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Review

Sorptive extraction techniques in sample preparation for organophosphorus pesticides in complex matrices☆

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ABSTRACT

Organophosphorus pesticides (OPPs), widely known as persistent organic pollutants, are the most popular contaminants in agriculture products in developing countries. The determination of OPPs in complex matrices, such as food, environmental and biological samples, usually requires extensive sample pretreatment. This review focuses on the sorptive extraction techniques applied as sample pretreatment for OPPs in complex matrices, including solid-phase extraction (SPE) and solid-phase microextraction (SPME). These methods are evaluated and the applications of each technique are demonstrated extensively with many practical examples.

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Contents

1. Introduction

Organophosphorus pesticides (OPPs) are widely used in agriculture by virtue of their biodegradable nature and short persistence. The use of OPPs can provide benefits for increasing agricultural production. The improper use of OPPs, however, may also result in the presence of their residues in agricultural products and thus eventually in animals and humans [1]. Moreover, OPPs are mostly sprayed over crops or applied to soils, leading to the direct transfer of OPPs from drainage of agricultural lands to other parts of surrounding environments, including ground and surface waters [2]. Therefore, there is an increasing concern with regard to the determination of these compounds. Up to now, OPPs analysis has been performed by the use of gas chromatography (GC) [3–5], high-performance liquid chromatography (HPLC) [6,7], capillary electrophoresis (CE) [8], biosensors [9–12] and many other methods [13,14]. However, due to the low OPP concentrations, the low maximum residue limits (MRLs), and the complexity of matrices, real samples cannot be directly analyzed without sample preparation. Since OPPs are usually present in complex matrices, such as food, environmental and biological samples, it is crucial to develop sensitive, selective, rapid and cost-effective analytical methods or devices for their determinations.

Sampling and sample pretreatment usually account for over 60% of the total analysis time, and the quality of these steps largely determines the success of an analysis from complex matrices. Ide-

Abbreviations: CE, capillary electrophoresis; CNTs, carbon nanotubes; GC, gas chromatography; HPLC, high-performance liquid chromatography; LLE, liquid–liquid extraction; LODs, limits of detection; MIP, molecularly imprinted polymers; MRLs, maximum residue limits; MHSPE, SPE method based on mixed hemimicelles (hemimicelles and admicelles); MS, mass spectrometry; MWCNTs, multi-walled carbon nanotubes; NIP, non-imprinted polymers; OC, organochlorine; OPPs, organophosphorus pesticides; OSWCNTs, oxidized SWCNTs; PDMS, polydimethylsiloxane; PPESK, poly(phthalazine ether sulfone ketone); PS-DVB, polystyrene divinylbenzene; RSD, relative standard deviation; SWCNTs, single-walled carbon nanotubes; SPE, solid-phase extraction; SPME, solid-phase microextraction; SBSE, stir-bar sorptive extraction.

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ally, sample preparation should be as simple as possible, because it not only reduces the time required, but also decreases the possibility of introducing contaminants. Recently, ad/absorption based methods using beds of solid enrichment sorbents have gradually replaced conventional liquid–liquid extraction (LLE) for sample pretreatment, and has gained wide acceptance because of its simplicity and economy in terms of time and solvent needs. Sorptive extraction technique mainly includes solid-phase extraction (SPE) and solid-phase microextraction (SPME). The aim of this review is to describe and evaluate the development and application of sorptive extraction technique for OPPs in complex matrices in recent years.

2. Sorptive extraction techniques for OPPs

2.1. Solid-phase extraction

Solid-phase extraction (SPE) was first introduced in the mid-1970 [15], and became commercially available in 1978. SPE is currently one of the most widespread extraction methods for the pretreatment of environmental [16–21], food [22,23] and biological samples [24,25]. The basic principle of SPE is the transfer of analytes from an aqueous phase to the absorption sites of the adjacent solid phase. Analytes are eluted from the solid medium with appropriate organic solvents and then are determined by GC or HPLC. Compared to traditional liquid extraction techniques, SPE is simpler, more convenient, and easier to automate. In addition, SPE possesses other distinct advantages including: (1) requires a lower volume of solvent than traditional liquid–liquid extractions; (2) involves simple manipulations which are not time consuming and makes it possible for field treatment of samples; (3) the SPE cartridges can be used for short-term storage of the species; (4) provides high enhancement factors proportional to the volume of water passed through the SPE cartridge.

After more than 20 years of development, the types of SPE adsorbents increase significantly and a wide range of SPE columns are commercially available. However, the conventional sorbents such as C_{18} silica, graphitized carbon black and macroporous polystyrene divinylbenzene (PS-DVB), show low retention for polar compounds [26,27]. In order to improve the extraction efficient for polar compounds, the development of new adsorbents and modification of the adsorbents by introducing the polar groups become a major research direction.

Nanomaterials are one kind of novel adsorbents. Carbon nanotubes (CNTs), including single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), are a kind of carbonaceous nanomaterial and have received significant attention in many fields [28,29]. CNTs are of super-large specific surface area, outstanding thermal and chemical stabilities, and can be synthesized in large scale. These eminent characteristics make CNTs become attractive adsorbent materials [30]. The applications of CNTs as SPE extraction sorbents for the extraction of OPPs from real samples have been reported in lots of literatures [17,31–33]. For example, Valliyaveettil and co-workers developed a MWCNTs-supported micro-solid-phase extraction procedure and apply it to extract OPPs from sewage samples [31]. Analytes were then desorbed in hexane and analyzed using gas chromatography/mass spectrometry (GC/MS). Under the optimized extraction conditions, the method showed good linearity in the range of 0.1–50 μg/L, good repeatability of the extractions (RSD 2–8%, $n = 4$), and superior limits of detection (1–7 pg/g).

Li et al. used Oasis HLB, SWCNTs, MWCNTs and oxidized SWCNTs (OSWCNTs) as SPE sorbents to enrich six typical polar OPPs in aqueous samples [17]. The corresponding chromatogram of these OPCs in the spiked seawater is shown in Fig. 1. All six OPPs were separated in baseline, and the peak heights of methamidophos and acephate extracted with OSWCNTs were much higher than those extracted with Oasis HLB. It indicates that OSWCNTs could provide higher extraction efficiency for polar OPPs.

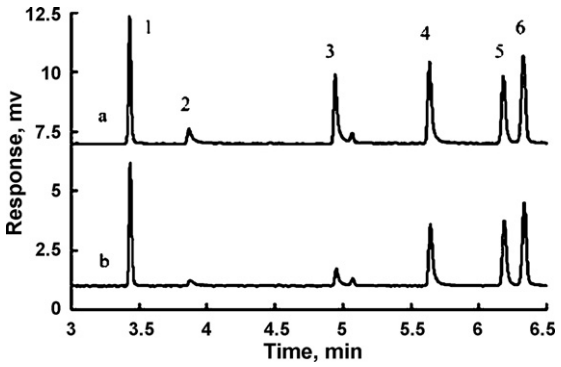

Fig. 1. Chromatograms of six OPCs (1.0 mg/L) in the spiked seawater extracted with: (a) OSWCNTs and (b) Oasis HLB (1, dichlorvos; 2, methamidophos; 3, acephate; 4, omethoate; 5, monocrotophos; 6, dimethoate).

Recently, a new SPE method based on mixed hemimicelles (hemimicelles and admicelles) (MHSPE) has been proposed for the preconcentration of a variety of organic pollutants from complex matrices [34]. Hemimicelles and admicelles are formed by the adsorption of ionic surfactants on mineral oxides, such as alumina, silica, titanium dioxide, and ferric oxyhydroxides. Hemimicelles consist of monolayer of surfactants adsorbed head down on the oppositely charged surface of the oxide, whereas admicelles have the bilayer structure with the ionic head group as the outmost surface [35]. Some specific benefits can be obtained from the use of these sorbents, such as high extraction yields, easy elution of analytes, high breakthrough volumes, and high flow rate for sample loading. One important development of MHSPE is magnetic nanomaterials entrapped SPE sorbents, which can provide high surface area, good chemical stability, and rapid magnetic separation [36–39]. The procedure of the surfactant coated Fe_3O_4/SiO_2 nanoparticle preparation and its application for enriching analytes are shown in Fig. 2 [36]. Unfortunately, this new method has rarely been applied to adsorb OPPs.

In recent years, molecular imprinting polymer (MIP) technology with high selectivity evolves rapidly. MIP technology is now well established for the preparation of tailor-made polymers with cavities those are capable to extract or clean-up of OPPs [40–45]. Their synthesis procedures are mainly based on weak non-covalent interactions (such as hydrogen bonds and/or ionic interactions) between target molecules (template) with functional monomers, followed by polymerization in the presence of cross-linker, usually in a non-polar and weakly polar solvent. Once the template is removed, selective molecular recognition sites, which often described as three-dimensional shapes within the polymer, are available for the selective rebinding of the target molecule and some structurally related compounds. Molecular recognition between receptor sites and target analytes in MIP technology is of higher specificity and better stability [46].

Tan and co-workers prepared a non-covalent MIP for the extraction of dimethoate pesticide from tea leaves [41]. Compared with non-imprinted polymers (NIP) that did not contain the template, the retention and the peak shape of dimethoate on the MIP clearly indicated the presence of the template binding sites in the imprinted polymer (Fig. 3). MIP can separate dimethoate very well from its impurity (additives in industrial grade dimethoate), whereas NIP not.

Immunoextraction technique is based upon a biomolecular recognition mechanism. The high affinity and the high selectivity

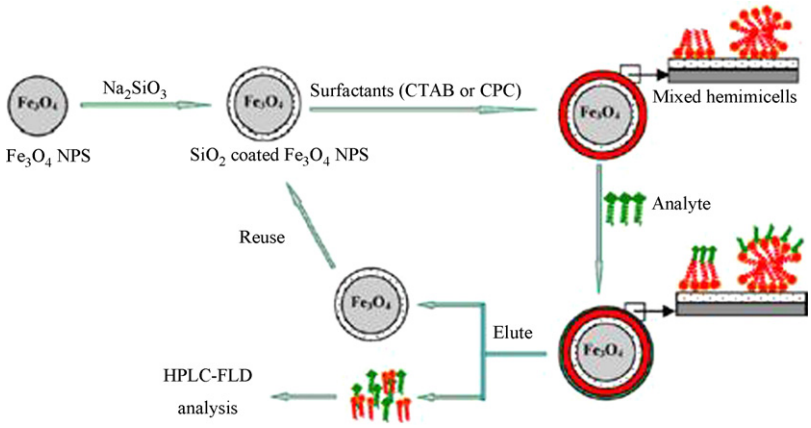

Fig. 2. Schematic illustration of the preparation of surfactants coated Fe_3O_4/SiO_2 NPs and its application for enriching analytes as SPE sorbents.

of the antigen–antibody interactions allow the specific extraction and the concentration of the analytes of interest in one step. Pesticides and their metabolites, PAHs, and biotoxins, are extracted by this technology, then separated by HPLC, and quantified by UV or fluorescence detection. However, there is no direct report about the extraction of OPPs by using this technology [47–50].

2.2. Solid-phase microextraction

Solid-phase microextraction (SPME) was first developed in 1989 by Pawliszyn and co-workers, and has been commercialized by Supelco since 1993 [51,52]. Analytes are absorbed into an absorption phase coated on a fused-silica fiber surface, and then desorbed either in an injection port of a GC by thermal desorption, or by solvent desorption for HPLC analysis. Adsorption follows the principle of equilibrium partitioning between sample molecules and absorption phase in a time-dependent manner [53]. Due to various restrictions enforced by government regulations, the solvents that can be used in sample preparation become less and less in many countries. The solvent-free characteristic of SPME technology improves greatly the working environment for operators, and minimizes the volume of discarded toxic solvents. SPME fiber can also be inserted directly into an injection port of any type of GC, saving 70% of sample preparation time. The SPME sorbents are polymeric materials, which have a gum-like, or even liquid-like state with properties similar to those of organic solvents. SPME technology can be performed in two ways: (1) direct immersion of the fiber into the aqueous sample to extract analytes dispersed in aqueous solution; (2) exposure of the fiber in the sample headspace to extract volatile targets that are partitioned between gaseous and liquid phases [54]. SPME has been applied to OPPs analysis in various matrices with high efficiency and good reproducibility [55–71].

Based on SPME, Hernández and co-workers explored the feasibility of the determination of organochlorine (OC) and OPPs in human body fluids, including serum and urine samples [60]. Their result demonstrates that SPME is a valuable tool in pesticide residue analysis of OC and OPPs in human fluids (Fig. 4). Guan and co-workers developed a new sol–gel technology for the preparation of SPME fiber, in which polydimethylsiloxane (PDMS) containing 3% vinyl group was physically incorporated into the silica sol–gel network, and then the PDMS was partly cross-linked at 320 °C, so it could withstand 290 °C desorption temperature [67]. Extraction and determination of OPPs in water, orange juice, and red wine

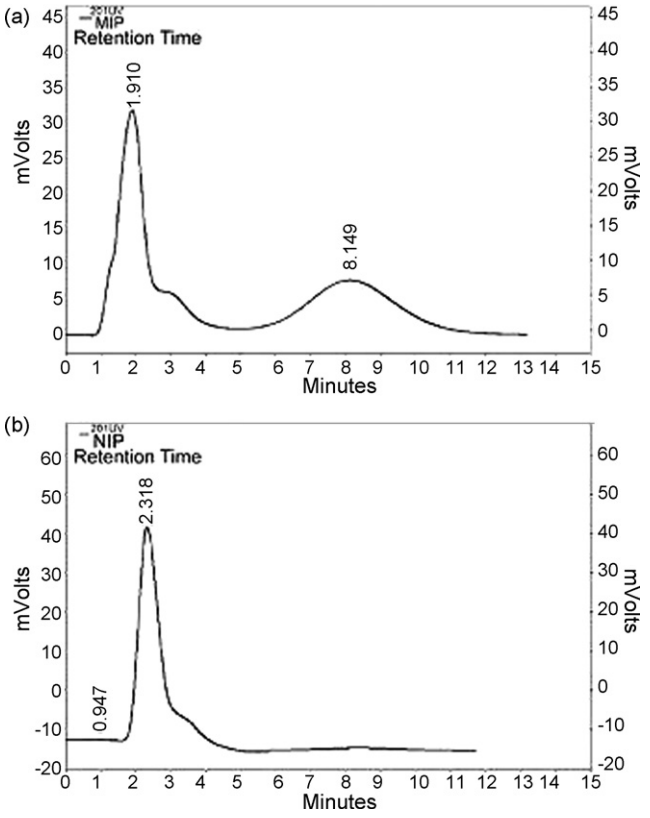

Fig. 3. Chromatograms of dimethoate sample for the HPLC separation on the columns packed with (A) MIP and (B) NIP. The first peak (retention time: 1.910 min) of (A) is the impurity (some additives) of industrial grade dimethoate, and the second peak (retention time: 8.149 min) of (A) is pure dimethoate.

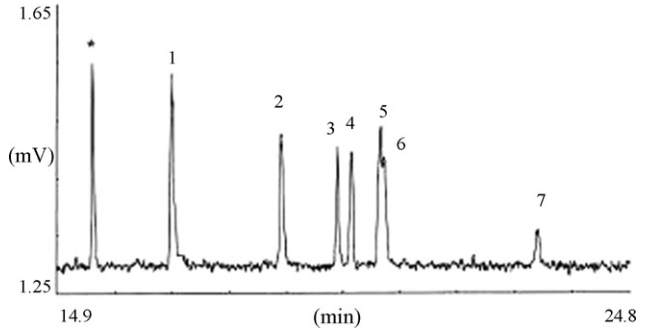

Fig. 4. Chromatograms obtained by GC/ECD or GC/FPD after SPME over spiked serum samples. 10 ng/mL OP pesticides (FPD): 1, diazinon; 2, parathion-methyl; 3, fenitrothion; 4, malathion; 5, fenthion; 6, chlorpyrifos; 7, methidathion; internal standard: *, phorate.

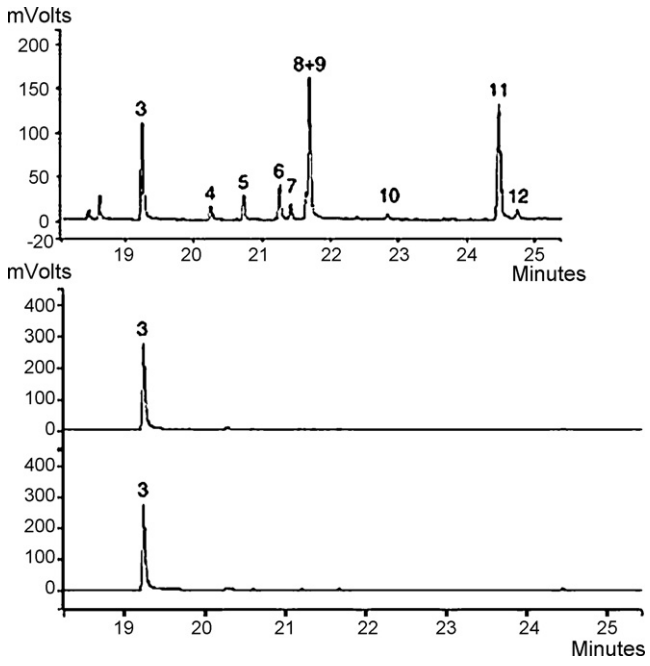

Fig. 5. Chromatograms of spiked water (A), orange juice (B) and red wine (C) samples by SPME–GC. Salt concentration: 15%; extraction time: 30 min; extraction temperature: 30 °C; stir rate: 1250 rpm; sample volume: 10 mL. Real life samples: diluted orange juice (1:20), and diluted red wine (1:10). 1: Momocrotophos; 2: phorate; 3: dimethoate; 4: parathion-methyl; 5: malathion; 6: fenitrothion; 7: fenthion; 8: chlorpyrifos; 9: parathion; 10: methidathion; 11: triazophos; 12: ethion.

by this fiber SPME coupled with GC thermionic specified detector (TSD) was validated. Limits of detection of the method for OPPs were below 10 ng/L except methidathion. Relative standard deviations (RSDs) were in the range of 1–20% (Fig. 5).

The SPME technique has been incorporated with commercial GC autosampler to realize automation of extraction, injection, thermal desorption, and fiber conditioning. Capillary solid-phase microextraction (in-tube SPME) technique was first proposed by Pawliszyn in 1997 [72]. In in-tube SPME, a thin coating on the internal surface of GC capillary was typically used to extract the analytes [73,74]. The water sample flows through the extraction column and the target constituents can diffuse into and concentrate gradually in the coating. In principle, the sample preparation can be on-line, and the sample size as well as the consumption of solvents can be substantially reduced with the in-tube SPME technique. It also can be easily coupled to micro-LC systems thus enhancing the sensitivity [75]. According to Web of Science (up to December 2009), however, only a few of applications of in-tube SPME coupled to capillary LC for OPPs are reported [64,76–78].

The reason for the lack of application is due to the hydrophobic nature of the non-polar extraction phase. A thin layer of air is trapped between the coating surface and water sample inside the capillary. Unlike the air layer between the coating on fiber SPME and water sample, where the air layer can be peeled off immediately by fast stirring in water samples, the air layer inside the capillary tube cannot be removed effectively by liquid flow. Thus the air layer in in-tube SPME is very stable, and retards normal extraction. To conquer this defect, Guan et al. developed a novel in-tube SPME device and coupled it with a capillary GC system [78]. The device consists of a six-port valve and three gas flow controllers, a homemade stainless steel micro-tee piece, a 5 m × 0.53 mm, 1.2-μm PDMS capillary extractor, and a mini water-circulating pump. A homemade oven capable of heating at a rate of 290 °C/min to temperatures greater than 320 °C provided fast and uniform heating for the capillary extractor. A deactivated fused-silica capillary of 1 m × 100 μm in close contact with a piece of heating resistor wire was used as the analyte transfer line from the in-tube SPME system to the GC system. An adiabatic sleeve covered the transfer line to maintain heat (Fig. 6). This in-tube SPME–GC method was used successfully to the on-line extraction, desorption, and sampling of various contaminants in water, followed by analysis with high-resolution GC of different detectors. OPPs in an aqueous sample were determined by this device, and the lowest detection limit was 0.05 μg/L for most of the analytes with an extraction time of only 5 min.

As the absolute amount of target compounds extracted from samples is very limited by using fiber SPME, the LOD of the analysis cannot always meet requirements. Stir-bar sorptive extraction (SBSE) technology, therefore, was introduced by Sandra et al. in 1999 as a novel sample preparation technique [79,80]. In SBSE, a magnetic stirring bar of glass or quartz coated with PDMS is used as the extractor instead of coated fiber. After a given extraction period, the analytes are thermally desorbed in a thermal desorption unit (TDU) and transferred into a GC injector, or desorbed with solvent extraction followed by using HPLC analysis [81]. The main advantage of SBSE is that the amount of PDMS coated on the stir bar is 50–250 times larger than that on SPME fiber, resulting in a significant increase in extraction capacity and overall sensitivity [82]. SBSE has been successfully applied to the extraction of OPPs from various types of samples in many fields, e.g. environmental, food, and biological samples [83–88]. Guan et al. determined OPPs in vegetables by SBSE and capillary GC with thermionic specific detec-

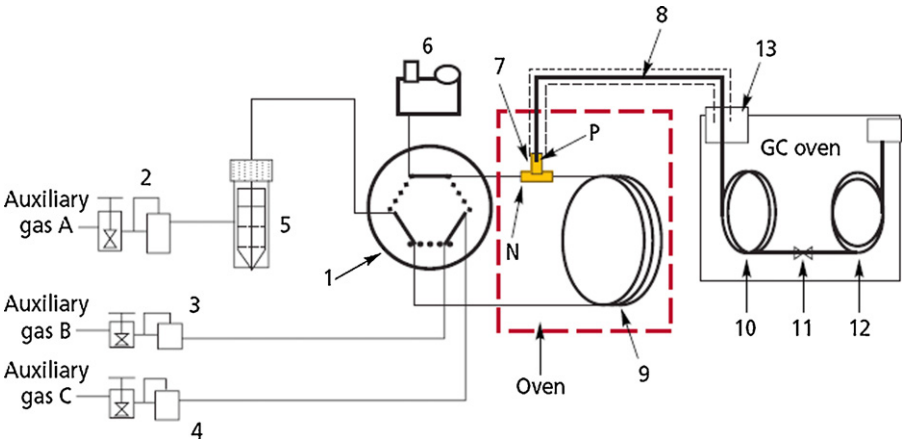

Fig. 6. Schematic diagram of the on-line in-tube SPME system coupled with a capillary GC system. 1: six-port valve; 2: flow controller for sampling; 3: flow controller for desorption gas; 4: flow controller for auxiliary gas; 5: sample vial; 6: mini water-circulating pump; 7: a micro-tee; 8: capillary transfer line; 9: capillary extractor; 10: precolumn; 11: press-fit or micro-union; 12: analytical column; 13: on-column injector.

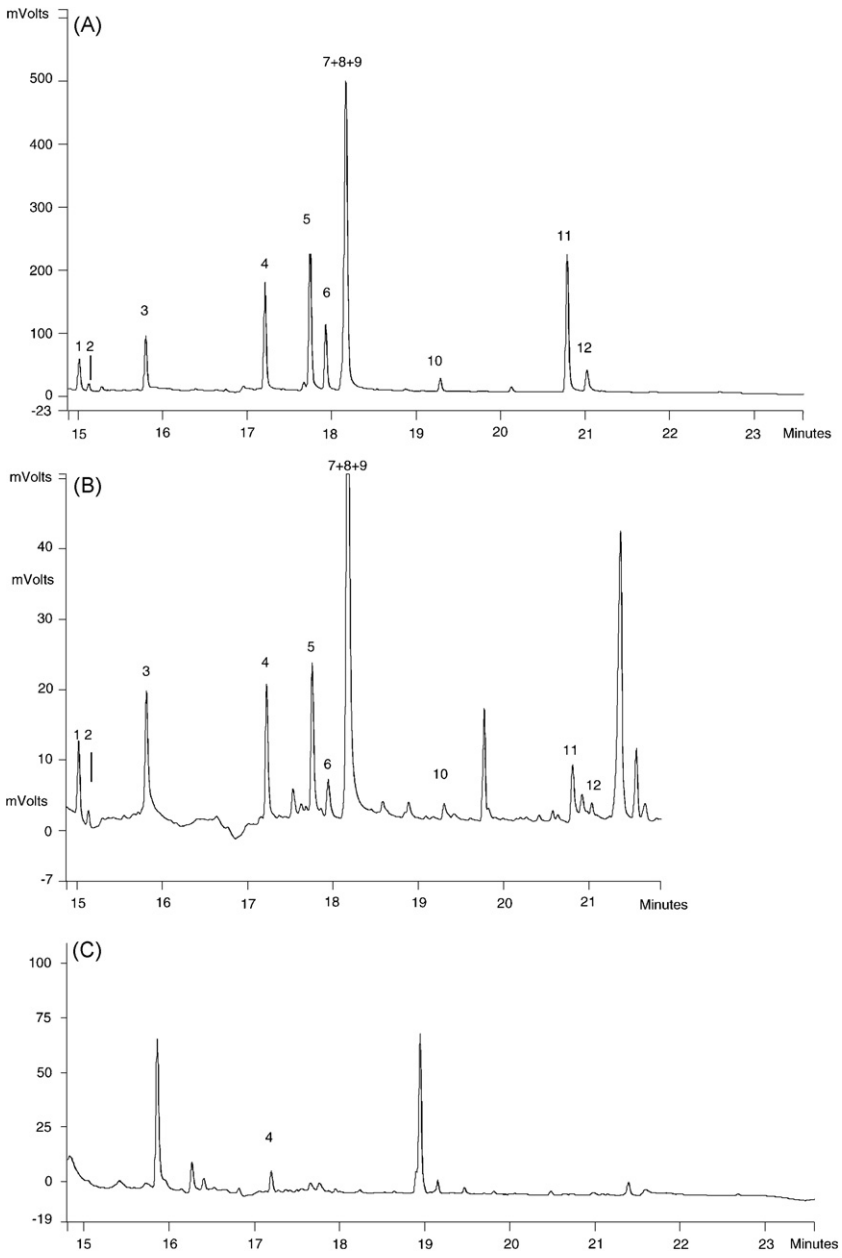

Fig. 7. GC–TSD chromatograms of OPCs obtained by the optimized SBSE method from: (A) water solution (800 ng/L); (B) spiked cucumber sample (0.5 ng/g) and (C) a potato incurred sample (0.5 ng/g). 1: Monocrotophos; 2: phorate; 3: dimethoate; 4: parathion-methyl; 5: malathion; 6: fenitrothion; 7: fenthion; 8: chlorpyrifos; 9: parathion; 10: methidathion; 11: triazophos; 12: ethion.

tion (TSD). Hydroxy-terminated PDMS coating prepared by sol–gel method was used as extraction phase. The detection limits of OPPs in water were between 0.06 and 1.22 ng/L [86]. The extracted and enriched OPPs from vegetable were desorbed completely at 260 °C for 5 min. The results demonstrated that sorptive stir bars prepared by sol–gel technology showed good extraction–desorption properties for OPPs in vegetable extracts. Linear ranges of extraction of OPPs in vegetable samples were 0.25–50 μg/L with detection limits ≤0.1 μg/L, and the repeatability of the method was better than 20% relative standard deviation (Fig. 7).

Because of the non-polar character of PDMS, the only commercialized coating for SBSE, the SBSE has been mainly applied to extract non-polar and weakly polar compounds. SBSE cannot be used to the extract strong polar compounds [89–92] unless derivatization was utilized. However, it is difficult to realize the derivatization of all polar analytes to get corresponding species with sufficient hydrophobicity. In order to overcome this limitation of SBSE, it is necessary to develop novel extraction phases that have better affinities to polar compounds, good mechanical properties, and tolerate high desorption temperature. A new dual-phase stir bar commercialized by Gerstel consisted of a short PDMS tube containing different carbon-based adsorbents [93]. The new stir bars showed enhanced extraction yield for polar compounds compared with those from conventional PDMS stir bar. Sol–gel technique has also been used to prepare stir bars because it provided direct chemical binding of the stationary phase to the quartz stir bar [94], and has been applied to the extraction of polycyclic aromatic hydrocarbons and OPPs [95]. A PDMS/β-cyclodextrin extraction phase has been prepared by using sol–gel technique and showed better selectivity to medium polar compounds estrogen and bisphenol A than pure PDMS stir bars [96]. A novel poly(phthalazine ether sulfone ketone) (PPESK) coated stir bars prepared by immersion

Table 1
Overview of sorptive extraction techniques for organophosphorus compounds in complex matrices.

Techniques	Matrices	Pretreatment	Characteristics	Elution	Detection	Recovery (%)	LOD	Ref.
SPE	Water	Filtered through 0.45 μm membranes	Oxidized carbon nanotubes	Acetone and methanol	GC/FPD	79.1–101.9	0.07–0.12 mg/L	[17]
SPE	Tap, surface and waste water	Added sodium thiosulphate (80 mg/L)	A Visiprep SPE manifold (Supelco, Bellefonte, PA, USA) Oasis HLB 200 mg cartridges	Methanol	LC/MS/MS	81–145	0.3 and 30 ng/L	[18]
SPE	Water	None	C_{18} cartridges		GC/MS/MS			[19]
SPE	Agricultural, ornamental and forestal soils	Soils were first ultrasound extracted with 10 mL 1:1 methanol/acetonitrile (v/v)	MWCNTs as an adsorbent	Dichloromethane	GC/NPD	54–91	2.97 and 9.49 ng/g	[20]
On-line SPM	River water	Filtered through 0.45 μm nylon filters	The Prospekt-2 system	1 mL of water	LC–ESI-MS/MS		Fenitrothion (50 ng/L)	[21]
SPE	Olives	Filtered	C_4, Chromasil	MeOH/water	GC/FID		0.18–0.38 mg/L	[22]
SPE	Baby food	The crude extract obtained by LLE, and reconstituted in ACN	A Sep-Pak Vac C18 6 cm^3 C18 cartridge (Waters, Milford, MA, USA)	Acetonitrile	HPLC	37–67	4.4–125.0 ng/mL	[23]
SPE	Human urinary	Acidified with 3 M hydrochloric acid	Automated solid-phase extraction, the styrene-divinyl benzene polymer-based SPE cartridges	Acetonitrile	GC/MS/MS	98–105	50–170 pg/mL	[24]
SPE	Human urinary	The urine was spiked with 20 μL internal standard working solution, acidified with 125 μL of 3 M HCl and vortex mixed	The ENV+ cartridges were placed on a Vacmaster SPE station with stopcocks	Acetonitrile	GC/MS/MS	79–113	0.1–1.0 μg/L	[25]
μ-SPE	Sewage sample	None	6 mg MWCNTs were packed inside a (2–1.5 cm) sheet of porous polypropylene membrane	Hexane	GC/MS		1–7 pg/g	[31]
SPE	Mineral water, ground water, and run-off water	Adjusted to pH 6.0 with 1.0 M HCl	MWCNTs of 10–15 nm O.D., 2–6 nm I.D., and 0.1–10 m length were used as stationary phase	Dichloromethane	GC/FTP	75–116 (mineral water), 67–119 (ground water) and 57–81 (run-off waters)	18–85 ng/L (Milli-Q water), 18–76 ng/L (mineral water), 19–102 ng/L (ground water) and 25–117 ng/L (run-off waters)	[32]
SPE	Tap water	Adjusted to suitable pH (4–10)	MWCNTs as an adsorbent	Acetonitrile	HPLC	95.2 ± 4.2	0.06 ng/mL	[33]
MHSPE	Rivers, wells	Calcium was removed by precipitation with SDS	Pure sodium dodecyl sulphate (SDS) and mixed tetrabutyl ammonium (TBA)–SDS hemimicelles and/or admicelles adsorbed onto alumina	Methanol and 0.3 M NaOH:methanol (90:10, v/v) solution	LC/UV	96–103	<100 ng/L	[34]

Table 1 (*Continued*)

Techniques	Matrices	Pretreatment	Characteristics	Elution	Detection	Recovery (%)	LOD	Ref.
MIP	Tea leaves	Extracted with hexane in microwave extraction system for 3 min and filtered through a 0.45 μm filter	Six functional monomers, including 4-VP, styrene, acrylamide, vinyl acetate, MMA and MAA	THF (5% acetic acid)	GC/FID; LC/UV	99		[41]
MIP	Water	None	The MCP imprinted polymer microspheres		GC/FTP			[42]
MIP	Aqueous media	None	Polymer particles (10 g) made by themselves were packed in a chromatography column (300 mm × 20 mm I.D.)	50 mL of methanol	IC	70		[43]
HS-SPME	Sewage sludge samples	None	A 100 μm poly(dimethylsiloxane) fiber	Thermal desorption at 250 °C for 3 min	GC/MS		21–93 pg/g	[4]
HFM-SPME	Sewage sludge samples	Added sodium chloride (5%, w/v) (pH = 8)	PDMS–DVB-coated fiber	Thermal desorption at 250 °C for 3 min.	GC/MS		10–67 pg/g	[4]
SPME	Apple juice, apple, tomato	HS-SPME (apple juice) 15 mL of diluted juice (1:30) with 5 g NaCl, extracted for 45 min at 70 °C. Direct SPME: 15 mL apple (1:50) and tomato (1:70) dilution with 5 g NaCl, for 60 min at 30 °C	Vinyl crown ether polar fiber: 80 μm	Thermal desorption at 270 °C for 5 min	GC/FPD	55–105	0.003–0.09 ng/g	[58]
DI-SPME	Blood, urine	None	The SPME fiber holder for manual use and the coated fibers (100 μm polydimethylsiloxane (PDMS) and 65 μm Carbowax™/divinylbenzene (CW/DVB)) were obtained from Supelco (Bellefonte, PA, USA)	Washed by immersion in deionised water for 5 s, and thermally desorbed in the injection port of the GC system for 1 min	GC	12.5–16.9; 24.5–27.9	10 ng/mL; 2 ng/mL	[59]
DI-SPME	Honey	None	100 μm PDMS	Desorpted at 280 °C for 5 min.	GC/AED	91	0.02–10 ng/g	[62]
SPME	Aquaculture-seawater samples	Filtered using cellulose ester membrane filters (HAWP, 47 mm, 0.45 μm; Millipore)	100-μm-thick PDMS fiber		GC/MS/MS	81–120	1.0–600 pg/mL	[63]
SPME	Environmental water	Filtered through 0.45 μm nylon membranes (Teknokroma)	A 30 cm × 0.25 mm I.D., 0.25 μm thickness coating column, and a 30 cm × 0.1 mm I.D., 0.1 μm of coating thickness column, the coating was 95% dimethylpolysiloxane (PDMS)–5% diphenylpolysiloxane	Methanol	LC		0.1–10 μg/L	[64]
HS-SPME	Water	None	A PDMS–DVB fiber	Desorbed at 270 °C for 5 min	GC/NPD			[65]

SPME	Tomatoes	Homogenized in a blender	The SPME holder for manual use and commercial fibers, including 75 μm carboxen-polydimethylsiloxane (CARPDMS), 65 μm polydimethylsiloxane-divinylbenzene (PDMS–DVB) and 85 μm polyacrylate (PA), were obtained from Supelco	Desorbed at 270 °C for 2 min	GC/NPD	82.5–90		[66]
SPME	Water, orange juice and red wine	Added NaCl (15%)	The extraction phase of PDMS containing 3% vinyl group	Desorbed at 290 °C	GC/FID		Below 10 ng/L except methidathion	[67]
SPME	Textiles	Simulative sweat solution was used to extract OPPs	Commercially available SPME fibers, 100 μm PDMS and 85 μm PA	Desorbed at 250 °C for 3 min	GC/MS	76.7–126.8	0.01–55 μg/L	[71]
In-tube SPME	Environmental water samples	Filtered through 0.45 μm nylon membranes	The coating was 95% PDMS–5% diphenylpolysiloxane	Injecting methanol	Capillary LC/UV		50–1000 μg/L	[64]
SBSE	Tap water, ground water and surface water	Added with 20% NaCl., $Na_2S_2O_3{\cdot}5H_2O$ was added to tap water	20 mm long PDMS stir bar	TSD at 280 °C for 6 min.	GC/MS		0.1–10.7 ng/L	[83]
SBSE	Aqueous samples	Suspending green tea (1.25 g) in 200 mL of boiling water for 5 min	Stir bars coated with 24 μL of PDMS (Twister)	Thermal Desorpted 30 min at 300 °C in a flow of helium	LTM–GC–MS	15–62	0.058–9.4 ng/L	[84]
SBSE	Water		Stir bars used were coated with 24 μL of PDMS and were supplied by Gerstel	A TDU heating rate of 600 °C/min to a final temperature of 260 °C	GC/FPD			[85]
SBSE	Brazilian sugarcane juice	Saturated with NaCl	The 10 mm long stir bars coated with a 0.5-mm-thick film of PDMS (Twister)	Desorpted 11 min at 250 °C	GC–MS (SIM)		0.002–0.71 μg/L	[88]
SBSE	Saffron	Added 1% methanol, 20% sodium sulphate anhydrous	0.5 mm film thickness, 20 mm length PDMS stir bars	Desorpted 5 min He inlet flow, 45 mL/min	GC/MS/MS		0.06–0.56 μg/kg	[89
SBSE	Water, grape and peach juice	None	The thickness of the PPESK coating is 250 μm	260 °C was reached in 2 min and held for 5 min	GC/TSD		0.09–1.5 ng/L (water), 0.17–2.25 ng/L (grape juice) and 2.47–10.3 ng/L (peach juice)	[97]

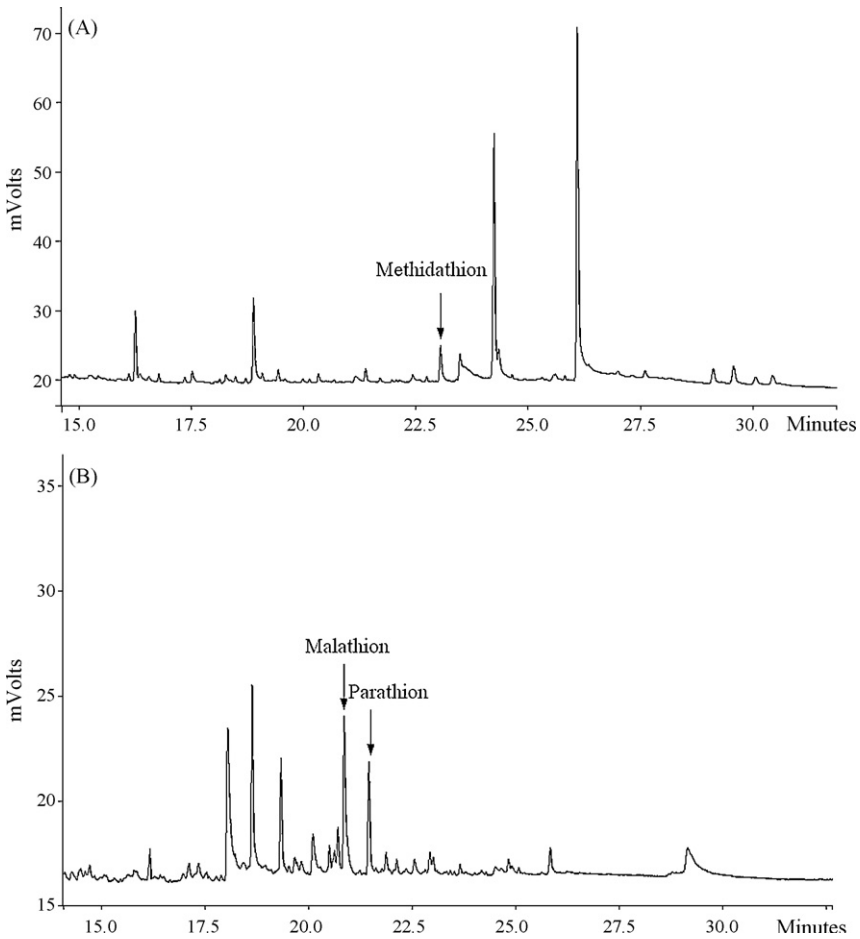

Fig. 8. SBSE/GC–TSD chromatogram of extracting OPCs in diluted grape juice and peach juice (B) with dilution ratio of 1:20 (v:v). Extraction temperature: 40 °C; extraction time: 30 min; desorption time: 5 min; desorption temperature: 260 °C; stir rate, 600 rpm; detector: TSD.

precipitation technique was reported for sorptive extraction of OC compounds in seawater samples and OPPs in juices [97]. As shown in Fig. 8 , methidathion was detected in diluted grape juice (1:20, v:v) at a concentration of 94.9 ng/L. Melathion and parathion were detected in diluted peach juice (1:20, v:v) at concentrations of 21.7 and 44.1 ng/L, respectively. Thus, the values in real samples were 434 ng/L for melathion, and 882 ng/L for parathion.

3. Applications

The applications of the various sorptive extraction techniques since 2006 for OPPs in biological samples, food and environmental analysis are compiled in Table 1. According to the scientific literature published so far, SPE and SPME are among the most widely used extraction techniques. The SBSE technique is getting popular in recent years because of high extraction capacities, minimal consumption of solvents, and small sample volume. Other techniques, such as MIP, and in-tube SPME, are still under development.

4. Conclusions and future outlook

After 20 years of development, sorptive extraction techniques and theories have become mature, and been widely used in extraction of trace OPPs in complex matrices, including water, food and biological samples. Future development is focused in the following directions: (1) design and synthesize novel coating materials of high selectivity to reduce the matrix effect, especially with specific functionalized phases; (2) new general-purpose extraction phases that can extract all acidic, alkaline, and neutral components simultaneously, and subsequently analyzed at one time; (3) integration of sorptive extraction techniques with other analytical instruments to enhance sensitivity and on-line determination of target compounds; (4) development of high-throughput and miniaturized device that could reduce the consumption of sample and reagent while increase the throughput 10 times or even higher.

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