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Recent advances in solid-phase sorbents for sample preparation prior to chromatographic analysis

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ABSTRACT

Sample preparation is a crucial bottleneck in the whole analytical process. Solid-phase sorbents (SPSs) have aroused increasing interest in research on sample preparation, as they have key roles in obtaining high clean-up and enrichment efficiency in the analysis of trace targets present in complex matrices. The objective of this review is to provide a broad overview of the recent advances and applications of SPSs in sample preparation prior to chromatographic analysis, during the period 2008–13. We include SPSs, such as molecularly-imprinted polymers, carbon nanomaterials, metallic nanoparticles and metal organic frameworks, focusing on solid-phase extraction, solid-phase microextraction, matrix solid-phase dispersion and stir-bar sorptive extraction of typical pollutants in environmental, biological, food and pharmaceutical samples. We propose remaining challenges and future perspectives to improve development of new SPSs and to apply them further.

Contents

Abbreviations: 2- or 4-VP, 2- or 4-vinylpyridine; AA, Acrylic acid; APTES, Aminosilica monomer; BPA, Bisphenol A; CNT, Carbon nanotube; CP, Chlorophenol; CTAB, Trimethylammonium bromide; DLLME, Dispersive liquid-liquid microextraction; DVB, Divinylbenzene; EDC, Endocrine-disrupting chemical; EGDMA, Ethylene glycol dimethacrylate; FID, Flame-ionization detector; FLD, Fluorescence detector; HEMA, 2-hydroxyethyl methacrylate; HLB, Hydrophilic-lipophilic balance; LOD, Limit of detection; LOQ, Limit of quantitation; MAA, Methacrylic acid; MAX, Mixed-mode/anion-exchange; MBAA, N,N-methylenebisacrylamide; MCX, Mixed-mode/cationic-exchange; MIP, Molecularly-imprinted polymer; MISPE, Molecularly-imprinted solid-phase extraction; MNP, Magnetic nanoparticle; MOF, Metal-organic framework; MSPD, Matrix solid-phase dispersion; MWCNT, Multi-walled carbon nanotube; NP, Nanoparticle; PAH, Polycyclic aromatic hydrocarbon; PDDA, Poly(diallyldimethylammonium chloride); PS-DVB, Poly(styrene-divinylbenzene); SBSE, Stir-bar sorptive extraction; SPME, Solid-phase microextraction; SPS, Solid-phase sorbent; SWCNT, Single-walled carbon nanotube; TRIM, Trimethylolpropane trimethacrylate; WAX, Weak anion-exchange.

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1. Introduction

Sample preparation is a crucial part of chemical/biological analysis and in a sense is considered the bottleneck of the whole analytical process. The main objectives of sample preparation are the removal of potential interferences, analyte preconcentration, and converting (if needed) the analyte into a more suitable form for detection or separation. In recent decades, solid-phase extraction (SPE) has played a crucial role in sample preparation, replacing the classic liquid–liquid extraction (LLE), in environmental, food and biological analyses [1–3]. In the past, some classic materials, such as C_8, C_{18}, hydrophilic-lipophilic balance (HLB, the sorbent of which is a macroporous copolymer made from a balanced ratio of two monomers including hydrophilic and lipophilic ones), mixed-mode/cationic-exchange (MCX), mixed-mode/anion-exchange (MAX) and weak anion–exchange (WAX) were commonly used for SPE [4]. More recently, a large number of new solid-phase sorbents (SPSs), such as molecularly-imprinted polymers (MIPs) [5], magnetic nanomaterials [6] and carbon nanoparticles (NPs) [7] have been proposed and applied for sample preparation. Moreover, although some powerful techniques (including HPLC-MS/MS and GC-MS/MS) are also subjected to improving the detectability for analytes in complex matrices, new objectives of sample preparation have been set, such as using small initial volume or weight of sample, improvement of selectivity in extraction, facilitating automation, and minimizing the amount of glassware and organic solvents to be used. Thus, some other sample-preparation methodologies, such as solid-phase microextraction (SPME), stir-bar sorptive extraction (SBSE) and matrix solid-phase dispersion (MSPD), have been effective for the above purposes. These methods, together with SPE, stimulated rapid advances of the new SPSs. A number of research efforts dealing with novel SPSs specifically developed for these applications in chromatography have been reported and some have been reviewed.

Lucena et al. [7] gave a general overview of the use of NPs mainly including carbon, metallic, silica and imprinted NPs to perform sample preparation in SPE and SPME.

Turiel and Martín-Esteban [8,9] reviewed the use of MIPs in SPE, SPME, MSPD and SBSE.

Augusto et al. [10] outlined progress in research on some new classes of sorbents, such as carbon nanotubes (CNTs), MIPs and sol-gel coatings for SPME fibers and related techniques, and for extraction and microextraction techniques.

Tankiewicz et al. [11] described some SPSs applied in SPE, SPME and SBSE.

Several recent reviews were released in 2013. For example, Mehdinia and Aziz-Zanjani [12] reviewed advances for sensitive, rapid and selective extraction in different configurations of SPME, containing some new SPSs.

Spieteluna et al. [13] summarized recent developments and future trends in SPME toward green analytical chemistry containing various novel SPSs.

Yang et al. [14] presented an overview of microextraction techniques for the determination of volatile and semi-volatile organic compounds from plants, involving SPS preparation and applications.

Namera and Saito [15] reviewed some new SPSs used in SPE and SPME methods for bioanalysis.

An important trend shared by the fundamental research on the above extraction techniques relates to the development and the characterization of new sorbents. It has become a hot issue to research new advanced materials, involving several branches of disciplines, such as materials science, nanotechnology, polymer synthesis and analytical chemistry. The development of SPSs generally aims for: high selectivity, good sorptive/adsorptive capacity, enhanced thermal, chemical or mechanical stability and improved lifetime of devices employing them as sorbent/adsorbent media [10]. In this review, we therefore provide an updated, essential summary of the most important features and applications of new materials as SPSs in SPE, SPME, MSPD and SBSE prior to chromatographic analysis. We summarize highlighted applications of these new SPSs for the extraction of environmental, biological, food and pharmaceutical samples. We also discuss the present limitations and expected future trends of SPSs in sample preparation for better advancement.

2. Novel solid-phase sorbents

Traditional SPSs, such as silica NPs, C_8, C_{18}, poly (styrene-divinylbenzene) (PS-DVB), methacrylate-DVB resins, macroporous poly (N-vinylpyrrolidone-DVB) polymers and some others, usually used mixed-mode ion-exchange sorbents, including MCX, MAX and WAX, which have already been reviewed in detail by Alberti et al. [4]. The present review focuses on the preparation and the applications of novel SPSs, mainly including MIPs, carbon nanomaterials, metallic NPs and metal-organic frameworks (MOFs).

2.1. Molecularly-imprinted polymers

In recent years, MIPs proved to be useful materials in several areas of analytical chemistry [5,16–20]. MIPs are synthetic materials with artificially-generated recognition sites able to specifically rebind a target molecule in preference to other closely-related compounds. Functional monomers and cross-linking agents are copolymerized in the presence of a template (the imprint molecule) in a suitable solvent, leading to a highly cross-linked three-dimensional network polymer. The monomers are chosen by considering their ability to interact with the functional groups of the template molecule. Subsequent removal of the imprint molecule leaves cavities with size, shape and chemical functionality complementary to those of the template. The inherently high selectivity associated with MIPs has made them ideal sorbents to be used in SPE, SPME, MSPD and SBSE [18]. Recently, our group reviewed recent advances in molecular imprinting technology, with particular emphasis on significant progress of novel imprinting methods and MIP materials, some challenges and effective strategies, and highlighted applications of MIPs [5].

The mechanism of MIP formation mainly includes free-radical polymerization and the sol-gel process. Use of free-radical polymerization became popular recently, including bulk polymerization, suspension polymerization, emulsion polymerization, seed polymerization and precipitation polymerization. During polymerization, the types of target molecule, monomer and cross-linker have an important effect. First, an ideal template molecule plays a key role in the polymerization. Nowadays, hormone drugs, triazine pesticides and phenolic compounds, such as bisphenol A (BPA), are the most widely used targets in preparing MIPs. The role of the monomer is to provide functional groups that can form a complex with the template by covalent or non-covalent interactions. For molecular imprinting, methacrylic acid (MAA), acrylic acid (AA), 2- or 4-vinylpyridine (2- or 4-VP), acrylamide, trifluoromethacrylic acid and 2-hydroxyethyl methacrylate (HEMA) are commonly used monomers. The role of the cross-linker is to fix functional groups of monomers around imprinted molecules, and thereby form highly cross-linked rigid polymers. Commonly used cross-linkers include ethylene glycol dimethacrylate (EGDMA), trimethylolpropane trimethacrylate (TRIM), N,N-methylenebisacrylamide (MBAA) and divinylbenzene (DVB) [5].

2.2. Carbon nanomaterials

Since the discovery of fullerene C_{60} in 1985 [21], carbon nanomaterial-based technology has developed as one of the most important trends in SPE. Carbon exists in a number of allotropic forms, such as fullerenes, CNTs, including single-walled CNTs (SWCNTs) and multi-wall CNTs (MWCNTs), carbon nanohorns, carbon nanocones, carbon nanodisks, carbon nanofibers, nanotube rings, graphene oxide (GO) and graphene (G), and diamonds [22–26]. However, to date, from the analytical point of view, the applications have mainly been focused on the use of fullerenes, CNTs and GO/G.

2.2.1. Fullerenes

Fullerenes are polyhedral nanostructures, in which carbons are bonded in arrangements of five-to-six-membered rings [7]. Although they are extremely insoluble in aqueous and organic media, their lower aggregation tendency facilitates their use as sorbents in miniaturized SPE procedures based on continuous-flow devices.

Gallego et al. [27] first fabricated a continuous-flow system, sorbed on a C_{60} fullerene mini-column for preconcentration of trace metals.

Serrano and Gallego [28] compared C_{60} fullerene, Tenax TA (a porous polymer resin based on 2.6-diphenylene oxide), and RP-C_{18} as SPE sorbents for the extraction of benzene, toluene, ethyl benzene and xylene isomers from water samples. The results showed C_{60} fullerene was the best choice in terms of sensitivity, precision, selectivity and reusability.

Recently, Jurado-Sánchez et al. [29] used fullerenes as SPSs in SPE for discrimination of aromatic and non-aromatic N-nitrosamines. An automatic SPE unit containing two sequential sorbent columns was constructed, and a comparative study of C_{60} and C_{70} fullerenes and nanotubes revealed C_{60} fullerene to be the best choice to retain the aromatic fraction selectively. Hence, the simple, fast SPE system (10 min per sample) coupled with a customary GC-MS instrument permitted quantification of these amines in complex matrices with considerable sensitivity and selectivity [29].

2.2.2. Carbon nanotubes

CNTs can be viewed as graphite sheets (sp^2 carbon) that have been rolled up into tiny tubes. CNTs usually have a diameter in the range from a few tenths to tens of nanometers and a length up to centimeters [30]. Thanks to their large surface area-to-volume ratios and high affinity, CNTs can be considered as excellent materials for SPSs [7]. There are basically two types of CNTs: MWCNTs (including two or more concentric cylindrical shells or G sheets coaxially arranged around a central core) and SWCNTs [30]. Both of them have exhibited excellent adsorption properties as SPSs. The first application of CNTs was that MWCNTs were used for SPE and highly efficient enrichment was successfully achieved for BPA, 4-*n*-nonylphenol and 4-*tert*-octylphenol from environmental water samples [31]. Recent advances of CNTs as SPSs (e.g., applied in SPE and SPME) were demonstrated by several excellent reviews [4,7,30].

2.2.3. Carbon nanohorns, nanocones, nanodisks and nanofibers

As well as CNTs, carbon nanohorns, nanocones, nanodisks and nanofibers are also rapidly evolving as sorptive materials and (pseudo) stationary phases in modern separation sciences because of their unique physicochemical and mechanical properties and large chemically active surface areas. These carbon-based nanomaterials applied in sample preparation have been excellently reviewed in detail by Lin and his co-workers lately [32].

Carbon nanocones were first synthesized by vapor condensation of carbon atoms on a graphite substrate in 1994 [33] and the allotropic forms were identified in 1997 [34]. The discrimination of each structure corresponds to the presence of a given number of pentagons in the seed from which it grew, including disks (no pentagons), five types of cones (1–5 pentagons, as shown in Fig. 1) and open tubes (six pentagons) [23].

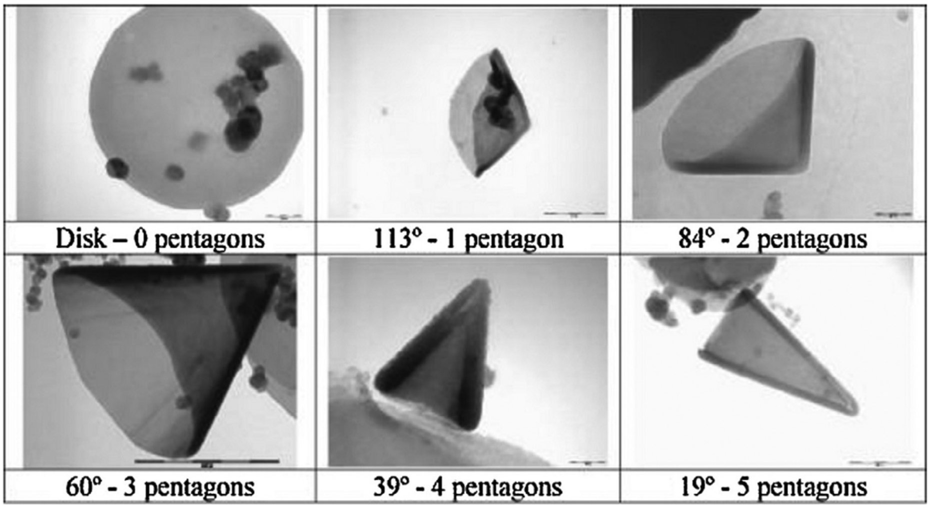

Fig. 1. Angles formed at the vertex of the carbon nanocones depending on the number of existing pentagons. (Reprinted with permission from [23]. © 2013 Elsevier).

Carbon nanofibers are solid carbon fibers with lengths in the order of a few microns and diameters below 100 nm, and specific surface area reported up to 1877 m^2/g, the highest ever reported for nanostructured materials [35].

2.2.4. Graphene and graphene oxide

G, an atomically thin honeycomb lattice of carbon atoms, recently sparked great excitement in the scientific community shortly after being discovered by Geim et al. in 2004 [36]. It attracted intensive interest in recent years due to its remarkable electronic, mechanical, optical and thermal properties [37], which make it the most promising carbon-based nanomaterial after fullerene and CNTs. G exhibits a high theoretical surface area of 2700 m^2/g [38]. It possesses most of the advantages of CNTs. Moreover, it is prepared from graphite without any residual heterogeneous materials, which usually include residual metallic impurities and NPs derived from catalysts [25]. As a result, G is currently a popular option for SPSs.

Like G, GO is a monolayer of two-dimensional carbon-based materials containing multi-functional groups, such as carboxyl, epoxy, ketone and hydroxyl groups, in its basal and edge planes [39]. Due to its good water dispersibility, high mechanical strength and versatile surface modification, GO is now a popular alternative SPS in sample preparation.

2.3. Metallic nanoparticles

Metallic NPs, involving a wide range of different inorganic NPs, have unique properties, such as large specific surface area, high adsorption capacity and low temperature modification. Nowadays, metallic nanomaterials used as SPSs reportedly include Fe_3O_4, TiO_2, Al_2O_3, ZrO_2, MnO, and CeO_2, modified with functional coatings [40–47]. Among them, magnetic NPs (MNPs) are particularly useful for extracting and enriching a large volume of target analytes, because they can provide high surface area-to-volume ratio, easy surface modification and strong magnetism [48]. The extraction of magnetic nanomaterials with analytes is generally based on hydrophobic interaction, electrostatic attraction, and/or covalent-bonding formation. Fe_3O_4 nanomaterials are the most popular, and possess strong magnetism, so they are easily isolated from sample solutions by an external magnetic field without additional centrifugation and filtration [48,49].

2.4. Metal-organic frameworks

MOFs are a new kind of hybrid inorganic–organic microporous crystalline material, self-assembled straightforwardly from metal ions with organic linkers via coordination bonds [50]. These materials have large surface areas in the range 1000–10400 m^2/g, tailorable polarity and pore size, and high thermal stability [51–53]. MOF materials have therefore attracted special attention in analytical applications.

In the past few years, MOFs emerged as a new class of porous hybrid material with great potential for applications in gas storage and separation [54]. Moreover, the promising MOFs, which offer a variety of topologies, porous networks, high surface areas, nanoscale porosity, tunable pore sizes, in-pore functions, and outsurface modification, have potential for the applications of catalysis [55], separation [54,56], gas storage [57] and drug delivery [58].

3. Solid-phase sorbents for sample preparation prior to chromatographic analysis

3.1. Molecularly-imprinted polymers as solid-phase sorbents

3.1.1. Molecularly-imprinted solid-phase extraction

Sample preparation using SPE was first introduced in the mid-1970s. As a classical sample-preparation method, SPE is still being used and developed, including off-line and on/in-line. Nevertheless, the major disadvantage of conventional SPE sorbents, such as C_{18}, ion-exchange and size-exclusion phases, is the lack of selectivity, leading to co-extraction of matrix-interference components with the target analytes. MIPs have attracted great attention because they show promise as compound-selective or group-selective media. So, MIPs as SPE sorbents, have become a most important application area, which has been reviewed by Chen's group [5,18,59], by coupling with various chromatographic technologies, such as HPLC, GC and CE. MISPE has been applied using off-line, on-line and in-line modes.

3.1.1.1. Off-line molecularly-imprinted solid-phase extraction. Off-line MISPE involves loading the MIPs into SPE cartridges. The operational process is very similar to that for other SPE sorbents, including pre-conditioning, sample loading, washing and elution steps.

- **Traditional MIPs.** Table 1 summarizes MISPE applied in extracting analytes from environmental, biological and food samples [60–87]. It can be seen from Table 1 that more applications of MISPE are before HPLC than GC or CE in recent years. Besides the applications mentioned in Table 1, there are some other novel SPE applications using MIPs as SPSs prior to chromatography. For example, Peng et al. [88] used MIP-layer-coated silica NPs as the sorbents of dispersive SPE (dMISPE) for extracting trace sulfonylurea herbicides from soil and crop samples. The times of adsorption and desorption were 30 min and 20 min, respectively. The performance was compared with commercial C_{18} sorbents, showing the binding capacity of the MIPs was much higher than that of C_{18}. The dMISPE-HPLC method exhibited high selectivity and sensitivity for the determination of sulfonylurea herbicides from spiked soil, rice, soybean, and corn samples.

Ebrahimzadeh et al. [89] combined dMISPE with dispersive liquid-liquid microextraction (DLLME) for ultra-preconcentration and determination of mono-nitrotoluenes in wastewater samples using gas chromatography-flame ionization detector (GC-FID), where 3-nitrotoluene, MAA and EGDMA were template, functional monomer and cross-linker, respectively. Although the time of dMISPE was a little long (about 13 h), the preconcentration factor of dMISPE-DLLME was high (~2800 under optimal conditions).

Lee et al. [90] used commercial MIPs and polypropylene flat sheet membrane to make a MIP micro-SPE (MI-μSPE) device. Under optimal conditions of the MI-μSPE-HPLC-fluorescence detector (FLD) method, ochratoxin A was selectively extracted and determined in roasted coffee samples.

Moreover, commercial MIPs materials can be purchased from different reagent companies. Also, MISPE cartridges purchased from these companies have exhibited excellent performance [91–93].

- **Novel MIPs.** Recently, magnetic SPE became a popular extraction mode of SPE based on the use of magnetic sorbents, when MIPs are grafted onto MNPs before MISPE.

Hiratsuka et al. [94] and Lin et al. [95] used magnetic MIPs as SPSs for the determination of estrogens in water samples. As the unique mechanical properties and extremely large surface area of MWCNTs, they can be an excellent candidate as the support material. Zhang et al. [96] used the MWCNTs as the support materials, and synthesized erythromycin-MIPs on the surface of MWCNTs according to surface imprinting technique. Under the optimized conditions, the erythromycin was purified and enriched from ethanol and chicken muscle by using the MWCNTs-MIPs, and the recoveries of erythromycin was in the range 85.3–95.8% in chicken muscle samples. Similarly, Gao et al. [97] also synthesized triclosan (TCS)-MIPs based on CNTs coated with silica. The scheme of the synthetic route for CNTs@TCS-MIPs is shown in Fig. 2. The whole process via a multistep procedure is involved in the formation of TCS-aminosilica monomer (APTES) complex, silica-shell deposition on the surface of CNTs, MIP-functionalized onto the silica surface and final extraction of TCS to generate the recognition sites. Then,

Table 1
Selected applications of the technique of molecularly-imprinted polymer-solid-phase extraction (MIP-SPE)

Template	Analyte	Matrix	Monomer/cross-linker	MIP synthesis	Analytical technique	LODs (ng/mL)	Ref.
Thiabendazole	Thiabendazole	Citrus fruits	MAA/EDMA	Grafted on porous polyethylene frits	HPLC-FLD	16^{a}	[60]
Quercetin	Quercetin,quercetin-4'-glucoside and quercetin-3,4'-diglucoside	Yellow onion	4-VP/EGDMA	Bulk	HPLC-UV	–	[61]
Bromhexine	Bromhexine	Human serum and urine	MAA/EGDMA	Bulk	HPLC-UV	0.1, 0.3	[62]
Oxytetracycline and Chlortetracycline	Tetracycline antibiotics	Lobster, milk and honey	MAA/TRIM	Precipitation polymerization	HPLC-UV	–	[63]
Rutin	Rutin	*S. chinensis*	AA and 2-VP/EGDMA and DVB	Bulk	HPLC-UV	6.7	[64]
Quercetin	Catechins	Red, white, green and black tea	4-VP/EGDMA	Bulk	HPLC-UV	–	[65]
Quercetin	Rutin and quercetin	Cacumen platycladi	AA/EGDMA	Bulk	HPLC-UV	–	[66]
Amiodarone	Amiodarone	Blood serum	4-VP/EGDMA	Bulk	HPLC-UV	20	[67]
Metolachlor deschloro	Chloroacetamide herbicides	Food samples	MAA/EGDMA	Suspension polymerization	HPLC-MS/MS	0.1–0.5^{a}	[68]
Trichothecene-2	Trichothecenes	Maize, barley and oat samples	MAA/EGDMA	Radical polymerization	HPLC-MS/MS	0.3–2.3^{a}	[69]
Oxytetracycline hydrochloride	Oxytetracycline residues	Milk	MAA/TEOS	Sol-gel technology	HPLC-UV	4.8–12.7^{a}	[70]
Citalopram	Citalopram	Human serum and urine	MAA/EGDMA	Bulk	HPLC-UV	0.4	[71]
Imidazole	Imidazole	Water samples	MAA/EDMA	grafted on silica	HPLC-UV	–	[72]
3-methylflavone-8-carboxylic acid	3-methylflavone-8-carboxylic acid	human urine	MAA/EGDMA	Bulk	ZHILC-UV	–	[73]
BPA Diphenolic Acid	BPA Diphenolic Acid	Water samples	APTES/TEOS	Grafted on silica	HPLC-UV	2	[74]
Propyl gallate	Antiplatelet active ingredients	Radix Salviae Miltiorrhizae	4-VP/EGDMA	Bulk	HPLC-MS/MS	–	[75]
Sudan I	Sudan I	Chili Sauce Samples	MAA/DVB	Multistep seed swelling polymerization	HPLC-UV	3.3, 5.0^{a}	[76]
Atrazine	Atrazine	Lettuce and corn samples	MAA/EGDMA	Precipitation polymerization	HPLC-UV	–	[77]
Atrazine	Triazines	Soil	MAA/DVB	Two-step swelling polymerization	HPLC-UV	2.8–9.6	[78]
Deltamethrin or cypermethrin	Pyrethroid insecticides	Aquaculture seawater	MAA/EGDMA	Bulk	GC-ECD	0.017–0.68	[79]
Methanidophos	Methanidophos	Surface water and soil	MAA/EGDMA	Bulk	GC-NPD	3.8^{a}, 0.010, 0.013	[80]
16 PAHs	16 PAHs	Seawater	PTMS/TEOS	Grafted on silica	GC-MS	0.052–0.126	[81]
4,4′-(hexafluoroisopropylidene)-diphenol	BPA	Water	4-VP/ TRIM	Bulk	GC-MS	10^{-5}	[82]
Diisononyl phthalate	Phthalates esters	Plastic bottled beverage products	AM/DVB	Precipitation polymerization	GC-FID	0.85–1.38	[83]
PAHs	PAHs	Air dust	4-VP/EGDMA	Bulk	GC-MS	1.5×10^{-4}	[84]
TMB	Polybrominated biphenyls	Water and fish	γ-MPTMS/TMOS	Grafted on silica	GC-ECD	0.002–0.008	[85]
BPA	BPA	–	MAA/EGDMA	Bulk	CE-UV	100	[86]
BPA	EDCs	Tap, waste, river and shrimp water	4-VP/TRIM	precipitation polymerization	CE-UV	1.8–84	[87]

AM, Acrylamide; BPA, Bisphenol A; EDC: Endocrine-disrupting chemical; GC-ECD, Gas chromatography-electron capture detector; GC-FID, Gas chromatography-flame ionization detector; GC-NPD, Gas chromatography-nitrogen phosphorus detector; HPLC-FLD, High-performance liquid chromatography-fluorescence detector; γ-MPTMS, γ-mercaptopropyltrimethoxysilane; PAH, Polycyclic aromatic hydrocarbon; PTMS, Phenyltrimethoxysilane; TMB, 3,3′,5,5′-tetramethylbenzidine; TEOS, Tetraethoxysilane; TMOS, Tetramethoxysilane; TRIM, Trimethylolpropane trimethylacrylate; ZHILC, Zwitterionic hydrophilic interaction liquid chromatography.

[a] ng/g.

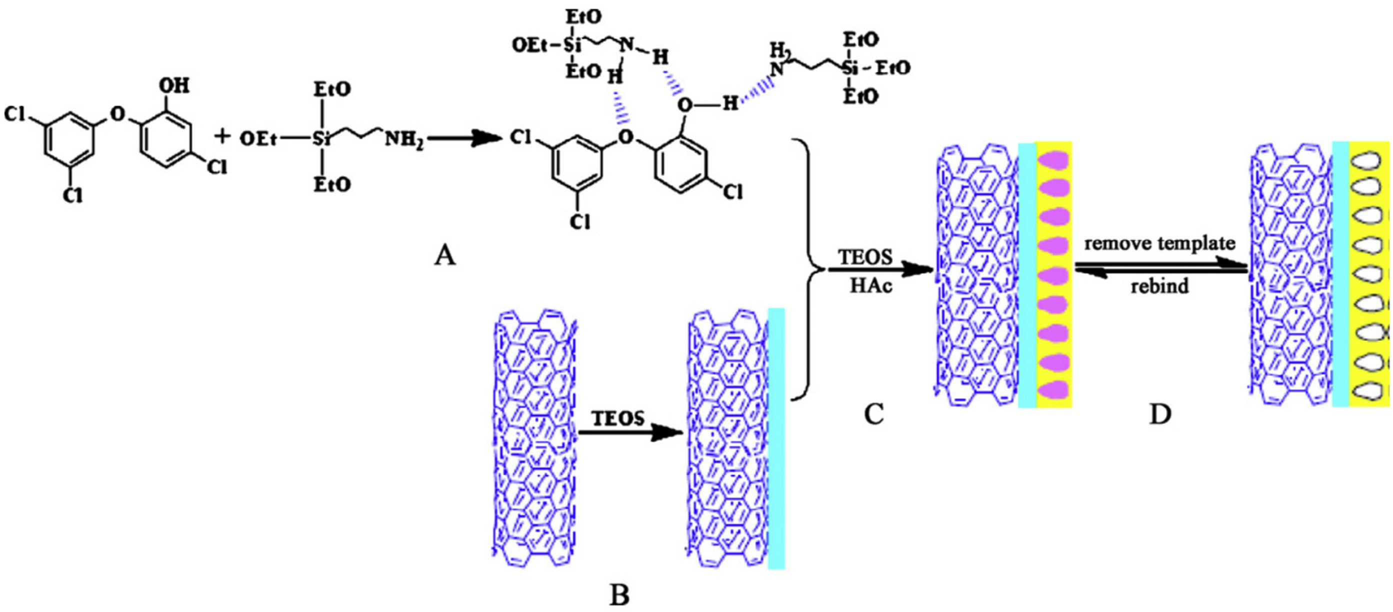

Fig. 2. The route of synthesis for CNTs@TCS-MIPs: (A) formation of template (TCS)-aminosilica monomer (APTES) complex; (B) transformation of the surface of purified CNTs to silica shell by a sol–gel process using TEOS and APTES in the presence of CTAB to obtain core@shell CNTs@SiO2; (C) reaction of CNTs@SiO2 with template-silica monomer complex to produce silica-surface functionalized with TCS-imprinted polymer; and, (D) removal of the TCS from polymer shells to obtain the CNTs@TCS-MIPs. (Reprinted with permission from [97]. © 2011 Elsevier).

CNTs@TCS-MIPs were used as the sorbents of dMISPE for the extraction of TCS in river-water and lake-water samples prior to HPLC. This method combined the merits of surface molecular imprinting and CNTs. The polymers showed fast kinetics, high capacity and favorable selectivity.

3.1.1.2. On-line molecularly-imprinted solid-phase extraction. In this format, a small SPE column packed with MIPs is usually placed in a six-port valve loop of HPLC. After the sample loading and washing out interfering compounds (the analytes are preconcentrated by the MISPE column), the analytes are eluted by the HPLC mobile phase [98–104]. These research works mainly focused on the analytes of Sudan dyes [98], Para Red [99], riboflavin [100], fluoroquinolone antimicrobials [101], tetracycline antibiotic residues [102], triazine residues [103] and estrogens [104] in samples from the environment (e.g., water and soil) and food (e.g., tomato sauce, chili sauce, egg, and milk).

Guo et al. [105] synthesized chlorsulfuron-MIPs by using vinylimidazolium ionic liquid as functional monomer. MIPs were also used as the on-line SPE-HPLC sorbents for the determination of chlorsulfuron in samples of reservoir water, pond water, detergent and tap water. The low limit of detection (LOD) and high recoveries showed that novel MIPs sorbents were excellent SPSs for the extraction of chlorsulfuron.

Like off-line MISPE, there are also some applications of MWCNTs-MIPs in the on-line MISPE mode. For example, MWCNTs-MIPs on-line SPE was developed for the determination of trace Sudan IV in chili-powder samples [106].

3.1.1.3. In-line molecularly-imprinted solid-phase extraction. Extraction, enrichment, separation and determination of target analytes can be achieved in one single step by the direct coupling of a MIP column in-line with the detection system, thanks to the high selectivity provided by MIPs. Also, the column of in-line MISPE is usually called an MI-monolithic column.

The first in-line MISPE was described by Sellergren for the determination of pentamidine in urine [107]. And the first evaluation of MIPs as in-line concentrator in CE was reported by Lara et al. [108].

Zhang et al. [109] demonstrated a novel light-emitting diode-induced polymerization technology that could be applied as an in-column MISPE concentrator in CE. The constructed concentrator exhibited good selectivity, high extraction efficiency, and little sacrifice of CE separation efficiency for the analytes, epitestosterone, methyltestosterone, and testosterone acetate.

Zheng et al. [110] reviewed the developments and the applications of the MI-monolithic column for HPLC and CE. The combination of monolithic column and MIPs integrated the high separation efficiency of modern chromatography and the high selectivity of MIPs.

Canale et al. [82] packed BPA-MIPs into monolithic column and installed it on an HPLC unit for the determination of BPA in real-world water samples. The monolithic column exhibited good selectivity and concentration capability in the analysis of BPA in water samples.

3.1.2. Solid-phase microextraction, matrix solid-phase dispersion and stir-bar sorptive extraction

Because MIPs present several advantages in terms of mechanical robustness, resistance to elevated temperatures and pressures, inertness to extreme pHs, easier and cheaper preparations, especially for their high selectivity for the target analytes, MIP materials are now becoming very popular in SPME, MSPD and SBSE methods. The combination of molecular imprinting and these three extraction methods would therefore ideally provide powerful analytical tools with the characteristics of simplicity, flexibility, and selectivity. The principles of the three extraction methods have been described in detail [59], and here we do not describe them again.

Table 2 summarizes some new applications of MIPs as SPSs in the three extraction methods. For SPME, the MIPs are usually coated on a fiber segment, and then the fiber is inserted into the SPME device for the extraction [111–126]. Sometimes, nanomaterials can

Table 2
Selected applications of molecularly-imprinted polymers (MIPs) as solid-phase sorbents (SPSs) in solid-phase microextraction (SPME), matrix solid-phase dispersion (MSPD) and stir-bar sorptive extraction (SBSE)

Template	Analyte	Matrix	Application methods	Analytical technique	LOD (ng/mL)	Ref.
17β-estradiol	Estrogens	Fish and shrimp tissue samples	SPME	HPLC-UV	0.98–2.39	[111]
Chlorogenic acid	Chlorogenic acid	Echinacea purpurea	SPME	HPLC-UV	0.08	[112]
Caffeine	Caffeine	Human serum	SPME	GC-MS	0.1	[113]
Ametryn	Triazines	Onion, maize and rice seeds	SPME	GC-FID	9–85	[114]
Sudan I	Sudan I–IV dyes	Hot chili powder and poultry feed	SPME	HPLC-UV	2.5–4.6[a]	[115]
Ephedrine	Ephedrine and pseudoephedrine	Human urine and serum	SPME (monolithic column)	CE-UV	0.96–200	[116]
Prometryn	Triazines	River water, wastewater and liquid milk	SPME	HPLC-UV	0.08–0.38	[117]
Testosterone	Anabolic steroids	Water and urine samples	SPME	GC-MS	0.008–0.020	[118]
17β-estradiol	EDCs	River water	SPME	GC-MS	0.0013–0.022	[119]
Thiamphenicol	Thiamphenicol	Milk and honey	SPME	HPLC-UV	3, 2[a]	[120]
Thiabendazole	Thiabendazole	Orange juice	SPME	HPLC-FLD	4	[121]
Ciprofloxacin	Fluoroquinolone antibiotics	Water	SPME	HPLC-MS/MS	0.0008–0.0081	[122]
α,α'-Azobis(isobutyronitrile)	Quinolones	Serum	MSPD	HPLC-UV	40–90[a]	[123]
Atrazine	Triazines	Soil, fruit and vegetable	MSPD	CE-UV	12.9–31.5[a]	[124]
Terbuthylazine	Triazines	Rice, apple, lettuce and soil	SBSE	HPLC-UV	0.04–0.12	[125]
Triadimefon	Triazole fungicides	Soil	SBSE	HPLC-UV	0.14–0.34	[126]

GC-ECD, Gas chromatography-electron capture detector; GC-FID, Gas chromatography-flame ionization detector; HPLC-FLD, High-performance liquid chromatography-fluorescence detector.

[a] ng/g.

be combined with MIPs in order to modify the extraction efficiency {e.g., CNTs [112,117]}.

Golsefidi et al. [112] reported that MWCNTs were added into the MIP solutions gradually to form a dispersed mixture. After that, 12 µL of the dispersed mixture was injected into a 2.5-cm long polypropylene hollow-fiber segment. Then, the MWCNTs-MIPs fiber was submerged in the sample solution and completed the extraction process [112].

Different from that, prometryn MWCNTs-MIPs were prepared by copolymerization of MAA and TRIM in the presence of prometryn on the surface of modified-MWCNTs [117]. This means the MWCNTs were used as support materials of MIPs. Then the MWCNTs-MIPs were introduced on a segment of polypropylene. After heat-sealing the two ends of the fiber, it was clamped onto a paper clip for microextraction [117].

Moreover, some metallic materials are used as support materials for MIPs. For example, an SPME fiber was fabricated through ultraviolet irradiation polymerization of ametryn-MIPs on the surface of anodized-silylated aluminum wire [114]. In order to investigate the extraction mechanism, four fibers were used for comparison, including cleaned aluminum wire, anodized aluminum wire, anodized and silylated aluminum wire, and anodized and silylated aluminum wire coated with a MIP layer. The chromatograms of extracted ametryn (Fig. 3) revealed that the extraction ability of the anodized-silylated aluminum-wire fiber was definitely higher than that of the other fibers.

Besides the SPME fiber, MIPs can be prepared by an *in-situ* polymerization method to form a MIP micro-monolithic column [116]. The polymerization mixture, consisting of template, functional monomer, cross-linker and initiator, was filled into a 30 cm × 530 µm capillary. The two ends of capillary were sealed with rubbers, then the capillary was placed in a water bath at 60°C to react for 24 h. After polymerization, the capillary was cut into 5-cm pieces. Then 1-cm silica wall at one end of the capillary was broken and peeled off mechanically with a blade. The cut portion of 1-cm MIP fiber was used for SPME. Finally, the capillary pieces were immersed in a solution to remove the template compound. Fig. 4 shows the whole implementation process of the micro-monolithic column. The fabricated MIP monolithic column can be immersed in the sample solution for microextraction. And, after solution desorption, the analytes can be determined by CE.

3.2. *Carbon nanomaterials as solid-phase sorbents*

Because of their large adsorption surface area-to-volume ratios and high affinity, good physical and chemical stability, and low cost, carbon nanomaterials are increasingly popular as SPSs in sample preparation prior to chromatography. CNTs and G/GO are the most widely used SPSs in extraction methods, including SPE, SPME, MSPD and SBSE. Table 3 summarizes recent popular applications of carbon nanomaterials used as SPSs in sample preparation prior to chromatography [23,25,31,127–173].

3.2.1. *Carbon nanotubes*

As seen from Table 3, MWCNTs, magnetic MWCNTs, functionalized MWCNTs and SWCNTs are used as the sorbents for SPE, SPME and MSPD. CNTs in sample preparation have been reviewed in detail by Zhang et al. [32]. Using magnetic MWCNTs as SPE sorbents can avoid tedious steps, such as centrifugation and filtration [135–138]. And self-assembled poly(diallyldimethylammonium chloride) (PDDA)-functionalized MWCNTs were used as anion-exchange sorbents for extraction of acidic degradation products of nerve agents [139].

By comparison with commercial strong anion-exchange and MAX, PDDA-MWCNTs presented superior recoveries, which may be attributed to the combined effects of the high charge density of the polyelectrolyte plus the highly hydrophobic CNT surface. Because at neutral pH, analytes exist as anions, they are expected to be retained on the cationic surface of PDDA-MWCNT composite *via* primary electrostatic interactions. However, secondary hydrophobic interactions between alkyl groups of analytes and the CNT surface also facilitate their retention. This means that there were two interactions between the analytes and the PDDA-MWCNT materials, so high charge density of polyelectrolyte plus the highly hydrophobic CNT surface may lead to high extraction recovery [139].

For dSPE and µSPE technologies, MWCNTs can be an excellent material for a quick, easy, cheap, effective, rugged and safe (QuEChERS) method. Zhao et al. [131] used MWCNTs as a reverse

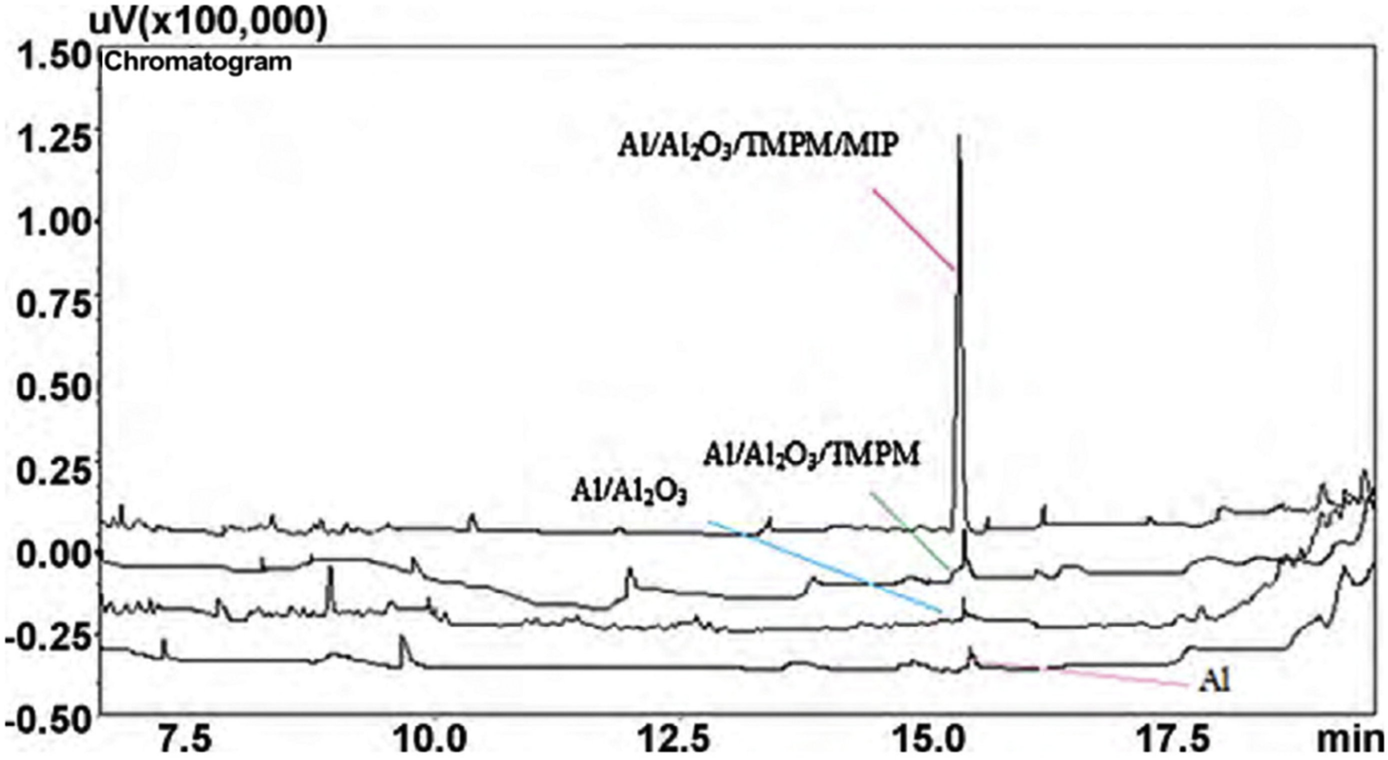

Fig. 3. Chromatography results of SPME procedure by different fibers. (Reprinted with permission from Ref [114]. © 2010 Elsevier).

dSPE material combining with GC-MS for the determination of 14 pesticides in leek, onion, ginger and garlic samples. The recoveries of the target analytes in the complex matrices at two concentration levels (0.02 mg/kg and 0.2 mg/kg) were 78–110%. The LODs for the analytes were 1–6 µg/kg. In the µSPE device, MWCNTs were employed as sorbents and were packed inside a porous polypropylene membrane “envelope”, whose edges were heat-sealed to secure the contents. The µSPE device was placed in a stirred sample solution to extract the analytes [134]. Wu et al. [134] used two micropipette tips to make an MWCNT-packed micro-column, followed by flow-injection SPE. Good linearity, reproducibility and LOD were obtained.

Although CNTs enjoy excellent properties, due to their rigidity, chemical inertness and self-aggregation with strong van der Waals forces, they are difficult to dissolve or to disperse in common organic solvents or polymeric matrices, which makes CNTs unsuitable as SPSs of SPME. Great efforts have been made to functionalize CNTs to improve their solubility. Sarafraz-Yazdi’s group has investigated poly(ethylene glycol) (PEG)-grafted MWCNTs as sorbents of SPME [140–143]. The –COOH-functionalized group-grafted MWCNTs enhanced their dispersion and compatibility [144,145].

Self-assembly amino-functionalized MWCNTs (MWCNTs-NH_2) were anchored to the stainless-steel wire as SPSs for the SPME of phenols compounds by Feng et al. [146]. Results showed that the

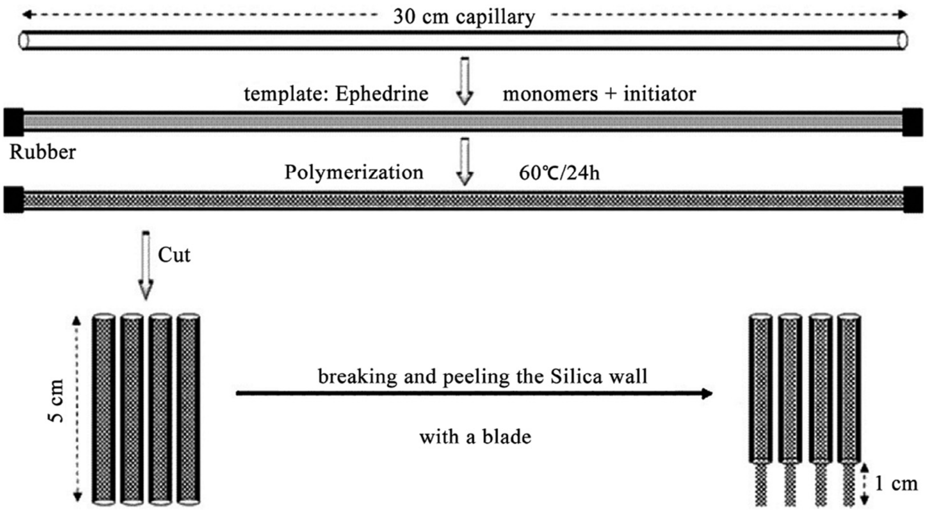

Fig. 4. MIP micro-monolithic column-preparation procedure. (Reprinted with permission from [116]. © 2010 Elsevier).

Table 3
Selected applications of carbon nanomaterials as solid-phase sorbents (SPSs) in in solid-phase microextraction (SPME), matrix solid-phase dispersion (MSPD) and stir-bar sorptive extraction (SBSE)

Carbon nanomaterials	Analyte	Matrix	Application methods	Analytical technique	LOD (ng/mL)	Ref.
MWCNTs	BPA etc.	Tap, river, waste water	SPE	HPLC-FLD	0.018–0.083	[31]
	Metsulfuron methyl and chlorsulfuron	Lake, creek, reservoir and underground water	SPE	CE-UV	0.40, 0.36	[127]
	Marine DOM	Sea water	SPE	SEC-UV	–	[128]
	16 PAHs	Tap, river, sea water	SPE	GC-MS	0.002–0.0085	[129]
	Organophosphorus pesticides	Peanut oil	dSPE	GC-MS	0.7–1.6[a]	[130]
	14 pesticides	leek, onion, ginger and garlic	dSPE	GC-MS	2–20[a]	[131]
	Quinolone antibiotics	Mineral, tap, waste water	dSPE	CE-UV	0.028–0.094	[132]
	16 PAHs	River water	µSPE	GC-MS	0.0042–0.0465	[133]
	16 PAHs	River water	µcolumn SPE	GC-MS	0.001–0.15	[134]
Magnetic MWCNTs	BPA and BPF	Tap, river, snow water	MSPE	GC-MS/MS	0.001–0.06	[135]
	Phthalate acid esters	Beverage and perfume	MSPE	GC-MS	0.0049–0.038	[136]
	Estrogens	Tap, mineral, Pearl River water and honey	MSPE	CE-UV	0.1–0.2	[137]
	Aconitines	Human serum	MSPE	HPLC-UV	3.1–4.1	[138]
PDDA grafted MWCNTs	Degradation products of nerve agents	Water	SPE	GC-MS	0.11–0.25	[139]
PEG grafted MWCNTs	BTEX	Tap, mineral, waste and well water	SPME	GC-FID	0.0006–0.003	[140]
	PAHs	Saffron	SPME	GC-FID	0.001–0.05	[141]
	Furan	Apple and orange juice, banana/wheat/milk and fruit/wheat/milk	SPME	GC-FID	0.00025, 0.001	[142]
	Non-steroidal anti-inflammatory drugs	Tap, river, waste and well water	SPME	GC-FID	0.007–0.03	[143]
-COOH grafted MWCNTs	Phenobarbital	Clinical wastewater	SPME	HPLC-UV	0.32	[144]
MWCNTs bonded on Au wires	Diazinon and fenthion	Ground, surface, lagoons and drinking water	SPME	GC-FID	0.2, 0.3	[145]
MWCNTs bonded on stainless steel wire	Phenols compounds	River water	SPME	GC-FID	0.01–0.02	[146]
SWCNTs	EDCs	Tap and sea water	On-line SPME	HPLC-UV	0.32–0.52	[147]
MWCNTs	Hormones	Butter	MSPD	GC-MS	0.2–1.3[a]	[148]
	9 Organophosphorus Pesticides	Fruit and vegetables	MSPD	LC-MS-MS	0.06–0.15[a]	[149]
G	Chlorophenols	Tap and river water	SPE	HPLC-UV	0.1–0.4	[151]
	Neurotransmitters	Rat brain	SPE	HPLC-FLD	23.4–67.5[a]	[152]
G-Fe_3O_4 MNPs	Triazine herbicides	Reservoir, lake and river water	MSPE	HPLC-UV	0.025–0.040	[153]
	Neonicotinoid insecticides	Reservoir, sea and river water	MSPE	HPLC-UV	0.004–0.01	[154]
	Phthalate esters	Bottled and river, Cola and green tea	MSPE	HPLC-UV	0.01–0.04	[155]
	Carbamate pesticides	River, pool and reservoir water	MSPE	HPLC-UV	0.02–0.04	[156]
	PAHs	Soil	µSPE	GC-MS	0.0017–0.0057[a]	[157]
	PAHs	River water	µSPE	GC-MS	0.0008–0.0039	[158]
G	Carbamates	Sea, lake and tap water	SPME	HPLC-UV	0.1–0.8	[159]
	Polybrominated diphenyl ethers	Canal water	SPME	GC-MS	0.0002–0.0053	[160]
	Triazine herbicides	Tap, sea and lake water	SPME	HPLC-UV	0.05–0.2	[161]
	Organochlorine pesticides	River water	SPME	GC-ECD	0.00016–0.00093	[162]
	Pyrethroid pesticides	Pond water	SPME	GC-ECD	0.00369–0.00694	[163]
	PAHs	River and pond water	SPME	GC-MS	0.00152–0.00272	[25]
	Phenols	Pond water	SPME	GC-FID	0.34–3.4	[164]
GO	PAHs	River water	SPME	GC-FID	0.005–0.08	[165]
G	16 PAHs	Tap and lake water	SBSE	GC-MS	0.005–0.429	[166]
	Polybrominated diphenyl ethers	Soil and fishes	MSPD	GC-ECD	0.0053–0.2126[a]	[167]
Nanohorns	PAHs	River, tap and bottled water	µSPE	GC-MS/MS	0.03–0.06	[168]
Nanohorns	Triazines	River, tap and bottled water	µSPE	GC-MS	0.015–0.1	[169]
Nanocones/disks	Chlorophenols	Drinking, swimming pool, water-tank and well water	SPE	GC-MS	0.3–8	[23]
Nanocones/disks	Toluene etc.	Drinking, well and river water	SPME	GC-MS	0.15–2	[170]
Nanofiber	Chlorotriazines and dealkylated metabolites	Ground, creek, tap water and soil	µSPE	HPLC-UV	0.004–0.03	[171]
Nanofiber	Aromatic amines	Wastewaters	µSPE	HPLC-UV	0.009–0.081	[172]
Nanofiber	Benzene etc.		SPME	GC-FID	0.01–0.08	[173]

BPA, Bisphenol A; BPF, Bisphenol F; BTEX, Benzene, toluene, ethyl benzene, and the xylene isomers (p, m, and o-xylenes); DOM, Dissolved organic matter; dSPE, Dispersive solid-phase extraction; EDC, Endocrine-disrupting chemical; G, Graphene; GC-ECD, Gas chromatography-electron capture detector; GC-FID, Gas chromatography-flame ionization detector; GO, grapheme oxide; G-Fe_3O_4 MNPs, graphene-based Fe_3O_4 magnetic nanoparticles; HPLC-FLD, high performance liquid chromatography-fluorescence detector; MSPE, Magnetic solid-phase extraction; PDDA, Poly(diallyldimethylammonium chloride); PEG, Poly(ethylene) glycol; SEC, Size-exclusion chromatography; µSPE, Micro-solid-phase extraction.

[a] ng/g.

fabricated MWCNT fiber had higher extraction efficiency than the commercially available fibers.

SWCNTs can also exhibit good extraction efficiency. For example, SWCNT fibers for SPME were prepared using the electrophoretic deposition method [147]. The fibers were immersed into sample solutions for extraction of endocrine-disrupting chemicals (EDCs). After that, the fiber was inserted into the desorption chamber of the interface. The desorbed analytes were delivered into the HPLC column by the mobile phase when the valve was switched from the load to the injection position.

Table 3 lists the applications of MWCNTs-MSPD [148,149]. For MSPD and SBSE, there are a few research works about CNTs as SPSs and further explorations are essential in future sample-preparation development.

3.2.2. *Graphene, graphene oxide and other carbon nanomaterials*

Sitko et al. reviewed the adsorptive properties of G and GO and their applications in preconcentrating organic compounds and trace-metal ions by SPE, SPME and magnetic SPE methods, including trace analysis of water, food, biological and environmental samples using chromatography and spectroscopy techniques [150]. Table 3 summarizes G/GO as SPSs used in SPE, SPME, MSPD and SBSE [25,151–167].

Like CNTs, there are also a lot of research works about G [151,152,159–162,166,167] and magnetic G [146–149] grafted onto the stainless steel fiber [162,163], functional G {e.g., polypyrrole/graphene composite-coated fiber [164]} and GO [165] used for SPSs. Usually, G-NPs are derived from deoxidized GO-NPs. For example, Zhang et al. prepared a G-coated SPME fiber following deoxidization of GO-NPs [25]. The whole fabrication included five processes (Fig. 5). The surface of the SiO_2 substrate was first modified by the amino group according to silanization reaction, and was then inserted into the GO dispersion solution to complete the GO modification. Finally, the fiber was deoxidized to give the G-coated SPME fiber. The fabricated G-coated fiber was exposed to the headspace above water solutions for extraction of polycyclic aromatic hydrocarbons (PAHs) followed by GC-MS determination. Under the optimized extraction and determination conditions, the LODs of eight PAHs were 1.52–2.72 ng/L and recoveries were 72.7–101.7% for samples of river water, pond water and soil.

Table 3 also lists the applications of other carbon nanomaterials, such as nanohorns, nanocones, nanodisks and nanofibers, as SPSs [23,168–173]. All the nanomaterials exhibited excellent extraction efficiencies in SPE, SPME, MSPD and SBSE.

3.3. *Metallic nanoparticles as solid-phase sorbents*

3.3.1. *Fe_3O_4 magnetic nanoparticles*

As mentioned above, MNPs are particularly useful for extracting and enriching a large volume of target analytes because they provide a large surface area-to-volume ratio, easy surface modification and strong magnetism. The MNPs can therefore be quickly isolated from matrix solutions using an external magnet after extraction and have excellent extraction efficiencies. Conventional SPE needs the sorbent to be packed into the column and time-consuming loading of large-volume samples, while the magnetic extraction method is not only convenient, economical and highly efficient, but also overcomes the above problems. However, pure iron-oxide NPs can easily form large aggregates, which may alter their magnetic properties. Moreover, these nm-sized metal oxides are not target selective and are unsuitable SPSs for samples with complicated matrices. A suitable coating is therefore essential to overcome such limitations. Chen et al. [174] reviewed the applications of magnetic materials, combined with other materials (e.g., silica, C_{18}, polymers and surfactants), for the separation and the preconcentration of pollutants in water samples.

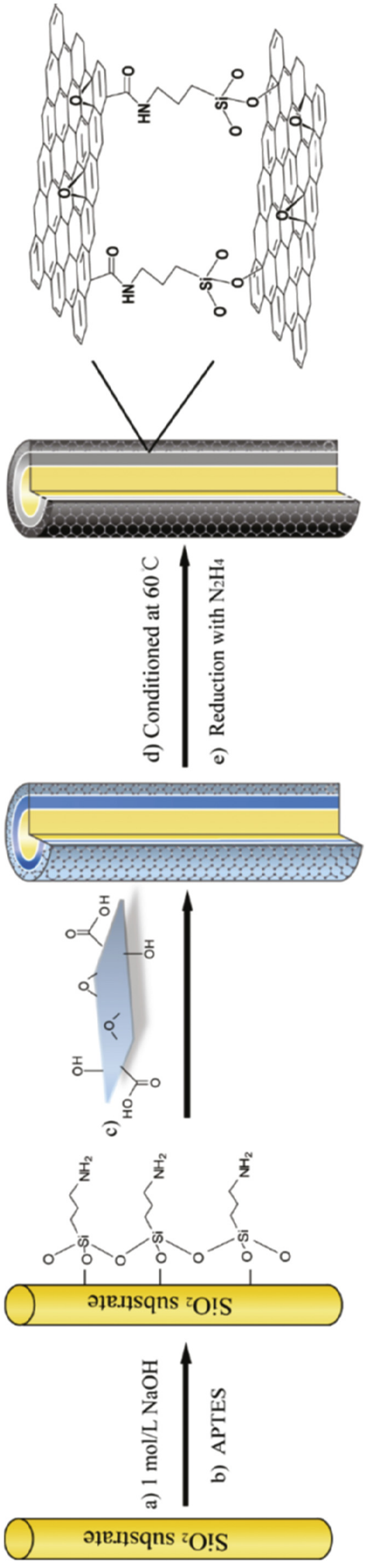

Fig. 5. The processes for fabricating G-coated SPME fiber. (a) The silica fiber was cut into small pieces and then treated to expose the maximum number of silanol groups. (b) The fiber was immersed into the APTES solution for 12 h at room temperature, then pulled out and immediately placed into an oven at 70°C to complete the silanization reaction. (c) The silylated fiber was inserted into aqueous GO dispersion for 2 h in a 70°C water bath. Then, it was taken out and dried in air to give a thin layer of GO coating. (d) The GO-coated fiber was conditioned in the GC injector under nitrogen at 60°C for 2 h (e) The GO-coated fiber was deoxidized in the mixture of distilled water (10 mL), hydrazine solution and ammonia solution at 70°C for 18 h to give the G-coated SPME fiber. (Reprinted with permission from [25]. © 2011 American Chemical Society).

In recent years, there were also some novel applications of Fe_3O_4-NPs functionalized with:

- Al_2O_3 for the extraction of alendronate in human urine samples [175] and glyphosate and aminomethylphosphonic acid in water and guava-fruit extract [176];
- carbon for the extraction of BPA and PAHs in water samples [177,178]; and,
- C_{18} for the extraction of PAHs and phthalate esters in water samples [179] and lidocaine in rat plasma samples [180].

In addition, the Fe_3O_4/SiO_2 core was functionalized with C_{18} for the extraction of PAHs [181] in water solutions, with polymerization (MAA-*co*-vinylbenzyl chloride-*co*-DVB) and poly (MAA-*co*-EGDMA) for the extraction of amphetamines in urine samples and benzimidazole residues in animal tissue [182,183]. Some other polymers, such as polyaniline [184], polydopamine [185] and polypyrrole [185,186], are used commonly. Also, surfactants, such as trimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) [187,188], are functionalized on the surface of the MNPs.

Recently, some novel materials grafted onto MNPs were reported. For example, an ion liquid, 1-hexadecyl-3-methylimidazolium bromide (C_{16}mimBr)-coated Fe_3O_4-MNPs as an adsorbent of mixed hemi micelles SPE, was investigated for the preconcentration of two chlorophenols (CPs) in environmental water samples prior to HPLC-UV [189]. The LODs of the analytes were 0.12 μg/L and 0.13 μg/L, respectively. Recoveries at three concentrations were 74–90%.

A sorbent based on the aptamer for ochratoxin A was immobilized onto MNPs and used to develop a magnetic SPE of ochratoxin A in food samples in conjunction with HPLC separation and fluorescence detection [190]. The highly selective sorbents showed excellent extraction efficiency.

Long et al. [191] modified triphenylamine on the surface of MNPs as a new sorbent for the extraction of PAHs in water samples. This method enabled selective, sensitive analysis of PAHs in complex environmental water at low LODs of 0.04–3.75 ng/L, and high recoveries of 80.21–108.33%.

For the selective extraction of PAHs from water and milk samples, biocompatible phosphatidylcholine bilayer and diphenyl were also coated on the MNPs and good results were obtained [192,193].

3.3.2. *Other metallic nanoparticles*

Among the metallic Fe_3O_4, TiO_2, Al_2O_3, ZrO_2, MnO and CeO_2 nanomaterials modified with functional coatings as SPSs [40–47], TiO_2 nanomaterials are also commonly used. As a new TiO_2 nanomaterial, TiO_2 nanotubes (NTs) have often been used as the photo catalyst for photo degradation. However, it should have much higher adsorption capacity and much greater potential for the trapping of compounds because it has a larger surface area [194]. For example, organophosphorus pesticides in water samples [194], benzoyl-urea insecticides [195] and polychlorinated biphenyls [196] in environmental water samples were extracted by SPE using TiO_2-NTs as SPSs. In μSPE, TiO_2-NTs were used to extract pyrethroid pesticides [46] and organochlorine pesticides [47] in water samples.

Some novel functionalized NTs were also reported. Zhou et al. [197] described a new method for rapid, sensitive determination of paraquat and diquat by SPE with an N-doped TiO_2-NT cartridge prior to CE. Under optimal conditions, the LODs were 1.95 mg/L and 2.59 mg/L for paraquat and diquat, respectively. The developed method was successfully applied to the analysis of paraquat and diquat in several environmental water samples.

Wang et al. [198] investigated Zr-doped TiO_2-NTs as SPSs for the enrichment of BPA in water samples. Under optimal conditions, an excellent linear range of 1–80 mg/L and an LOD of 0.016 mg/L were obtained. Four different real water samples were used for validation, and the spiked recoveries were satisfactory in the range 102.9–108.8%.

Like TiO_2-NT, TiO_2 wire was also introduced for SPSs. A novel SPME fiber was fabricated through the anodization of Ti-wire substrates in an electrolyte containing ethylene glycol and NH_4F [45]. The SPME fiber coupled with GC was then used to extract PAHs from real water samples, exhibiting high selectivity for PAHs.

Pan et al. [199] used the adsorbent of Ti wire, on which TiO_2-NTs were first formed by anodization and then AuNPs and *n*-octadecanethiol were modified, for the extraction of PAHs in water samples.

3.4. *Metal-organic frameworks as solid-phase sorbents*

As mentioned above, MOFs are inorganic-organic solids that form porous crystalline structures and can be synthesized by using a wide range of metal ions and organic ligands [200]. Because of their unique properties, MOFs were increasingly used recently as SPSs.

Yan's group has widely explored the analytical applications of MOF materials, ranging from sample collection to chromatographic separation [201–205]. MOFs used as chromatographic solid phases were also investigated [206–208] {e.g., a tubular MOF, MOF-CJ3, was chosen as stationary phase to prepare a capillary GC column via a verified dynamic coating procedure. The column offered good separations of linear and branched alkanes, as well as aromatic positional isomers [206]}.

Some MOFs with modification are also used in chromatography separation. For example, a bipyridinium ligand with a charge separated skeleton was introduced into a MOF to yield a porous material with charge-polarized pore space, which exhibited selective adsorption for polar guest molecules and could be further used in GC for the separation of alcohol–water mixtures [207].

Yu et al. have reviewed some applications of MOFs as stationary phases in chromatography [209]. For sample preparation, Ouyang's group has reviewed MOFs as SPSs (e.g., for SPE and SPME) [210,211]. Yang et al. prepared and evaluated MOFs and used them as new SPE materials for the determination of PAHs in environmental waters, coupling with HPLC [212]. Under the optimized experimental conditions, good sensitivity levels were achieved with low LODs in the range 0.4–4.0 ng/L and a linearity 0.004–20 μg/L ($R^2 > 0.996$).

Since most of the biological and environmental samples contain water, water-stable MOFs are very popular in biological chemistry. For example, MOF MIL-101 was fabricated in a polyetheretherketone (PEEK) tube as micro-trapping device, and applied to sorptive extraction of naproxen and its metabolite in urine samples [213]. MIL-101 exhibited higher extraction capacity for naproxen than C_{18}-bonded silica and MWCNTs. The method proved to be highly sensitive with the linear range of 0.05–6.0 μg/L and LODs of 0.034 μg/L and 0.011 μg/L for naproxen and 6-O-desmethylnaproxen, respectively.

Novel PDMS/MOFs coated stir bars were prepared by sol–gel technique [214]. The PDMS/MOF coating for SBSE coupled with the HPLC-UV method was developed for the determination of seven target estrogens in environmental waters. Under optimal experimental conditions, the LODs (S/N = 3) were found to be in the range 0.15–0.35 μg/L.

4. Conclusions and perspectives

This review of SPSs for sample preparation prior to chromatography includes an enormous variety of materials (e.g., MIPs, carbon nanomaterials, metallic NPs and MOFs). Undoubtedly, the use of SPSs in sample-preparation methods, such as SPE, SPME, MSPD and SBSE, has become a hot topic in analysis. In sample preparation, all SPSs

Table 4
General advantages and disadvantages of various solid-phase sorbents (SPSs)

SPSs	Advantages	Disadvantages
MIPs	Large specific surface area, low cost, easy synthesis, high stability to harsh chemical, physical conditions, excellent reusability, selective adsorbents for target analytes.	Hard to imprinting water-soluble biological macromolecules and hydrophilic compound, heterogeneous binding sites which have a bad effect on binding, incompatibility with aqueous media, leakage of template molecules.
Carbon nanomaterials	Large adsorption surface-to-volume ratios, high affinity, Easily modified with functional groups and easily covalently or non-covalently functionalized.	Cause high pressure in the SPE column, easily escape from the SPE column.
Metallic nanoparticles	Large specific surface area, high adsorption capacity, low temperature modification, quickly isolated from matrix solutions by using an external magnet, economical and highly efficient, excellent reusability.	Less selectivity, MNPs with functional groups on the surface tend to aggregate in water solution, unsuitable for samples with complicated matrices.
MOFs	Large surface areas, excellent adsorption capability for gaseous molecules, easily embedded into organic polymers which was good for SPME.	Moisture sensitive (extraction efficiency decreases significantly when applied to adsorption in aqueous matrix), microporous (the small size of their cavities restricts the choice of incorporated species and thus induces low diffusion rates).

have their own advantages and disadvantages, as outlined in Table 4. The common property of all the SPSs is their large specific surface area, which makes them very suitable as SPSs. However, every material has its own characteristics (e.g., carbon nanomaterials may cause high pressure in the SPE column, which is not favorable for the diffusion of target analytes). Also, because of the special properties of MOFs (e.g., excellent adsorption capability for gaseous molecules, and easily being embedded into organic polymers), they are very suitable as SPSs for SPME. The investigations reported not only included exploration of new SPSs that can overcome the disadvantages mentioned above, but also included exploration of new sample-preparation methods. Three major issues associated with their preparation and applications are yet to be resolved for continuous improvement of SPSs, as follows.

First, the primary requirements of SPSs are to possess high selectivity and enrichment capability (i.e., they can specifically adsorb targeted analytes while eliminating matrix interferences and thereby assist to attain high detectability). Each of the sorbents has their own advantages (e.g., MIPs have high selectivity, physical robustness, and thermal stability, low cost and easy preparation). New techniques and methods of synthesis are increasingly being developed for new SPSs with continually improved selectivity and other features. Significantly, vigorously developing combined SPSs by coupling various materials and their characteristics can rapidly advance SPSs, demonstrating improved selectivity and adsorption ability (e.g., MIPs coated on MNPs and G/GO).

Second, the major trends in the SPSs will be towards more MSPD and SBSE applications. Because of the traditional usage of SPE and easy operation of SPME, many research works have been reported on these two extraction techniques, including improving sorbents and instruments. However, although applications of MSPD and SBSE are still in their infancy, they could become tools, routinely used in sample preparation in the near future, especially for carbon NPs used in SBSE.

Third, the developments of on/in-line mode of extraction methods and monolithic columns will be accelerated to facilitate preparing more novel SPSs. In order to satisfy the general objectives of sample preparation, such as smaller sample amounts, reduction or elimination of organic solvents, integration of several preparation steps into one (e.g., applications of passive samplers for simultaneous sampling, extraction and enrichment of analytes from complicated matrices), and potential for automation, on/in-line mode of extraction methods and monolithic column are popular. We therefore strongly encourage new explorations of SPS-based monolithic column and extraction methods, and thereby push forward sample preparation.

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