antibody. Simultaneously, acetonitrile was proved can realize better elution effect more than methanol to prevent antigen-antibody interaction [129]. Qian et al. successfully established a method that immunoaffinity chromatography combined with LC-MS/MS analysis for selective enrichment and quantitative detection of phosphorylated butyrylcholinesterase in human plasma [130].

Normally, the objective of IAC is only one kind of analytes. In recent, many investigations about IAC for multiple-analytes have received increasing interest, as an example of Deng team. The IAC column that simultaneously selective extraction of four Sudan dyes (Sudan I, II, III, and IV) was first prepared by them, and the extraction conditions were optimized in detail. Using this column, Sudan I-IV that multi-analytes were successfully separated from food samples, and then were detected via HPLC. The study justifies that the immunosorbent has good extraction efficacy and good reproducibility, what's more, this method is enough competent to the simultaneous enrichment as well as analysis of Sudan dyes [131].

#### 4.9. Monolith solid phase extraction

As a kind of sorbents in SPE, monoliths have received increasing attention since the materials were first used. The development of monolith makes it not only avoid some disadvantages occurred in the traditional SPE method to some extent, e.g. slow mass transfer, time consuming as well as low extraction efficiency, but also has good advantages, such as easy separation, low extraction pressure, high adsorption capacity, good reusability [132]. The monolith adsorbents are fricated via in situ polymerization. Prior to transferring into column, the mixture consisting of a certain amount of monomer, initiator, cross-linking agent and porogen are uniformly

dispersed in the aqueous solution, and the column needs to be conditioned using organic solvents (e.g. ethanol or acetone) to remove the residual impurities on the surface, and then dried [133]. Subsequently, the mixture is shifted into the capillary column, short stainless steel column or syringe. This column will be prepared under a certain temperature for a period of time to complete the reactions. During separation, the sample solutions will pass through column from side to side. This approach reduces the adverse effects of low extraction ability resulting from solution cannot completely fill the space between particles [132].

Based on the difference of materials used, monolith can be divided into silica, organic monolith and hybrid monolithic. To date, a number of studies about polymer monoliths has been reported due to porous structure of polymer and large surface area increase the adsorption sites of adsorbents, and facilitate the adsorption between adsorbents and probe analytes [19]. Hilder et al. prepared porous polymer monoliths and packed it into SPE column for separation and enrichment of five homologues of benzene, subsequently the extraction efficiency of this porous polymer adsorbents and two commercial adsorbents were compared. As a consequence, this material possesses higher adsorption ability than other particulate adsorbents, and this results also indicate that large surface area of sorbents is beneficial for purification of target analytes, and better extraction performance can be obtained due to porous structure improve fast mass transfer [134].

Herein, introducing metal–organic frameworks (MOFs) into polymer monoliths is an effective method to increase activated adsorption site of sorbents. Nowadays, MOFs are widely applied as materials for fabricating adsorbents in separation and preconcentration fields on account of large surface area, good thermal stability and ease of preparation of these materials. Yan successfully prepared aluminum terephthalate MOF (MIL-53(Al)) on the basis of capillary monolithic column for highly effective extraction non-steroidal anti-inflammatory drugs (NSAIDs) from water and urine samples. Compared with pure polymer monolith column, the MIL-53(Al) incorporated monolith column is equipped with higher extraction performance due to the use of MIL-53(Al) can enlarge the surface area of polymer material. Furthermore, the impacts of polymer monolith microextraction for enrichment of NSAIDs were optimized. Under the optimum conditions, the method presented good extraction ability of real samples, and good reproducibility also makes this

polymer monolith column can be a promising adsorbent for preconcentration of NSAIDs in water and urine samples [135]. As is the use of MIL-53(Al)-polymer monolith column, Lin group also made an effort and realized success. In this study, the sorbents were synthesized by filling a capillary tube with prepared Al-MOF-polymer solution using microwave-assisted polymerization. They discussed and confirmed optimum extraction conditions for penicillins. Alternatively, the effect of different Al-based MOFs was investigated as well. High recovery and low detection of limits demonstrate that MIL-53(Al)-polymer is a potential sorbents used in monolith column for preconcentration of hydrophilic compounds [136].

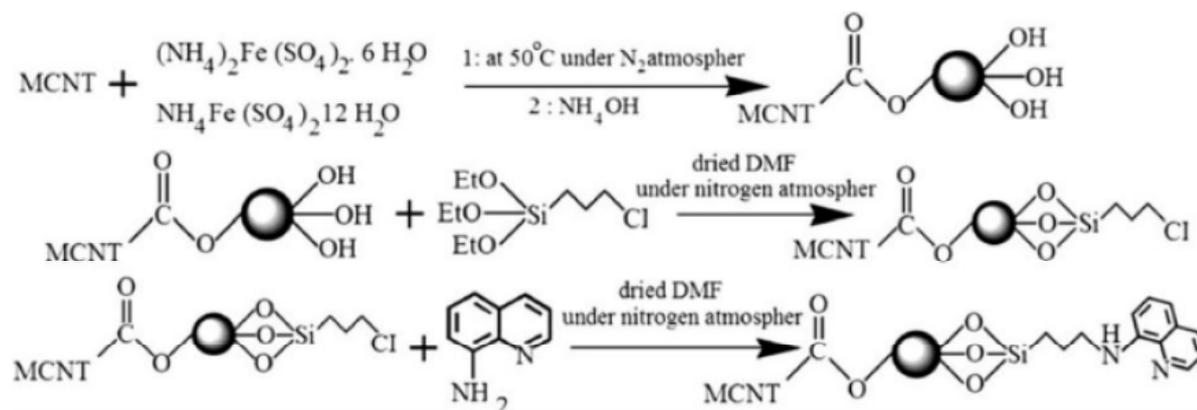
In addition to the monoliths proposed above, molecularly-imprinted monoliths (MIMs) are also utilized in SPE for high selectivity towards target analytes. Similar to MISPE, MIMs are synthesized via polymerization of template molecule, initiators, porogen, monomer as well as crosslinkers, following that the target template molecule will be removed. The only difference between these two methods is that the polymerization is occurred in columns, as an example capillary column. Molecular imprinting (MIP) technique combined with monoliths can also obtain good results and improve the accuracy and effectivity, such as Chen [137], Li [138] and Chen [139] groups.

## 5. APPLICATIONS OF SOLID PHASE EXTRACTION

### 5.1. Extraction of the heavy metal ions in environmental waters

There are a great number of heavy metals in nature, such as cadmium, copper, zinc, lead, cobalt, etc., they are necessary trace elements in the human body. Yet, once they have more than normal amounts, it is bound to result in significantly adverse effects on the environment and human body. Especially, human body will be declined such as minamata disease (mercury pollution) and osteoporosis (cadmium pollution), if the heavy metals are taken in via food polluted, such as vegetables as well as fruits, and so on. Thus, there is rapid demand to seek and find suitable methods for preconcentration of the heavy metals in environment samples.

The suitable adsorbent can play a multiplier effect. Various adsorbents were applied for determination of heavy metal ions, including activated carbon, silica, carbon nanotubes, etc. [70-75]. Acti-



**Fig. 8.** Schematic illustration of synthesis of magnetic multiwalled carbon nanotube, reprinted with permission from M. Taghizadeh, A.A. Asgharinezhad, N. Samkhaniy, A. Tadjarodi, A. Abbaszadeh and M. Pooladi // *Microchim. Acta* 181 (2014) 597, (c) 2014 Springerlink.

ivated carbon is employed as the effective sorbent due to its large specific surface area, high chemical and physical property for the target objects. When grated with different chemical groups, activated carbon will possess more adsorption capability. Chang et al. packed activated carbon modified by zinc (AC-ZCN) into the PTFE column to enrich and separate two metal ions of trace Cr(b!) and Pb(II) in the yellow river, then the content of the metal ions was monitored by inductively coupled plasma optical emission spectrometry (ICP-OES). The analysis of Cr(b!) and Pb(II) in the sample cannot be disturbed in pH 4.0, even though Zn(II), Fe(b!), Ni(II), Cu(II), Cd(II) and Hg(II) can be adsorbed with the recoveries are from 60-80%. At the same time, the relative standard deviation is less than 3.5%. The results in the experiment are in agreement with the standard values certified by utilized the standard materials [1]. However, the adsorb ability of activated carbon modified perhaps is limited because of the reduction of pore size. As a consequence, other alternative sorbent also be used. For instance, a novel magnetic multi-walled carbon nanotube composite functionalized with 8-aminoquinoline was employed for preconcentration of cadmium, nickel, and lead ions in water samples, fish and sediment samples, soil sample, with the limit of detection are 0.09, 0.72, 1.0 ng/mL, respectively. The adsorbents were synthesized according to the Fig. 8 [140]. Taghizadeh et al. prepared and developed a magnetic metal organic framework (MOF) nanocomposite by using  $\text{Fe}_3\text{O}_4$  nanoparticles decorated with dithizone and a copper-(benzene-1,3,5-tricarboxylate) MOF as re-

actant for extraction of Cd(II), Pb(II), Ni(II), and Zn(II) ions [141]. Zhou et al. used  $\text{TiO}_2$  nanotubes as the extractant in SPE for concentration and enrichment of two heavy metals, nickel and cadmium in four real water samples prior to the detection of the flame atomic absorption spectrometry. As a result, the mean recovery values of the heavy metals are about 90.2%-99.2%. This fast, simple, sensitive and high selective method could be used in detection of the trace levels of Cd(II) and Ni(II) in other analogous environmental fields [142].

Hossein Abdolmohammad-Zadeh et al. synthesized and applied Mg-Al-Fe( $\text{NO}_3$ ) ternary layered double hydroxide nanomaterial as a SPE sorbent for enrichment and separation of trace As(b!) and As(V) before the determinant of the electrothermal atomic absorption spectrometry. In the experiment, the RSD relative standard deviation is 3.9% in the optimum conditions. Possessing higher selectivity and adsorption capacity, great accuracy and other good advantages, this method could be available in the real water samples to separate and extract As(b!) as well as As(V) [143].

## 5.2. Extraction of organic contaminants in real water samples

Generally speaking, the organic contaminant is a kind of organic matter that mainly caused by human industrial or daily activities and affects the environment. It is mandatory requirements that the organic matter need to be disposed to the emission

standards before discharged. In fact, not all the organics are released after strict management. Several progressive technologies are used for preconcentration of the organic contaminants, including pesticides and pharmaceuticals by the mean of SPE with GC [25]. Nnaphthalene and acenaphthene via SPE combined with ionic liquid (IL) dispersive liquid–liquid microextraction (DLLME) were determined by HPLC [49]. By the mean of magnetic solid-phase extraction (MSPE), polyaromatic hydrocarbons (PAHs) was detected by GC [144]. Many kinds of contaminants, such as isoproturon, dimethomorph [145], pirimicarb, baygon [28], carbendazim, thiamethoxam [146], and vancomycin [147] have been enriched and observed via SPE with HPLC. All these methods have their own advantages.

### 5.2.1. Extraction of pesticides in waste waters

Recently, because an increasing number of pesticides are used in agriculture, the residual pesticides in vegetables, fruits and food are seriously overweight. To handle this problem, Chinese Ministry of Agriculture and Ministry of Health have made strict provisions about the kind of residual pesticides, the maximum residue limits as well as daily intake. Similarly, the United States and the European Union also have corresponding rigorous rules. SPE, as the advanced technique, have been used for detecting pesticides successfully.

Zhou et al. successfully detected four carbamate pesticides content using graphene-modified TiO<sub>2</sub> nanotube arrays. The excellent adsorption properties of graphene and the great sample isolation characteristic of the SPME were combined well, the four model analytes, metolcarb, carbaryl, isoprocarb, and diethofencarb were separated fully with HPLC. And the mean values of recovery range from 83.9%–108.8% [148]. Wunderlin et al. used the reversed-phase silica supporter bonded with C18 as an adsorbent in SPE cartridges, combining with SPME for effectively selective preconcentration and enrichment of pesticides in the waste water sample prior to the determinant of GC-MS. After conditioning the column in SPE, the target analytes flows through the reverse phase C18 column, then the samples were eluted by employing methanol and acetonitrile as eluents, following by evaporation to exsiccation. Afterwards, the dry residue was diluted by acetone and ultrapure water. Next, the SPME procedure was performed. The analytes were extracted utilizing 85  $\mu$ m polyacrylate fiber from sample solu-

tion for 30 min, while the temperature was designed as 70 °C, desorption step was executed at 280 °C for 5 min. Then, the target analytes was determined through GC-MS. The analysis results suggested that this method combining the SPE with SPME has good resolution. In all the experiments, the recoveries ranged within 63–104%, with RSD from 4% to 23%. The SPE-SPME-GC-MS method evaluated was available for identification and quantification other varieties of pesticides in rivers. On the other hand, this method could avoid the loss of the pesticides in a degree in studies [149].

Additionally, nanomaterial can also be employed as adsorbent in the aspect of extraction of pesticides. Zhou et al. first utilized TiO<sub>2</sub> nanotubes as the solid phase extraction adsorbents. The target analytes of o,p\_-DDT, [1,1,1-trichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl)ethane, p,p\_-DDT, [1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane] and their respective metabolites in water samples are enriched and separated by the material. Briefly, the SPE process was concentrated by following steps: firstly, the SPE column was packed with adsorbents and disposed with methanol and water. And then four water samples flowing through the column, the column was purified with Mill-Q water. After the column was dried, the analytes were eluted with dichloromethane and dried in nitrogen gas. Subsequently, the analytes were redissolved in methanol and injected into HPLC. And the results are good and satisfying. Indeed, the recoveries of the analytes are 81.2%–115% [150]. In fact, coupled with superior detection instrument, the accurate value and desire results are able to be received. Except for pesticides, other organic contaminants also have received considerable attention in recent years.

### 5.2.2. Extraction of phenols and aromatic compounds in environmental waters

Other organic pollutants such as polycyclic aromatic hydrocarbons (PAHs), bisphenol A (BPA), affect seriously the health of human and environment once these harmful substances are released into the environmental water. For extraction of these substances from water samples, numerous examples were published in the previous literature.

The desirable results of the extraction of 40 different analytes, including PAHs, were obtained by Ziarrusta group. In the experiment, the optimal conditions of extraction were established. After extracting samples using adsorbents, the extract was eluted with pure dichloromethane (DCM), afterwards,

the dried product was dissolved into n-hexane to be analyzed with GC–MS or GC–MS/MS. The limits of detection ranged from 0.010 to 2.74 ng/ml, and  $R^2$  within 0.980–0.9996 [151].

In addition, ion exchange resin is also able to reach the analytical goals. Nerín et al. used DSC-SCX SPE cartridges for preconcentration and enrichment of 22 primary aromatic amines (PAAs) before the analysis of LC-MS. In the study, the recovery values of all the objects are 81%–109% and the RSD are 4.5%–13.4%, the limits of the detection are lower. Because this method has obtained highly selective ability and high recoveries, it is the appropriate method to monitor the main aromatic amines in the environmental samples [152].

### 5.2.3. Extraction of DNA and RNA in biological matrices

The biological samples are pretty sophisticated, and various endogenous substances are mixed in it. These substances not only react with drugs and metabolites, but reduce interference for the detection of target objects. In general, the preconcentration of the biological samples is particularly important process during the separation and analysis of the entire system.

Consequently, it is necessary to execute several steps such as isolation, purification, and enrichment to get the analytes from the complex biological samples. Recently, as one of advanced methods for analyzing samples in SPE, microchip SPE technology is used for determination for the biological analytes, including DNA, RNA from intricate matrices since its distinct characteristic, including high throughput, miniaturization, multifunction, low consumption, etc.

Ferrance et al. first synthesized macro-porous silica sol-gel by using tetraethoxyorthosilicate (TEOS) material, and applied DNA as the model analyte to evaluate the extraction procedure. This micro-sized silica could be formed in the microchip galleries, and equipped with high surface area and other advantages. All the factors increase the effect of extraction of DNA. In relatively simple human blood samples, the average recovery of human genomic DNA of 85% is obtained, while in complicated biological matrix, the average recovery of DNA of 70% is acquired, respectively. Nevertheless, there is one disadvantage using this  $\mu$ chipSPE technique. When many extractions are reduplicating just in one device, a group of compounds will block the holes on the silica, so that the extraction efficiency would be decreased [153]. Furthermore, Landers group eluted

the DNA from complicated biological mixtures by utilizing the mchipSPE technique. When pH is lower in some degree, it is useful to increase the elution speed [154]. Klapperich et al. successfully isolated viral RNA from mammalian cells infected with influenza A (H1N1) virus by using plastic microchip combined with ichipSPE through in situ photopolymerization, and the target analytes are collected via reversible binding way. This procedure is rapid, simple for settlement of the extraction of viral RNA. Moreover, the risk of degradation of RNA has been decreased in some degree. The separation of the sample is justified to be available and enough efficient for the experiments about the preconcentration of nucleic acid [155]. Except for isolation and enrichment of analytes with microchip SPE, molecule imprinting technique is also a pervasive method to realize the purpose of concentration.

### 5.2.4. Extraction of antibiotics in water and milk samples

Antibiotics have been pervasively used for treating a variety of bacteria and pathogenic microorganisms, since the last century 70's [156]. Wang group prepared and applied a pseudo-template molecularly imprinted solid-phase extraction (MISPE) for selectively extraction of  $\beta$ -lactam antibiotics (BLA) in tap water and river. However, two challenges are required to be taken into consideration carefully. In MISPE technique, generally, the phenomenon of template bleeding maybe occurred while the target is employed as template, so that the purity of the samples, the accuracy and precision will be affected accordingly. On the other hand, the chemical instability of  $\beta$ -lactam ring of BLA under high temperature will have a significant influence on the molecularly imprinted polymer. To solve these two problems, the authors used the nafcillin, a structural analogue of the BLA, as the template to prepare the MIP sorbent by UV-initiated photopolymerization at 15 °C. Contrast to the thermal polymerization at 40 °C (2,2'-azobis (2,4-dimethylvaleronitrile) (ABDV) as initiator) and 60 °C (2,2'-azobisisobutyronitrile (AIBN) as initiator), the former has higher imprinting factors (IF) for four BLA-MIP, except for ampicillin-MIP, and the more homogenization effect can be achieved. This method was available for determination and analysis of the trace level of the BLA in river water at the downstream of antibiotics manufacturers [156].

Simultaneously, some antibiotics cannot kill effectively the bacteria since these bacteria possess high antibiotic-resistance rate. As the typical ex-

ample, *Staphylococcus aureus* has resistance to many antibiotics. Penicillin binding protein 2a (PBP2a) is regarded as the optimal substance to detect the existence and content of *staphylococcus aureus*. Therefore, the detection of this protein is also particularly important. A highly selective and specific antibody-linked immunoaffinity solid phase microextraction was developed by Pawliszyn group. The performance of this method was evaluated by serving penicillin binding protein 2a (PBP2a) as the objective, with LC-MS/MS system as the detection tool. To effectively resolve the problem of non-specific binding of antigen protein in use of IAC, bovine serum albumin (BSA) was used to deal with the glass surface of container, PBP2a extraction solutions was held in it, by blocking active sites on the surface. The sorbents then could be retained steadily onto the BSA for the purpose of extraction of protein PBP2a. The good result was obtained with the limit of the detection as low as 10 ng/mL [157].

All of these advanced techniques are used frequently for isolation of target objects from a variety of samples, not only about natural water, waste water, soil, milk, but also milk product, food, etc. With these different SPE techniques, and legitimately using advanced instrumentation, the purpose and desired results are able to be obtained since the high sensitivity, accuracy, celerity and other advantages.

## 6. CONCLUSION AND OUTLOOK

In this paper, we give a detailed and systematic review about concept, main principles and characters of the a series of solid phase extraction techniques, including solid phase extraction, molecule imprinting solid phase extraction, solid phase microextraction, dispersive solid phase extraction, matrix solid phase dispersion, magnetic solid phase extraction, microchip solid phase extraction, stir bar sorptive extraction, immunoaffinity solid phase extraction, monolith solid phase extraction.

The preconcentration of sample plays a pretty critical role in the whole process of analyzing sample. Herein, SPE is the significant core. Except for the differences of extraction methods, adsorbent also is an important impactor that affect the efficiency of separation and enrichment for the target analytes from a variety of samples. A collection of sorbents are used for extraction, e.g. silica, activated carbon, carbon nanotubes, graphene. Distinct physical and chemical properties (large surface area, rich functional groups, stability in acidic and alkaline solutions as well as high mechanical strength) make

them possess good adsorption performance. At the same time, the use of advanced analysis devices, such as GC, HPLC, ICP, MS, what's more, also enhance the accuracy of results to a large extent. With multidisciplinary endeavors, more and more advanced solid phase extraction technologies will be explored and used in preconcentration of sample, and hold great promise for the future.

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