Trends in Analytical Chemistry 71 (2015) 186–193

Contents lists available at ScienceDirect

Trends in Analytical Chemistry

journal homepage: www.elsevier.com/locate/trac

Recent advances and developments in matrix solid-phase dispersion

Anna Laura Capriotti, Chiara Cavaliere, Patrizia Foglia, Roberto Samperi, Serena Stampachiacchiere, Salvatore Ventura, Aldo Laganà *

Department of Chemistry, Università di Roma "La Sapienza", P. le Aldo Moro 5, Rome 00185, Italy

ARTICLE INFO

Keywords:
Carbonaceous sorbent
Clean-up
Co-sorbent
Extraction
Matrix solid-phase dispersion
MIP
Molecularly-imprinted polymer
MSPD
Sample preparation
Sorbent

ABSTRACT

Matrix solid-phase dispersion (MSPD) is a sample-preparation process first introduced in 1989 for the extraction of drug residues from animal tissue. The feasibility and the versatility of MSPD mean it is still widely employed and applicable to a large variety of analytes and samples. The research papers reporting the development of analytical methods with a MSPD-based sample preparation are novel mainly by employing innovative or unusual materials as dispersants and/or the mode of analyte elution. This review gives an update on MSPD from the literature in the period 2012–October 2014, focusing attention on improvements and the outlook for the technique.

Contents

Abbreviations: ACN, Acetonitrile; CE, Capillary electrophoresis; DLLME, Dispersive liquid-liquid microextraction; ECD, Electron-capture detector; FID, Flame-ionization detector; FLD, Fluorescence detector; FPD, Flame-photometric detector; FQ, Fluoroquinolone; HFR, Halogenated flame retardant; HLLME, Homogeneous liquid-liquid microextraction; IL, Ionic liquid; LOQ, Limit of quantification; MEKC, Micellar electrokinetic chromatography; MeO-PBDE, Methoxy- polybrominated diphenyl ether; MIM, Methylimidazolium; MIP, Molecularly-imprinted polymer; MWCNT, Multi-walled carbon nanotube; NCI, Negative chemical ionization; NP, Normal phase; OCP, Organochlorine pesticide; OH-PBDE, Hydroxy-polybrominated diphenyl ether; OPP, Organophosphorus pesticide; PAH, Polycyclic aromatic hydrocarbon; PBDE, Polybrominated diphenyl ether; PCB, Polychlorobiphenyl; PSA, Primary-secondary amine; QuEChERS, Quick, Easy, Cheap, Effective, Rugged, and Safe; RP, Reversed phase; SPME, Solid-phase microextraction; SBSE, Stir-bar sorptive extraction; UA, Ultrasound-assisted; WCX, Weak cation-exchange.

* Corresponding author. Tel.: +39 06 49913679; Fax: +39 06 490631.
E-mail address: aldo.lagana@uniroma1.it (A. Laganà).

http://dx.doi.org/10.1016/j.trac.2015.03.012
0165-9936/

1. Introduction

Sample preparation is a crucial step in every analytical process, because it significantly affects the total time required to complete the analysis, the quality of the results, and the cost of analysis [1]. An ideal sample-preparation procedure should concentrate the analyte while removing the potential interferents [2], avoiding analyte degradation and/or formation of artifacts; furthermore, the procedure should be robust, reproducible, and independent of sample-matrix variations.

In recent decades, sample-preparation techniques attracted much attention, due to the pressing need for accurate, fast determinations of a constantly increasing number of analytes at low concentrations in complex matrices [3]. In most cases, sample-preparation procedures involve a large number of steps and manipulations prior to analysis, including when selective techniques, such as mass spectrometry (MS) coupled to a chromatographic separation, are used for detection. This trend began to change only more recently due to the introduction of the latest generation of high-sensitivity mass spectrometers that have allowed the development of multiresidual liquid chromatography (LC)-MS methods based on the dilute-and-shoot approach, which requires only limited sample preparation. However, in this way, the presence of many matrix-interferent compounds could lead to a high ionic signal suppression or enhancement (namely matrix effect) during the atmospheric pressure ionization phase, affecting both method sensitivity and trueness.

Among the various sample preparations, methodologies based on employing sorbents are most suitable to obtain a high level of clean-up, enrichment efficiency, and analysis of trace targets present in complex matrices [4]. Therefore, in recent decades, solid-phase extraction (SPE), solid-phase microextraction (SPME), membrane-protected micro-SPE, stir-bar sorptive extraction (SBSE) and matrix solid-phase dispersion (MSPD) mostly replaced classical solvent-extraction methods, thus stimulating the development of new and improved sorbent materials [4]. The exception is the very popular Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) protocol [5], based on water/acetonitrile partitioning in salting-out conditions. SPE, SPME and SBSE are also commonly used for solid samples after a solubilization step in water or organic solvent.

The MSPD technique was first introduced in 1989 by Barker et al. [6] for the extraction of drug residues from bovine tissue. Since then, it has proved to be an efficient, versatile technique for isolating several classes of substances, such as pesticides, drugs, pollutants, and naturally-occurring compounds, from a wide variety of animal and plant samples [7]. Although MSPD was developed for extracting solid samples by disrupting their architecture, its application soon extended to viscous and liquid samples, such as milk.

The success of MSPD is due to its simplicity (it does not require any instrumentation or specific equipment), flexibility and ruggedness compared to other sample-preparation methods. The mild extraction conditions (i.e., room temperature and atmospheric pressure) preserve analytes from degradation and denaturation. Nevertheless, sometimes MSPD has been employed in conjunction with pressurized liquid extraction to increase recoveries of compounds that interact strongly with the solid matrix [8]. The choices of solid support and elution solvent determine the efficiency and the selectivity of the process. Generally, MSPD requires a low consumption of organic solvents, especially if miniaturized [9]. Although extraction based on this technique is quite rapid, it cannot be fully automated, and this represents an obstacle when routine analyses have to be performed on large sample sets. In most cases, samples prepared or extracted by MSPD are then analyzed by gas chromatography (GC)-MS or LC-MS.

Over the past 10 years, there have been detailed reviews on MSPD (mechanism, applications, recent developments and trends) [7,8,10–15], and research papers reporting applications and improvements for MSPD regularly appear in the literature. We therefore aim to give an update on MSPD literature from 2012 to October 2014, discussing selected recent applications and pointing out the latest developments and the future prospects for this technique.

2. General principles of MSPD

The basic procedure and the physical principles of MSPD were described in depth by its inventor [6,11]. The procedure consists of three main steps, as shown in Fig. 1; an additional SPE clean-up step can be carried out by adding a co-sorbent to the bottom of the extraction column (see Fig. 1) or using an external column [16].

Unlike SPE, where the sample is retained in the first few millimeters of the sorbent, in MSPD, the sample is homogeneously dispersed throughout the entire extraction column [15], and the retention mechanism seems a mix of partition, adsorption and ion/pair chromatography [8].

Several dispersant materials have been employed in MSPD. Inert solid supports, such as sea sand, have a simple abrasive role to ensure complete matrix disruption, but materials commonly used as SPE phases can enhance the technique selectivity and perform the clean-up together with the extraction step. Reversed-phase (RP) materials, such as C18- and C8-silica bonded phases, are used in most works, whereas alumina, silica and Florisil are typically used as normal-phase (NP) materials. The different behavior of RP and NP phases has been discussed elsewhere [6,11]. More recently, new MSPD sorbents, such as molecularly imprinted polymers (MIPs) [2,17], and carbon-based materials [18,19] were also proposed.

A critical parameter is the ratio of sample-to-solid material (generally 1:1–1:4), which depends on sample type and physical-chemical features of the material. The choice of eluent depends on the strength of the interactions between solid support and target analytes.

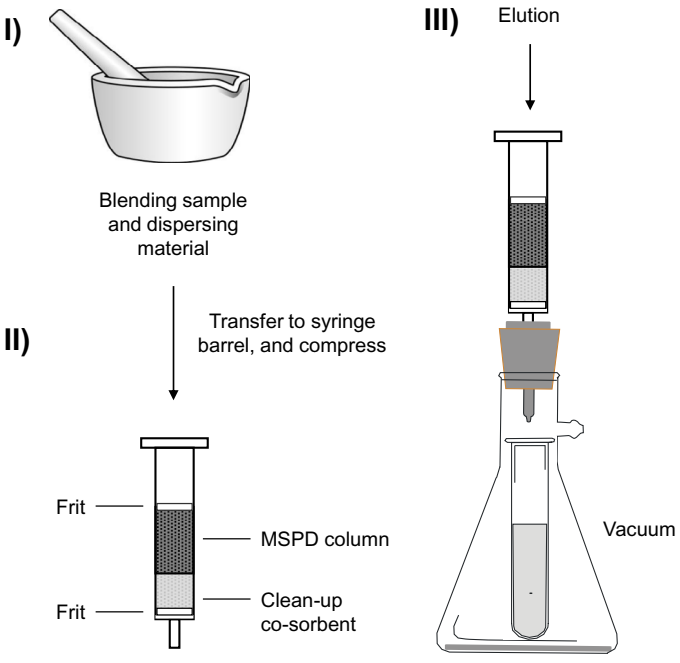

Fig. 1. Outline of the main steps of the matrix solid-phase dispersion extraction procedure: I) the sample is blended with the dispersant material in a mortar with a pestle; II) the homogenized powder is transferred into a solid-phase extraction cartridge, and compressed; III) elution with a suitable solvent or solvent mixture is performed by the aid of a vacuum pump. Reprinted with permission from Elsevier [8].

To optimize all the main parameters of MSPD (i.e., sample amount, amount and type of dispersant material, possible clean-up step, composition of eluent), experimental design is often used [20–26].

3. New sorbent materials

The main innovation in MSPD concerns the employment of new or improved dispersant materials, such as carbon-based materials and MIPs. As far as silica-based materials are concerned, innovations are more limited, since they have already been extensively studied in the past. The use of new mixed-mode silica-based materials is the only exception. These hybrid materials can be designed to exploit the different properties of the moieties bound to the silica to achieve a higher selectivity for the target analytes. In this sense, very recently, Zhu et al. [27] synthesized a RP/weak cation-exchange mixed-mode silica-based material (silica-WCX) with alkyl and carboxyl groups. The synthesized silica-WCX sorbent was then investigated as MSPD dispersant for the extraction of clenbuterol and ractopamine in porcine liver, and it performed better than commercial single-mode sorbents and other mixed-mode sorbents.

3.1. Carbon-based materials

Carbon nanotubes (CNTs) [18] and, more recently, graphene [19] have been introduced as novel MSPD dispersing materials. Multi-walled CNTs (MWCNTs) are carbon-based nanomaterials characterized by an extremely large, hydrophobic surface area and peculiar structural features that confer on them excellent adsorption properties [8]. In a very recent paper, chitosan-grafted MWCNTs were synthesized, characterized and used in the development of an MSPD method for trace determination of acrylamide in foods [28]. The authors reported that the modified MWCNTs were more effective in acrylamide adsorption than unmodified MWCNTs, also displaying faster kinetics.

In 2011, graphene was used in a method for the determination of polybrominated diphenyl ethers (PBDEs) and their structural analogues, hydroxy-PBDEs (OH-PBDEs) and methoxy-PBDEs (MeO-PBDEs), in soil, tree bark and fish [19]. The very large surface area and the flexible nanosheet morphology of graphene led to higher recoveries (90–105% for the three classes) than those obtained with classical MSPD materials, namely C18 silica and Florisil, and MWCNTs, which performed worse for OH-PBDEs (~10% recovery). However, since then, no new application using graphene in MSPD has been published in the literature, probably due to the difficulties of using this support, such as its fragile structure, which means that it is unsuitable for completely disrupting the sample architecture, and the small amount required (sample-to-support ratio 10:1) that, with the adhesion forces to the mortar surface, complicate transfer of the powder to the SPE cartridge.

3.2. Molecularly-imprinted polymers

Molecularly-imprinted polymers (MIPs) are synthetic materials obtained by polymerizing functionalized monomers around a template molecule, leading to a highly cross-linked three-dimensional network polymer. The presence of a template during their synthesis provides them with molecular recognition abilities, making MIPs able to rebind specifically to a target molecule in preference to other closely-related compounds [2]. They have therefore found several applications as selective materials in extraction techniques. Despite the specificity being lower than that of antibodies, MIPs possess attractive features that make them competitive with antibodies, because they are easy to prepare, have lower cost, and do not require immobilization on a suitable support [2]; moreover, MIPs are stable and resistant to a wide range of pH values, solvents and temperature.

However, one of the main drawbacks with MIPs is template bleeding that could seriously affect the accuracy of the method, especially in trace analysis [29]. It is known that, even after exhaustive washing [30], residual template remains in the polymer network, so its leakage might occur during the SPE elution step. To circumvent this inconvenience and thus the unreliability of analyte quantification, the use of an analogue of the target analyte as MIP template has been proposed [29], but, in this way, the molecular recognition ability of the polymer is reduced. In this sense, a very interesting alternative is use of a stable-isotope-labeled compound as template.

Since the first application of MIPs in MSPD in 2007 [31] to extract fluoroquinolone (FQ) residues from chicken eggs and swine tissues, these polymers have been employed in several works, mainly applied to liquid and viscous samples, such as water [32] and milk [33,34], but also to samples of vegetable [25,35] and animal tissue [36]. To overcome the problem of template leakage, a dummy template, daidzein, was used to create specific molecular recognition sites for FQs in the synthesized MIP [37]; the polymer was then used in the MSPD extraction of FQs from fish muscle. Specific interactions between FQs and the selected MIP were observed; the low selectivity of the MIP for two analytes, namely enrofloxacin and pefloxacin, was mostly due to highly hydrophobic, non-specific interactions, resulting from their relatively high hydrophobicity (octanol/water partition coefficients 0.22 and 0.31, respectively, while those of the other six FQs were below zero).

For the analysis of trace steroids [34], 0.2 mL of goat's milk was blended with 0.048 g of MIP-E2, together with Na_2SO_4 and sea sand to obtain a dry mixture, thus facilitating its transfer into the cartridge. The five target steroids were eluted directly from the cartridge without any previous washing step. With this miniaturized MIP-MSPD procedure, analyte recoveries were 80–110%, with the lowest values observed for the MIP template; only 17α-ethinylestradiol showed a marked matrix effect when the extract was analyzed by micellar electrokinetic chromatography with diode-array detection. However, method limits of quantification (LOQs) were quite high (see Table 1).

Using MSPD, MIPs were employed to extract organophosphorus pesticide (OPP) residues from fruit samples using 4-(dimethoxyphosphorothioylamino)butanoic acid as the template [35]. The novel MIP exhibited good recognition ability and fast adsorption-desorption dynamics toward OPPs. The procedure described was suitable even for a sample-to-sorbent ratio of 4:1 and with samples containing a large amount of water (pear, apple and orange), since the authors did not use any other solid materials (e.g., Na_2SO_4) to adsorb the water excess.

3.3. Ionic liquids

Ionic liquids (ILs) are inorganic and organic salts with melting points below 100°C, and they are emerging solvents in analytical chemistry [49–51]. Their success is due to their unique, fascinating characteristics as non-molecular solvents, with a negligible vapor pressure associated with high thermal stability, tunable viscosity and miscibility with water and organic solvents. ILs generally comprise an organic cation (e.g., imidazolium, pyrrolidinium, pyridinium, tetraalkyl ammonium or tetraalkyl phosphonium) and an inorganic or organic anion (e.g., tetrafluoroborate, hexafluorophosphate, or bromide). In addition, the large number of possible combinations provides a long list of ILs with different chemical and physical

Table 1
Selection of matrix solid-phase dispersion (MSPD) methods published in the period 2012-October 2014

Analyte	Sample	Sorbent	Sample:sorbent ratio (*w/w*)	Elution solvent	Clean-up	Rec (%)	Detection	Method LOQ (ng g^{-1})	Ref.
PBDEs, OH-PBDEs, MeO-PBDEs	Soil (0.5 g), lettuce (0.25 g freeze-dried) carrot (0.5 g freeze-dried)	C18	1:1 (soil, carrot); 1:2 (lettuce)	10 mL 75:25 (*v/v*) Hex:DCM (PBDEs, MeO-PBDEs) + 30 mL DCM (OH-PBDEs)	0.5 g SiO_2 + 1.75 g acidified SiO_2	81–129	GC-NCI-MS	0.01–1.8	[38]
PBDEs, HFRs	Mollusks (0.5 g freeze-dried)	PSA	1:1	10 mL DCM	1.75 g acidified SiO_2 + 0.5 g SiO_2 + 1.75 g Florisil	46–120	GC-NCI-MS	0.01–2.11	[39]
Alkanes	Soil (0.1 g)	chitosan-ZnO	1:2	1 mL EtOH	50 mg chitosan- ZnO + FA-DLLME	ca. 90	GC-FID	0.2–5.0	[40]
Pesticides	Onion (0.5 g)	C18	1:2	10 mL ACN	-	87–100	LC/ESI-MS/MS	10–100	[41]
OCPs	Soil (0.5 g)	C18:SiO_2 1:9 (*w/w*)	1:4	8 mL DCM:Hex 1:1 (*v/v*)		59–93	GC-ECD	0.3–6.0	[23]
OCPs and PCBs	Vegetable oils (0.5 g)	SiO_2 (H_2S-impregnated)	1:7	10 mL Hex:DCM 70:30 (*v/v*)	0.8 g SiO_2 gel	70–105	GC-ECD	0.14–2.45	[42]
OCPs and PCBs	Post-mortem lung tissue (0.5 g)	Florisil (+2 g Na_2SO_4)	1:4	15.45 mL DCM:Hex 89:11 (*v/v*)	1.54 g Florisil	65–106	GC-ECD (GC-MS)	0.5–1.6 (1.4–3.9)	[22]
OPPs	Fruit (apple, pear, orange) (2.0 g)	MIP	4:1	5.0 mL MeOH:AcOH 95:5 (*v/v*)		85–125	GC-FPD	n.r.	[35]
Pyrethroids	Soil (0.1 g)	SiO_2	1:3	3 mL acetone	DLLME	84–99	GC-ECD	1.51–3.77	[43]
Triazines	Soil, strawberry and tomato (0.2 g)	MIP	1:1 (soil); 1:3 (other samples)	5 mL MeOH (soil); 5 mL acetic ester (strawberry); 10 mL DCM (tomato)	0.05 g C_{18}	53–98	MEKC-DAD	45–105	[25]
Triazines	Seaweeds (1.0 g)	C8	1:2	25 mL ethyl acetate:ACN 80:20 (*v/v*)	0.5 g ENVI-CarbII/ 0.5 g PSA	80–92	HPLC-DAD	4.1–7.3	[44]
Isothiazolinone biocides	Cosmetics and household products (0.5 g)	Florisil	1:4	5 mL MeOH	0.5 g Florisil	45–100	LC/ESI-MS/MS	6.6–60	[20]
Benzotriazoles	Sediments (0.5 g)	Diatomite + Na_2SO_4	1:2	5 mL DCM	0.5 g SiO_2	78–110	GC-EI-MS/MS	3–15	[21]
UV filters	Mollusks (0.5 g freeze-dried)	Florisil	1:4	5 mL ACN	1 g C18	80–101	GC-EI-MS	4–28	[45]
Fragrance allergens and preservatives	Cosmetics (0.1 g)	Florisil (0.4 g) + Na_2SO_4 (0.2 g)	1:4	1 mL ethyl acetate or Hex:acetone 1:1 (*v/v*)	0.1 g Florisil	66–114	GC-EI-MS , GC-EI-MS/MS	n.r.	[26]
Perfluorinated compounds	Mollusks (0.5 g freeze-dried)	Diatomite	5:2	20 mL ACN	4 g SiO_2	64–126	LC/ESI-MS/MS	0.2–1.0	[24]
FQs	Fish (200 mg)	daidzein-MIP	4:3	4.0 mL ACN:TFA 99:1 (*v/v*)	50 mg MIP	88–103	HPLC-FLD	n.r.	[37]
Cocaine and opiates	Human hair (0.05 g)	Alumina	1:45	2 mL MeOH:AcOH 98:2 (*v/v*)	Oasis HLB (linked column)	93–109	GC-EI-MS; ESI-MS/MS	80–360	[46]
Flavonoids	Citrus fruit juices and body fluids (0.15 mL)	C18	3:4	0.5 mL MeOH	-	85–101	HPLC-UV	75–141	[9]
Synthetic dyes	Condiments (0.50 g)	Diatomite + [C6MIM][BF4]	1:3	6 mL H_2O	HLLME with 1 mL 2.0 mol L^{-1} NH_4PF_6	91–113	HPLC-UV	16–58	[47]
Acrylamide	Potato, flour, chip, toast (1.0 g) and 2.0 g of CS/MWCNTOX	Chitosan/MWCNTs	1:2	4.0 mL MeOH: H_2O: AcOH 90:10:2 (*v/v/v*)	-	85–95	HPLC-UV	n.r.	[28]
Phenolic acids and flavonoids	Propolis (0.05 g)	silica supported- [C_6MIM]Cl	1:4	15 mL MeOH	20 mL Hex (prior to elution)	66–92	HPLC-UV	19–74	[48]
Steroids	Goat milk (0.2 mL)	MIP-E2 (0.048 g) + Na_2SO_4 (0.126 g) + sea sand (0.126 g)	ca. 2:3	1 mL ACN		81–110	MECK-DAD	(2.0–7.3) × 10^3	[34]

DCM, Dichloromethane; Hex, Hexane; PCBs, Polychlorobiphenyls; Rec, Recovery.
n.r., not reported.

features, such as polarity, hydrophobicity and viscosity [52]. In recent years, ILs were also immobilized onto silica or polymeric supports to take advantage of their chemical functionality and, as a result, new groups of stationary phases emerged and were employed in different fields, with applications in extraction (e.g., SPME and SPE) and separation (e.g., GC, LC and CE) [53].

Wang et al. [47] proposed an IL-MSPD method coupled to homogeneous liquid-liquid microextraction (HLLME) for the extraction of four synthetic dyes from condiments. A 0.50-g aliquot of condiment sample (chili, curry, ginger, and star anise powders) was dispersed with 1.50 g of diatomite and 120 μL of 1-hexyl-3-methylimidazolium tetrafluoroborate ([C6MIM][BF4]) in the mortar. The homogenized mixture was transferred into a glass column with a layer of absorbent cotton at the bottom; a second layer of absorbent cotton was placed on the top of the sample mixture (the role of these two cotton layers was not explained). Elution of target analytes was performed with 6 mL of water. Then, ion-pairing agent NH_4PF_6 was added into the eluate to favor the separation of the newly formed $[C_6MIM][PF_6]$ IL phase. Finally, ACN was added to dilute the IL and an aliquot was injected into the ultra-performance LC (UPLC)-ultraviolet (UV) system. The IL $[C_6MIM][BF_4]$ performed better than analogs 1-butyl ($[C_4MIM][BF_4]$) and 1-octyl ($[C_8MIM][BF_4]$). The lower analyte recoveries shown by $[C_4MIM][BF_4]$ were due to the higher solubility in water of $[C_4MIM][PF_6]$ than homologs with longer chain length; however, increasing alkyl chain length also led to an increase in the solution viscosity, with negative effects on mass transfer and analyte recovery.

In a second work, Wang et al. [48] prepared a silica-supported IL for MSPD extraction of phenolic acids and flavonoids in raw propolis. The IL {$[C_6MIM]Cl$} was immobilized on the surface of silica gel {10% content of $[C_6MIM]Cl$}, and 0.050 g of sample was dispersed with 0.20 g of supported IL. After blending, the homogeneous mixture was packed into the SPE cartridge, as described above. First, 20 mL of hexane were passed for defatting, then the analytes were eluted with 15 mL of MeOH. Also, in this case, three ILs (C4, C6 and C8) were compared: $[C_8MIM]Cl$ gave the worst recovery, probably because of the strong interaction with the target compounds. The authors stated that, with respect to ultrasound-assisted (UA) extraction and Soxhlet extraction, their method allowed lower consumption of sample and organic solvents, and a shorter extraction time, even if the extraction yields obtained by supported IL-based MSPD were slightly below those obtained by ultrasound. However one must keep in mind that the defatting/elution step required at least 35 mL of organic solvents, which should also be taken into account.

3.4. Nanoparticles

One of the most apparent advantages for polymer–inorganic nanoscale hybrids is the good adsorption capacity and good chemical stability in a wide pH range, due to ease functionalization by different polymeric units [54]. The interaction between sorbent and target compound is probably physical adsorption or Van der Waals interaction.

Chitosan-zinc oxide nanoparticles (NPs) were used as a sorbent for miniaturized MSPD combined with flotation-assisted dispersive liquid-liquid microextraction (FA-DLLME) for the simultaneous determination of 13 *n*-alkanes (C_8H_{18}–$C_{20}H_{42}$) in soil samples [40]. The recoveries of analytes by these hybrid NPs were slightly higher than those obtained with alumina, silica, and C18.

The use of magnetic NPs, such as tetraethylenepentamine-functional Fe_3O_4 polymers, as MSPD dispersant to preconcentrate Cr(VI) at ultratrace levels from water [55], offered the possibility of isolating the NP-Cr(IV) complex under a magnetic field; finally, Cr(VI) was eluted with NaOH solution.

4. Assisted MSPD extraction

4.1. Ultrasound-assisted MSPD (UA-MSPD)

UA extraction involves the application of ultrasound irradiation using an ultrasonic bath or a probe to decrease the time and to increase significantly the efficiency of the liquid-solid extraction step. In a miniaturized UA-MSPD method to extract seven flavonoids from citrus fruit juice, and human urine and plasma samples, Barfi et al. [9] loaded a 150-μL sample directly into a 1-mL syringe barrel fitted with a PTFE frit and containing 200 mg of C18. Then, both ends of the syringe were closed with polypropylene caps and the syringe was immersed in ultrasonic water bath for 6 min at room temperature to disperse the sample. Analytes were finally eluted with 500 μL of methanol. They showed that, compared to classical MSPD, the UA-MSPD protocol gave better extraction efficiency and analytical performance (recovery increasing by 10–25% with sonication).

The use of sonication instead of mortar and pestle provides advantages and makes the method rapid and simple, and allows it to reduce solvent consumption. However it is at the boundary between MSPD and SPE. Even if the liquid is dispersed by sonication through all the surface of the sorbent, the analytes are still likely be retained on the top of it.

In another work, a hair-dye sample (0.2 g) was diluted to 25 mL with 0.1 mol L^{-1} methanesulfonic acid in a glass tube, then 0.4 g of neutral alumina and 0.5 mL of hexane were added [56]. The solution was heated, subjected to vibration and sonication, and centrifuged to sediment the fine alumina particles. Finally, the upper organic phase was removed and the lower phase was analyzed by HPLC-UV. The hexane was needed to dissolve lipids, the acid solution to disperse the matrix and extract the analytes, and the sorbent to retain interfering components. Extraction took only 9 min.

4.2. Vortex-assisted MSPD (VA-MSPD)

VA-MSPD substitutes the SPE elution step with vortex agitation followed by centrifugation. Briefly, after dispersion of the sample in the mortar with the solid support, the resulting homogeneous powder is placed into a centrifuge polypropylene tube with the appropriate elution solvent to obtain a suspension. Then, the tube content is vortexed for 1 min and centrifuged for 10 min to collect the final extract [57]. Compared to traditional MSPD with elution in a vacuum manifold, recoveries of pesticides in fish liver [57] obtained with the vortex-assisted procedure were slightly, but not significantly, lower. However the advantage of faster extraction claimed by the authors was not so evident. The dispersant material was reused C18 (i.e., C18 removed from SPE cartridges that had been used to pre-concentrate pesticides in drinking waters and checked to ensure contamination absence). Nevertheless, the idea of recycling the adsorbent material does not seem to have earned favor in the scientific community, probably because of the time required to remove the C18 from the old cartridges and check for residual contamination.

5. New applications of conventional materials

5.1. MSPD-assisted enzymatic hydrolysis

Several sample pre-treatments for the isolation of drugs from hair are available in literature (e.g., the use of acid and alkaline aqueous solvents, organic solvents and enzymatic hydrolysis). Enzymatic hydrolysis has the advantage of operating in mild extraction conditions (pH and temperature), thus minimizing target-analyte transformation. The possibility of assisting enzymatic hydrolysis procedures by MSPD sample-disruption mechanisms has been explored

for isolating cocaine and opiates from human hair [46]. The sample (0.05 g) was dispersed with alumina (2.25 g); once the cartridge was packed, the dissolved enzyme was loaded onto the hair-alumina solid phase. The procedure allowed an on-column clean-up/preconcentration procedure for the isolated targets by attaching an Oasis HLB cartridge to the end of the MSPD syringe. Analytes were eluted from the Oasis HLB cartridge with 2 mL of 2% (*v/v*) acetic acid in methanol. The proposed approach might be used for screening and quantifying drugs of abuse in hair specimens from polydrug abusers.

5.2. Environmental contaminants

For the analysis of PBDEs and new halogenated flame retardants (HFRs) in mollusk samples, Villaverde-de-Sáa et al. [39] dispersed freeze-dried samples with the mixed-mode sorbent primary-secondary amine (PSA), while silica, acidified silica and Florisil were used as clean-up sorbents. PSA performed better in extracting the target analytes than the other tested dispersants [i.e., RP (C18), NP (silica, Florisil and alumina), and inert (diatomaceous earth) materials]. The great affinity of PSA toward the analytes reduced their recovery when higher amounts of the dispersing material were employed. The clean-up step was necessary to remove lipids and other interfering substances, but the use of an assemblage of three different sorbents complicated preparation of the SPE column.

Iparraguirre et al. [38] determined PBDEs and their metabolites (OH-PBDEs and MeO-PBDEs) for 25 compounds in soil, lettuce and carrot samples. The MSPD protocol, modified from the previous work [39], allowed fractionated extraction of PBDEs and MeO-PBDEs from OH-PBDEs and simultaneous clean-up; also, low amounts of solvent and sample were required. The main modification involved dispersion with C18 instead of PSA, because the latter showed a very strong affinity with OH-PBDEs due to the formation of hydrogen bonds between the amino groups of PSA and the hydroxyl groups of OH-PBDEs, leading to unsatisfactorily low recoveries. OH-PBDEs required derivatization before GC-MS determination with negative chemical ionization (NCI).

MSPD and QuEChERS methods are characterized by low use of organic solvents and rapidity in comparison with most of the traditional sample-preparation methods, so Rodrigues et al. [41] compared their performances in extracting five pesticides (namely dimethoate, methalaxyl-M, tebuconazole, azoxystrobin and difenoconazole) in onion samples. In particular, comparison was based on extraction time, required sample amount, solvent-volume consumption, recovery, precision, matrix effect, LOD and LOQ by LC/ESI-MS/MS determination. With both MSPD and QuEChERS, extraction yields were high; QuEChERS allowed faster extractions and lower LOQ values (2–20 times), whereas MSPD had greater ruggedness (i.e., small variations for recoveries when significant changes were applied, e.g., C18 amount, different interaction times after fortification, different elution solvents and different sorbents) and fewer matrix effects.

A Box-Behnken design was implemented to study the optimal conditions for MSPD extraction of organochlorine pesticides (OCPs) and some of their degradation products in soil [23]. Performance of the selected solvents (dichloromethane, hexane and their mixture) in extracting and eluting the analytes from soil was independent of the composition of the selected dispersing material or its weight-to-sample ratio; however, composition of the dispersing material (silica with variable percentages of C18) and its weight-to-soil ratio showed relatively strong interaction and affected the method performance. As the model showed, when the dispersant weight-to-soil ratio was set at its minimum (1:1), mixing some C18 with silica gel in the dispersant material nearly became ineffectual. However, using the highest sample-to-sorbent ratio (1:4) caused a significant difference between C18 and silica gel, considering their contribution to the overall average response of the method for all 16 analytes. Finally, dichloromethane:hexane (1:1, *v/v*) as elution solvent, 1:4 ratio of sample-to-dispersant amount and 10% C18 in silica gel were chosen to provide optimal extraction efficiency. The authors correctly commented that those optimized conditions were deduced for the geometrical average of analytes responses and hence might not lead to the best performance when individual pesticides or a different set of target analytes were considered, so the set of optimum factor levels could be considered as practical guidance only.

Wang et al. [43] performed a miniaturized MSPD extraction of pyrethroids from soil, using silica as sorbent. The extract was then cleaned up by DLLME.

For the extraction of triazine residues [44], seaweed samples were blended with C8 and cleaned using a dual layer (separated by a frit) of ENVI-CarbII/PSA as co-sorbent. ENVI-Carb has strong affinity towards planar molecules, whereas PSA can retain fatty acids, organic acids, sugars and some polar pigments. After washing the cartridge with 10-mL hexane, analytes were eluted with 25 mL of ethyl acetate:ACN. The high volume of elution solvent was probably due to the strong interaction between triazines and the graphitized carbon clean-up sorbent.

Carpinteiro et al. [21] studied various dispersants, co-sorbents and elution mixtures for extracting benzotriazoles from sediments. Inert diatomaceous earth and silica were selected for sample dispersion and clean-up, respectively. Ethyl acetate and hexane were ineffective in eluting the target analytes, whereas the highest recoveries were obtained using dichloromethane (pale yellowish extract); the mixture hexane:dichloromethane (1:1, *v/v*) gave lower extraction efficiencies, but the extract was colorless.

Diatomaceous earth was also employed for the MSPD extraction of perfluorinated compounds from mollusks [24].

A micro-MSPD protocol followed by GC-MS detection was used for the analysis of 38 cosmetic ingredients (25 fragrance allergens and 13 preservatives) in personal-care products [26]. Only 0.1 g of cosmetic sample, after dispersion with 0.4 g Florisil, was packed into a Pasteur pipette and eluted with 1 mL of ethyl acetate.

Other applications are reported in Table 1.

6. Conclusions

MSPD is a well-consolidated sample-preparation process. Many dispersant materials can be used, and classical inert, RP and NP sorbents still predominate, whereas new solid supports proposed have rarely been adopted by the scientific community. Surely, among them, MIPs are the most fascinating, because they allow selective isolation of a structurally-related group of compounds present at ultratrace levels even from a very complex matrix without MS detection. However, they also present some limits, because it is not always possible to synthesize a MIP able to interact selectively with an entire chemical class of compounds, but often the retention capability of the polymer is restricted to a few substances, and the choice of the template is one of the critical parameters in MIP design. For these reasons, multiresidual analysis of commercial classes of compounds (e.g., pharmaceutical, personal-care products, antibiotics, and pesticides) is precluded.

The optimization of experimental conditions remains an open issue in MSPD. The variables involved are too many to be treated by a simple experimental design and a compromise must be accepted between simplicity and effectiveness to maintain the ruggedness that is one of the most attractive characteristics of the technique.

Although MSPD presents some limitations, it should be kept in mind that its performance is quite similar to those of more expensive or more solvent-consuming sample-preparation techniques.

References

[1] T. Hyötyläinen, Critical evaluation of sample pretreatment techniques, Anal. Bioanal. Chem. 394 (2009) 743–758.
[2] E. Turiel, A. Martín-Esteban, Molecularly imprinted polymers for sample preparation: a review, Anal. Chim. Acta 668 (2010) 87–99.
[3] L. Ramos, Critical overview of selected contemporary sample preparation techniques, J. Chromatogr. A 1221 (2012) 84–98.
[4] Y. Wen, L. Chen, J. Li, D. Liu, Recent advances in solid-phase sorbents for sample preparation prior to chromatographic analysis, Trends Anal. Chem. 59 (2014) 26–41.
[5] M. Anastassiades, S.J. Lehotay, D. Stajnbaher, Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) approach for the determination of pesticide residues, 18th Annual Waste Testing and Quality Assurance Symposium, WTQA 2002 - Proceedings, pp. 231–241. 2003.
[6] S.A. Barker, A.R. Long, C.R. Short, Isolation of drug residues from tissues by solid phase dispersion, J. Chromatogr. 475 (1989) 353–3361.
[7] A.L. Capriotti, C. Cavaliere, A. Laganà, S. Piovesana, R. Samperi, Recent trends in matrix solid-phase dispersion, Trends Anal. Chem. 43 (2013) 53–66.
[8] A.L. Capriotti, C. Cavaliere, P. Giansanti, R. Gubbiotti, R. Samperi, A. Laganà, Recent developments in matrix solid-phase dispersion extraction, J. Chromatogr. A 1217 (2010) 2521–2532.
[9] B. Barfi, A. Asghari, M. Rajabi, A. Barfi, I. Saeidi, Simplified miniaturized ultrasound-assisted matrix solid phase dispersion extraction and high performance liquid chromatographic determination of seven flavonoids in citrus fruit juice and human fluid samples: hesperetin and naringenin as biomarkers, J. Chromatogr. A 1311 (2013) 30–40.
[10] E.M. Kristenson, L. Ramos, U.A.T. Brinkman, Recent advances in matrix solid-phase dispersion, Trends Anal. Chem. 25 (2006) 96–111.
[11] S.A. Barker, Matrix solid phase dispersion (MSPD), J. Biochem. Biophys. Methods 70 (2007) 151–162.
[12] S. Bogialli, A. Di Corcia, Matrix solid-phase dispersion as a valuable tool for extracting contaminants from foodstuffs, J. Biochem. Biophys. Methods 70 (2007) 163–179.
[13] M. García-López, P. Canosa, I. Rodríguez, Trends and recent applications of matrix solid-phase dispersion, Anal. Bioanal. Chem. 391 (2008) 963–974.
[14] J. Moreda-Piñeiro, E. Alonso-Rodríguez, P. López-Mahía, S. Muniategui-Lorenzo, D. Prada-Rodríguez, V. Romarís-Hortas, et al., Matrix solid-phase dispersion of organic compounds and its feasibility for extracting inorganic and organometallic compounds, Trends Anal. Chem. 28 (2009) 110–116.
[15] L. Ramos, Matrix solid-phase dispersion, in: J. Pawliszyn (Editor), Comprehensive Sampling and Sample Preparation, Elsevier Inc., 2012, pp. 299–310.
[16] Y. Chen, Z. Guo, X. Wang, C. Qiu, Sample preparation, J. Chromatogr. A 1184 (2008) 191–219.
[17] A. Martín-Esteban, Molecularly-imprinted polymers as a versatile, highly selective tool in sample preparation, Trends Anal. Chem. 45 (2013) 169–170.
[18] B. Socas-Rodríguez, A.V. Herrera-Herrera, M. Asensio-Ramos, J. Hernández-Borges, Recent applications of carbon nanotube sorbents in analytical chemistry, J. Chromatogr. A 1357 (2014) 110–146.
[19] Q. Liu, J. Shi, J. Sun, T. Wang, L. Zeng, N. Zhu, et al., Graphene-assisted matrix solid-phase dispersion for extraction of polybrominated diphenyl ethers and their methoxylated and hydroxylated analogs from environmental samples, Anal. Chim. Acta 708 (2011) 61–68.
[20] G. Alvarez-Rivera, T. Dagnac, M. Lores, C. Garcia-Jares, L. Sanchez-Prado, J.P. Lamas, et al., Determination of isothiazolinone preservatives in cosmetics and household products by matrix solid-phase dispersion followed by high-performance liquid chromatography-tandem mass spectrometry, J. Chromatogr. A 1270 (2012) 41–50.
[21] I. Carpinteiro, B. Abuín, M. Ramil, I. Rodríguez, R. Cela, Matrix solid-phase dispersion followed by gas chromatography tandem mass spectrometry for the determination of benzotriazole UV absorbers in sediments, Anal. Bioanal. Chem. 402 (2012) 519–527.
[22] G.N. Rallis, V.A. Sakkas, V.A. Boumba, T. Vougiouklakis, T.A. Albanis, Determination of organochlorine pesticides and polychlorinated biphenyls in post-mortem human lung by matrix solid-phase dispersion with the aid of response surface methodology and desirability function, J. Chromatogr. A 1227 (2012) 1–9.
[23] A. Salemi, E. Shafiei, M. Vosough, Optimization of matrix solid phase dispersion coupled with gas chromatography electron capture detection for determination of chlorinated pesticides in soil, Talanta 101 (2012) 504–509.
[24] E. Villaverde-De-Sáa, J.B. Quintana, R. Rodil, R. Ferrero-Refojos, E. Rubí, R. Cela, Determination of perfluorinated compounds in mollusks by matrix solid-phase dispersion and liquid chromatography-tandem mass spectrometry, Anal. Bioanal. Chem. 402 (2012) 509–518.
[25] Y. Wen, L. Chen, J. Li, Y. Ma, S. Xu, Z. Zhang, et al., Molecularly imprinted matrix solid-phase dispersion coupled to micellar electrokinetic chromatography for simultaneous determination of triazines in soil, fruit, and vegetable samples, Electrophoresis 33 (2012) 2454–2463.
[26] M. Celeiro, E. Guerra, J.P. Lamas, M. Lores, C. Garcia-Jares, M. Llompart, Development of a multianalyte method based on micro-matrix-solid-phase dispersion for the analysis of fragrance allergens and preservatives in personal care products, J. Chromatogr. A 1344 (2014) 1–14.
[27] Y. Zhu, S. Yang, G. Chen, J. Xing, Single “click” synthesis of a mixed-mode silica sorbent and application in matrix solid-phase dispersion extraction of β-agonists from porcine liver, J. Chromatogr. A 1354 (2014) 101–108.
[28] H. Zhao, N. Li, J. Li, X. Qiao, Z. Xu, Preparation and application of chitosan-grafted multiwalled carbon nanotubes in matrix solid-phase dispersion extraction for determination of trace acrylamide in foods through high-performance liquid chromatography, Food Anal. Methods (2014) doi:10.1007/s12161-014-0022-5 in press.
[29] F.G. Tamayo, E. Turiel, A. Martín-Esteban, Molecularly imprinted polymers for solid-phase extraction and solid-phase microextraction: recent developments and future trends, J. Chromatogr. A 1152 (2007) 32–40.
[30] A. Ellwanger, C. Berggren, S. Bayoudh, C. Crescenzi, L. Karlsson, P.K. Owens, et al., Evaluation of methods aimed at complete removal of template from molecularly imprinted polymers, Analyst 126 (2001) 784–792.
[31] H. Yan, F. Qiao, H.R. Kyung, Molecularly imprinted-matrix solid-phase dispersion for selective extraction of five fluoroquinolones in eggs and tissue, Anal. Chem. 79 (2007) 8242–8248.
[32] P.P. Zhan, W.J. Gong, Y.G. Zhao, Use of core-shell nanoring amino-functionalized superparamagnetic molecularly imprinted polymer for matrix solid phase dispersion extraction and preconcentration of ultratrace levels of BPA from water samples, Anal. Methods 6 (2014) 5546–5553.
[33] J. Gañán, A. Gallego-Picó, R.M. Garcinuño, P. Fernández-Hernando, S. Morante, I. Sierra, et al., Development of a molecularly imprinted polymer-matrix solid-phase dispersion method for selective determination of β-estradiol as anabolic growth promoter in goat milk, Anal. Bioanal. Chem. 403 (2012) 3025–3029.
[34] J. Gañán, S. Morante-Zarcero, A. Gallego-Picó, R. María Garcinuño, P. Fernández-Hernando, I. Sierra, Evaluation of a molecularly imprinted polymer for determination of steroids in goat milk by matrix solid phase dispersion, Talanta 126 (2014) 157–162.
[35] X. Wang, X. Qiao, Y. Ma, T. Zhao, Z. Xu, Simultaneous determination of nine trace organophosphorous pesticide residues in fruit samples using molecularly imprinted matrix solid-phase dispersion followed by gas chromatography, J. Agric. Food Chem. 61 (2013) 3821–3827.
[36] F. Qiao, J. Du, Rapid screening of clenbuterol hydrochloride in chicken samples by molecularly imprinted matrix solid-phase dispersion coupled with liquid chromatography, J. Chromatogr. B 923–924 (2013) 136–140.
[37] X. Sun, J. Wang, Y. Li, J. Yang, J. Jin, S.M. Shah, et al., Novel dummy molecularly imprinted polymers for matrix solid-phase dispersion extraction of eight fluoroquinolones from fish samples, J. Chromatogr. A 1359 (2014) 1–7.
[38] A. Iparraguirre, R. Rodil, J.B. Quintana, E. Bizkarguenaga, A. Prieto, O. Zuloaga, et al., Matrix solid-phase dispersion of polybrominated diphenyl ethers and their hydroxylated and methoxylated analogues in lettuce, carrot and soil, J. Chromatogr. A 1360 (2014) 57–65.
[39] E. Villaverde-de-Sáa, C. Valls-Cantenys, J.B. Quintana, R. Rodil, R. Cela, Matrix solid-phase dispersion combined with gas chromatography-mass spectrometry for the determination of fifteen halogenated flame retardants in mollusks, J. Chromatogr. A 1300 (2013) 85–94.
[40] M. Khajeh, H. Yan, E. Arefnejad, M. Bohlooli, Matrix solid-phase dispersion with chitosan-zinc oxide nanoparticles combined with flotation-assisted dispersive liquid-liquid microextraction for the determination of 13 n-alkanes in soil samples, J. Sep. Sci. 37 (2014) 3292–3298.
[41] S.A. Rodrigues, S.S. Caldas, M.H. Scherer Kurz, L. Da Costa Cabrera, F.A. Duarte, R. Zanella, et al., Comparison of matrix solid-phase dispersion and modified QuEChERS methods for extraction of pesticide residues from onion, Anal. Methods 4 (2012) 1820–1824.
[42] J. Li, D. Liu, T. Wu, W. Zhao, Z. Zhou, P. Wang, A simplified procedure for the determination of organochlorine pesticides and polychlorobiphenyls in edible vegetable oils, Food Chem. 151 (2014) 47–52.
[43] H. Wang, H. Yan, J. Qiao, Miniaturized matrix solid-phase dispersion combined with ultrasound-assisted dispersive liquid-liquid microextraction for the determination of three pyrethroids in soil, J. Sep. Sci. 35 (2012) 292–298.
[44] N. Rodríguez-González, M.J. González-Castro, E. Beceiro-González, S. Muniategui-Lorenzo, D. Prada-Rodríguez, Determination of triazine herbicides in seaweeds: development of a sample preparation method based on Matrix Solid Phase Dispersion and Solid Phase Extraction Clean-up, Talanta 121 (2014) 194–198.
[45] N. Negreira, I. Rodríguez, R. Rodil, E. Rubí, R. Cela, Optimization of matrix solid-phase dispersion conditions for UV filters determination in biota samples, Int. J. Environ. Anal. Chem. 93 (2013) 1174–1188.
[46] M. Míguez-Framil, P. Cabarcos, M.J. Tabernero, A.M. Bermejo, P. Bermejo-Barrera, A. Moreda-Piñeiro, Matrix solid phase dispersion assisted enzymatic hydrolysis as a novel approach for cocaine and opiates isolation from human hair, J. Chromatogr. A 1316 (2013) 15–22.
[47] Z. Wang, L. Zhang, N. Li, L. Lei, M. Shao, X. Yang, et al., Ionic liquid-based matrix solid-phase dispersion coupled with homogeneous liquid-liquid microextraction of synthetic dyes in condiments, J. Chromatogr. A 1348 (2014) 52–62.
[48] Z. Wang, R. Sun, Y. Wang, N. Li, L. Lei, X. Yang, et al., Determination of phenolic acids and flavonoids in raw propolis by silica-supported ionic liquid-based matrix solid phase dispersion extraction high performance liquid chromatography-diode array detection, J. Chromatogr. B 969 (2014) 205–212.
[49] T.D. Ho, C. Zhang, L.W. Hantao, J.L. Anderson, Ionic liquids in analytical chemistry: fundamentals, advances, and perspectives, Anal. Chem. 86 (2014) 262–285.
[50] Z.Q. Tan, J.F. Liu, L. Pang, Advances in analytical chemistry using the unique properties of ionic liquids, Trends Anal. Chem. 39 (2012) 218–227.
[51] L. Ruiz-Aceituno, M.L. Sanz, L. Ramos, Use of ionic liquids in analytical sample preparation of organic compounds from food and environmental samples, Trends Anal. Chem. 43 (2013) 121–145.

[52] L. Vidal, M.L. Riekkola, A. Canals, Ionic liquid-modified materials for solid-phase extraction and separation: a review, Anal. Chim. Acta 715 (2012) 19–41.
[53] N. Fontanals, F. Borrull, R.M. Marcé, Ionic liquids in solid-phase extraction, Trends Anal. Chem. 41 (2012) 15–26.
[54] M. Khajeh, S. Laurent, K. Dastafkan, Nanoadsorbents: classification, preparation, and applications (with emphasis on aqueous media), Chem. Rev. 113 (2013) 7728–7768.
[55] X.P. Yao, Z.J. Fu, Y.G. Zhao, L. Wang, L.Y. Fang, H.Y. Shen, Use of tetraethylenepentamine-functional Fe_3O_4 magnetic polymers for matrix solid phase dispersion extraction and preconcentration of Cr(VI) in water samples at ultratrace levels, Talanta 97 (2012) 124–130.
[56] Z. Zhong, G. Li, Y. Wu, Z. Luo, B. Zhu, Ultrasound-assisted matrix solid-phase dispersive liquid extraction for the determination of intermediates in hair dyes with ion chromatography, Anal. Chim. Acta 752 (2012) 53–61.
[57] S. Souza Caldas, C. Marian Bolzan, E. Jaime De Menezes, A. Laura Venquiaruti Escarrone, C. De Martinez Gaspar Martins, A. Bianchini, et al., A vortex-assisted MSPD method for the extraction of pesticide residues from fish liver and crab hepatopancreas with determination by GC-MS, Talanta 112 (2013) 63–68.