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Review

Solid-phase microextraction in pesticide residue analysis

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Abstract

The applications of solid-phase microextraction (SPME) for sample preparation in pesticide residue analysis are reviewed in this paper taking into account the different approaches of this technique coupled mainly to gas chromatography but also to high-performance liquid chromatography. A complete revision of the existing literature has been made considering the different applications divided according to the pesticide families (organochlorine, organophosphorus, triazines, thiocarbamates, substituted uracils, urea derivatives and dinitroanilines among others) and the sample matrices analysed which included environmental samples (water and soil), food samples and biological fluids. Details on the analytical characteristics of the procedures described in the reviewed papers are given, and new trends in the applications of SPME in this field are discussed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Solid-phase microextraction; Reviews; Pesticides

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1. Introduction

Pesticide residue analysis in environmental and biological samples has received increasing attention in the last few decades as can be deduced by the great number of papers published dealing with this subject [1]. Samples of different matrix complexity such as water, soils, food or biological fluids have been analysed in order to obtain qualitative and quantitative information on the presence of pesticides. Most applications are based on chromatographic determination, both by gas chromatography (GC) and high-performance liquid chromatography (HPLC) using the various existing detection systems. As is already known, determination of pesticides by chromatographic techniques (mainly in GC analysis)

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requires an extensive and time consuming step of sample preparation, previous to final determination, that usually includes an extraction step and a clean-up procedure in order to obtain a final extract fully compatible with the chromatographic determination. In the few last years, several papers can be found dealing with some of the new trends in pesticide residue analysis, focused mainly in the reduction of the sample preparation as this is the main source of errors and the most time consuming [2]. In this way, several authors [2–5] indicate the need for a major simplification in the sample preparation accounting for a miniaturisation in scale which will also result in a reduction of time and solvent consumption [5].

Solid-phase microextraction (SPME) appears to be a solvent-free extraction technique that presents some of the characteristics outlined before as primordial in new sample preparation strategies. The initial concepts on SPME application were published in 1989 by Belardi and Pawliszyn [6], and the following rapid development resulted in first SPME device in 1990 [7]. Finally, the SPME device based on a reusable microsyringe was commercialised in 1993 by Supelco, together with the coated fibres used for extraction, which were initially polydimethylsiloxane (PDMS) and polyacrylate (PA), and that have now extended to other coatings as Carbowax–divinylbenzene, PDMS–divinylbenzene and Carboxen–PDMS.

Since its development, SPME has been applied to the determination of several organic compounds in gas, liquid and solid samples, paying special attention to determination of volatile compounds as benzene, toluene, ethylbenzene and xylenes (BTEXs) [8] and volatile organic compounds (VOCs) [9]. Several review papers published since 1995 can be found dealing with the determination of micropollutants in environmental samples that include a section dedicated to the potential and applications of SPME pointing out its characteristics, mainly as a simple and solvent-free technique that reduces sample preparation allowing the extraction and concentration steps to be focused in a single step [2,10–12].

Accounting for the increasing introduction of the SPME technique in the analysis of organics in water, Eisert and Levsen published in 1996 a review with 55 references [13] which already included 10 references dealing with pesticide determination in water samples. Later, Eisert and Pawliszyn [14] published a paper discussing the applications and high potential of the technique, which was also compared to classical sample preparation techniques. Recently, a paper published by Prosen and Zupancic-Kralj [15] also included some applications of SPME to pesticide determination in water samples.

In 1997 Pawliszyn published a monograph entitled "Solid-Phase Microextraction – Theory and Practice" [16] which describes SPME considering both theoretical and practical aspects, as well as selected applications including some pesticide determinations. More recently two new books [17,18] dealing with SPME have appeared including in both cases special chapters dedicated to environmental analysis which included pesticide residue analysis in several matrices. It has to be pointed out that, due to the actual relevance of SPME in environmental analysis, this technique is also considered in recent books about general extraction methods [19].

The goal of this paper is to review the state of the art of SPME as an emerging technique in the field of pesticide residue analysis in different types of samples.

2. Solid-phase microextraction optimisation

As in any other solid-phase extraction (SPE)-based procedure, SPME consists of two separate stages, absorption (retention of analytes on the stationary phase) and desorption. Development of a particular procedure for determination of pesticides using the SPME technique usually requires the optimisation of the variables related to both extraction and desorption steps. In this way, most of the reviewed papers include a specific section for procedure optimisation as can be seen in Table 1, where the studied variables are listed.

As can be seen, there are several variables studied including almost inevitably fibre type, extraction time and ionic strength for the extraction step; and temperature and time in the desorption step. Most papers describe the use of polydimethylsiloxane (PDMS) and polyacrylate (PA) coatings as these were the first developed SPME fibres. Nowadays, there are a number of coatings commercially available covering a wider range of polarities (some of them such as Carbowax–divinylbenzene commer-

Table 1
Variables considered in SPME procedure optimisation

Variable	Remarks	Refs.
Extraction step		
Fibre type		[20–33]
Extraction time	30 s to 120 min	[20,23,25,27,34–37]
	up to 16 h	[24,28,38–42]
Ionic strength	NaCl 0% to saturated	[21,23,26,34,35,37–41,43]
	Other mono and divalent salts	[22]
pH	2–11 using buffer solutions	[26,35,40]
	pH 1–7	[25]
	pH 2.5,4 and 6	[37]
	pH 4–7	[42]
Temperature	4°C to 80°C	[24,28,37–39,42]
	Up to 100°C	[41,44,45]
Matrix effects	Methanol content (up to 20%)	[21,38]
	Humic acid conc. (0.1–100 mg l^{-1})	[43]
	SDS, organic matter content	[28]
Sample volume	1–2 ml	[46]
	37–153 ml	[41]
Fibre position		[47,48]
Agitation	Stirring, fibre vibration, flow	[48]
	stirring rate (0–1600 rpm)	[28]
Other	Liner dimensions	[49]
Desorption step		
Temperature	140–220°C	[20]
	240–290°C	[23]
	210–310°C	[50]
Desorption time	Up to 7 min	[23,25,50]
	Up to 60 min	[39]
Focusing oven temperature	40–100°C	[20]
Desorption solvent and volume	ACN	[39]

cialised only recently). The introduction of these new phases is due to the interest in extracting more polar compounds and its application in the SPME–HPLC technique, but it has to be pointed out that stability is a major drawback for these fibres under particular conditions.

Although in nearly every paper the effect of extraction time over extracted amount is studied (up to several hours), and the equilibrium time is determined, extraction times shorter than the equilibrium are, usually, selected due to experimental considerations [23,32,47,51]. According to the chemical characteristics of the pesticides determined, extraction efficiency can be influenced by sample pH, thus while most authors state that pH is not a controlling variable for neutral pesticides [22,26,35,38,40,42,51,52], when considering the extraction of ionizable compounds as acidic herbicides [25] or chlorophenol derivatives [50] sample pH has to be adjusted to 1 prior to SPME. Another extraction parameter whose effect is well established in other extraction techniques (liquid–liquid partition and SPE) is the salting out effect obtained by adding ionic salts to the sample. This effect has also been

studied in SPME applications mainly by addition of NaCl and alternatively divalent salts as Na_2SO_4 [22]. Most authors agree on the positive effect of the addition of NaCl to the sample over extraction efficiency of most compounds; however some discrepancies have been found and no direct relation between extraction efficiency and salt addition has been pointed out in some cases [23,34,39,41,53]. Additionally, it has been reported that high salt concentrations can led to negative effects on fibre stability when using the new Carbowax–divinylbenzene fibre [31,54]. This fibre has a limitation in the maximum NaCl content, being necessary to achieve a compromise between extraction efficiency and fibre stability (more than 100 uses have been reported working with less than 20% NaCl) [54]. Optimisation of extraction temperature is generally more important when dealing with headspace SPME [41,44,45] than when working by direct immersion of the fibre in the aqueous sample. In spite of this, in several papers the effect of extraction temperature on pesticide recoveries has been studied, showing that in particular cases it is recommended to increase the temperature to around 60°C to improve extraction of different organochlorine, organophosphorus and triazine pesticides [24,28,39,52,55].

As is already known, SPME technique is based on distribution of the analytes between two (or three) phases, and it is generally accepted that the reduction of the diffusion layer is essential in order to reach equilibrium faster, which is easily achieved by sample agitation. In this way, most applications of SPME rely on stirring of sample during absorption step. Eisert and Pawliszyn [48] made a study comparing the use of magnetic stirring, fibre vibration (using a commercial autosampler from Varian) and flow-through cell extraction for the determination of several triazine herbicides. These authors conclude that there are only small differences between the three agitation systems with similar precision in all cases, but pointing out the advantage of the fibre vibration method using the autosampler, which allows the complete automation of the SPME procedure increasing the sample throughput.

Although in most cases optimisation is carried out by a step-by-step procedure (modifying a variable at a time), Batlle et al. [55] in a recent paper described the use of a systematic approach to optimise SPME by carrying out 16 experiments working simultaneously with six experimental variables (quantitative and qualitative).

3. Application of solid-phase microextraction to pesticide residue analysis

Although the introduction of SPME was first referenced in 1989 [6] it was in 1994 when the first applications on pesticide determination appeared [47,53]. Eisert et al. [53] used a PDMS (100 μm) fibre for the extraction of six organophosphorus pesticides in Milli-Q and river water reaching detection limits in the range of low parts per billion. Popp et al. [47] published later in that year a paper dealing with the application of SPME to the determination of hexachlorocyclohexanes in aqueous samples (soil solutions). Nowadays, according to the data available through the electronic search of Analytical Abstracts database, there are around 400 references about the SPME technique, where roughly 60 of them are devoted to pesticide residue analysis. Among the different chemical classes of pesticides, organochlorine, organophosphorus and triazine compounds have received especial attention accounting for more than 70% of the references at the moment of writing this paper. In relation to the matrices to which the SPME technique has been applied, most of the papers reviewed dealt with the determination of pesticides in water samples (more than 60% of papers), although some applications to soil samples, biological fluids and foods can also be found.

3.1. Water analysis

As indicated above, most applications of SPME to the determination of pesticides residues involve extraction of water samples, not only because its environmental relevance but because the technique fits perfectly to extraction of aqueous matrices. In addition, even when other matrices different from water are studied most authors include a section dealing with water samples as a preliminary optimisation step [22,31,34,35,54].

Table 2 presents experimental details for the determination of different pesticides in aqueous samples, including ultrapure water, environmental

waters (surface and groundwater) and drinking water samples. Data on experimental conditions for SPME and analytical characteristics are also given in Table 2. Quantitation in water analysis by SPME is usually carried out by a calibration using external standards prepared with ultrapure water adding a minimum volume of pesticide standard solution (acetone or methanol) and extracting them in the same way that the sample.

As can be seen in Table 2, there is, up to now, a vast number of applications of SPME for the analysis of different type of pesticides in water samples. So, SPME could nearly be considered as a well established technique. In this sense, in 1996 a first interlaboratory study on pesticide analysis by SPME was carried out [64], with participation of 11 laboratories from Europe and North America. A total of 12 pesticides representing all main groups of compounds at low ppb levels were included in the study, using PDMS (100 μm) fibre for the extraction. Results of the test showed that SPME was an accurate and fast method of sample preparation and analysis. More recently, other interlaboratory study for the analysis of triazine herbicides and their metabolites at ppb levels in aqueous samples using SPME with CW–DVB fibres was made [29]. The repeatability and reproducibility obtained (lower than 14 and 17%, respectively) and the good accuracy of the results proved that SPME is a reliable technique for the quantitative analysis of these compounds in water at a concentration level around the European limit of 100 ng l^{-1} for individual pesticides in drinking water (detection limits between 4 and 24 ng l^{-1}).

In most papers reviewed, determination of pesticides is carried out by gas chromatography using mainly mass spectrometry (MS), electron-capture detection (ECD) and nitrogen–phosphorous detection (NPD) (although other detection systems have also been used). SPME followed by HPLC with UV detection has been applied for the analysis of organophosphorus pesticides, thiocarbamate herbicides and fungicides in water samples [39]. Eisert and Pawliszyn [61] developed an automated SPME–HPLC system called in-tube SPME, where a section of fused-silica GC column placed between the needle and the injection valve of an HPLC autosampler works as SPME fibre. In the absorption step, the water sample is repeatedly aspirated and dispensed through the SPME capillary (GC column piece); desorption is carried out by flushing the SPME capillary with a volume of organic solvent which is finally injected on-line in the HPLC system. This approach improves the SPME selectivity for polar compounds by using more polar stationary phases such as Carbowax. The technique has been applied for the determination of six phenylurea herbicides comparing three common capillary column coatings for their efficiency in extracting the pesticides. The relatively polar Omegawax 250 coating extracted the largest amount of analytes by a wide margin over the SPB-1 (similar to PDMS) and SPB-5 coatings.

Eisert and Levsen [60] have developed a fully automated quasi-continuous sampling system for online analysis. The system consists of a flow-through cell and an automated SPME unit, coupled in-line to the gas chromatograph and it has been used for the determination of triazine herbicides with good repeatability. The system combines the advantages of SPME with those of automated processing of aqueous samples as a less time-consuming, efficient and continuous technique.

Many polar, thermally unstable and/or low volatile priority pesticides cannot be directly analysed by GC and require the application of derivatisation procedures as a preliminary step to GC determination. In this sense, the combination of derivatisation and SPME has been reported [25] for the analysis of phenoxyacid herbicides using a procedure based on the derivatisation of acidic herbicides adsorbed on the fibre coating (PDMS or PA) of the SPME device with diazomethane gas. In a similar way, Nilsson et al. [36] evaluated different conditions of derivatisation (using benzyl bromide and pentafluoribenzyl bromide) and SPME followed by GC–MS for the analysis of phenoxy acid herbicides in water. The most satisfactory results corresponded to aqueous-phase derivatisation with benzyl bromide and subsequent SPME of the derivatives.

3.2. Soil samples

Determination of pesticides in soil samples by SPME has received only limited attention in the last 5 years, as only a few references on this subject could be found. Table 3 gives details on the applica-

Table 2
Applications of SPME to determination of pesticides in water samples

Pesticide group	Matrix	Fibre type	Mode of application	Determination	Procedure	LOD (µg l^{-1})	Precision (%)	Ref.
Organophosphorus pesticides	Groundwater, surface water	PDMS 100 µm	Direct immersion (manual)	GC–NPD GC–MS	4 ml stirred sample saturated with NaCl at pH 7 extracted for 20 min; desorption at 220°C for 5 min	0.03–37.5 (NPD) 0.01–8.13 (MS)	8–17	[38]
Organophosphorus pesticides	Groundwater	PDMS 100 µm PA	Direct immersion (manual)	GC–NPD	3 ml stirred sample with 15% NaCl extracted for 60 min; desorption at 270°C (PDMS) or 250°C (PA) for 4 min	0.02–0.5 (PDMS) 0.006–0.12 (PA)	7–19 (PDMS) 6–13 (PA)	[23]
Organophosphorus pesticides	Groundwater	PDMS 100 µm PA	Direct immersion (manual)	GC–NPD	3 ml stirred sample extracted for 25 min; desorption at 220°C for 5 min	0.003–0.13 (PDMS) 0.001–0.09 (PA)	0.8–10.5 (PDMS) 1.4–18.1 (PA)	[21]
Organophosphorus pesticides	River water	PDMS 100 µm	Direct immersion (manual)	GC–AED	3 ml sample extracted for 20 min; desorption at 205°C for 3 min	0.5–1 (C 193 nm) 1–5 (S 181 nm)	8–12	[53]
Organophosphorus pesticides	Tap water, sea water, wastewater	PA	Direct immersion (manual)	GC–NPD	2 ml stirred sample extracted at 60°C for 45 min; desorption at 260°C for 2 min	0.006–0.136	2–13	[28]
Organophosphorus pesticides	Groundwater, surface water	PDMS 100 µm PA	Direct immersion (manual)	GC–MS	4 ml stirred sample extracted for 50 min; desorption at 250°C for 5 min	0.001–0.05 (PDMS) 0.001–0.06 (PA)	6–13 (PDMS) 2–17 (PA)	[34]
Organophosphorus pesticides	Surface water	PA	Direct immersion (manual)	GC–FID GC–NPD GC–MS	4 ml stirred sample extracted for 45 min; desorption at 250°C for 3 min	0.25–5.2 (FID) 0.01–0.5 (NPD) 0.002–0.1 (MS)	<25% (FID, NPD) <15% (MS)	[26]
Organophosphorus pesticides	Wastewater	PA	Direct immersion (manual)	GC–MS	5 ml stirred sample saturated with NaCl extracted for 30 min; desorption at 250°C for 2 min	0.03–7.2 (SCAN) 0.003–0.09 (SIM)	3–15	[43]
Organophosphorus pesticides	Ultrapure water	PDMS–DVB 65 µm	Direct immersion (manual)	GC–FID	20 ml stirred sample extracted for 30 min; desorption at 250°C for 2 min	0.5	–	[33]
Organophosphorus pesticides	Ultrapure water	XAD 15 µm PA 85 µm PDMS 100 µm	Direct immersion (automated)	GC–NPD	1.5 ml stirred sample extracted for 30 min; desorption at 270°C (XAD), 280°C (PA) or 300°C (PDMS) for 20 min	–	7.1–82 (XAD) 7.5–170 (PA) 4.8–122 (PDMS)	[30]
Organophosphorus pesticides	Drinking water, river water	CW–DVB	Direct immersion (automated)	GC–NPD	11 ml stirred sample (pH 7 and 4 *M* NaCl) extracted for 30 min; desorption at 280°C for 2 min	0.02–0.08	6–9	[56]
Organophosphorus pesticides	Surface water	PA	Direct immersion (automated)	HPLC–UV	15 ml stirred sample with 270 g l^{-1} NaCl extracted for 180 min at 60°C; desorption with acetonitrile for 30 min	1–12	6–15	[39]
Organochlorine pesticides	Drinking water, wastewater	PDMS 100 µm	Direct immersion (manual)	GC–ECD	1.8 ml stirred sample extracted for 15 min; desorption at 260°C for 5 min	–	–	[49]
Organochlorine pesticides	Drinking water	PDMS 7 µm	Direct immersion (manual)	GC–ECD	1.2 ml sample extracted for 30 min; desorption at 280°C for 2 min	0.04–0.23	5–28	[57]
Organochlorine pesticides	Groundwater	PDMS 30 µm	Direct immersion (automated)	GC–ECD	1.5 ml stirred sample with 0.15 g NaCl extracted for 20 min; desorption at 260°C for 10 min	–	18.5 (average)	[58]
Organochlorine pesticides	River water	PDMS 100 µm	Direct immersion (manual)	GC–ECD	1.7 ml stirred sample extracted for 2 min; desorption at 250°C for 2 min	0.005–0.02	<30	[46]
Organochlorine pesticides	Groundwater, surface water	PDMS 100 µm PA	Direct immersion (manual)	GC–MS	4 ml stirred sample extracted for 90 min; desorption at 275°C for 5 min	0.0006–0.002 (PDMS) 0.0001–0.002 (PA)	2–20 (PDMS) 5–14 (PA)	[34]

Organochlorine pesticides	Surface water	PDMS 100 μm	Direct immersion (manual)	GC–FID GC–ECD GC–MS	35 ml stirred sample extracted for 90 min; desorption at 275°C for 2 min	2–9000 (FID) 0.06–4.7 (ECD) 0.02–800 (MS)	4–51 (FID) 3–20 (ECD, MS)	[40]
Organochlorine pesticides	Soil solution	PDMS 100 μm	Direct immersion (manual)	GC–ECD GC–MS	4 ml stirred sample extracted for 10 min; desorption at 200°C for 2 min	0.005–0.032 (ECD) 0.012–0.080 (MS)	–	[47]
Organochlorine pesticides	Drinking water, surface water	PA	Direct immersion (manual)	GC–MS	3.5 ml stirred sample with 5 g l^{-1} NaCl extracted for 45 min at 55°C; desorption at 250°C for 2–5 min	0.01–0.02 (SCAN) 0.001–0.005 (SIM)	6–21 (SCAN) 10–24 (SIM)	[52]
Organochlorine pesticides	Groundwater	PDMS 100 μm	Headspace (manual)	GC–ECD GC–MS	15 ml stirred sample saturated with NaCl extracted for 45 min at 87°C; desorption at 250°C for 23 min	0.003–0.06	7–21	[41]
					110 ml stirred sample saturated with NaCl extracted for 60 min at 87°C; desorption at 250°C for 23 min	0.0003–0.0011	6–15	[41]
Organochlorine pesticides	Ultrapure water	PDMS 7 μm	Direct immersion (manual)	GC–ECD	4 ml stirred sample extracted for 40 min; desorption at 250°C for 2 min	0.0015–0.125	–	[59]
Organochlorine pesticides	Drinking water, surface water	CW–DVB	Direct immersion (automated)	GC–NPD	11 ml stirred sample (pH 7 and 4 *M* NaCl) extracted for 30 min;desorption at 280°C for 2 min	0.1–0.2	6	[56]
Triazine herbicides	Groundwater	PA	Direct immersion (manual)	GC–NPD	3 ml stirred sample extracted for 25 min; desorption at 240°C for 5 min	0.01–0.09	1.3–7.1	[21]
Triazine herbicides	Groundwater, surface water	PDMS 100 μm PA	Direct immersion (manual)	GC–MS	4 ml stirred sample extracted for 50 min; desorption at 250°C for 5 min	0.004–0.023 (PDMS) 0.006–0.019 (PA)	3–37 (PDMS) 4–20 (PA)	[34]
Triazine herbicides	Surface water, sewage water	PA	Direct immersion (automated)	GC–FID GC–ECD	On line SPME: sample is pumped through the cell with the fibre for 10 min at a constant flow (300 ml min^{-1}); desorption at 300°C for 5 min	–	4–13	[60]
Triazine herbicides	Ultrapure water	PA	Direct immersion (manual)	GC–FID GC–NPD GC–MS	4 ml stirred sample extracted for 50 min; desorption at 230°C for 5 min	1–14 (FID) 0.04–6.0 (NPD) 0.0003–0.03 (MS)	9–22 (NPD) 2–14 (MS)	[35]
Triazine herbicides	Drinking water, surface water	PA	Direct immersion (manual)	GC–MS	3.5 ml stirred sample with 5 g l^{-1} NaCl extracted for 45 min at 55°C; desorption at 250°C for 2–5 min	0.02–0.2 (SCAN) 0.01–0.02 (SIM)	6–21 (SCAN) 10–24 (SIM)	[52]
Triazine herbicides	Wastewater	PA	Direct immersion (manual)	GC–MS	5 ml stirred sample saturated with NaCl extracted for 30 min; desorption at 250°C for 2 min	0.75–0.25 (SCAN) 0.007–0.01 (SIM)	3–10	[43]
Triazine herbicides	Ultrapure water	PDMS 100 μm	Direct immersion (automated)	GC–NPD	Multiple extraction (whole procedure repeated three times): 1.2 ml sample extracted for 10 min; desorption at 220°C for 5 min	–	6–20	[20]
Triazine herbicides	Groundwater, surface water	PDMS 100 μm	Direct immersion (manual)	GC–NPD GC–MS	4 ml stirred sample saturated with NaCl and at pH 7 extracted for 20 min; desorption at 220°C for 5 min	0.04–0.40 (NPD) 0.01–0.04 (MS)	7–19	[38]
Triazine herbicides	Drinking water, river water	CW–DVB	Direct immersion (automated)	GC–NPD	11 ml stirred sample (pH 7 and 4 *M* NaCl) extracted for 30 min; desorption at 280°C for 2 min	0.03–0.1	3–6	[56]

Table 2. Continued

Pesticide group	Matrix	Fibre type	Mode of application	Determination	Procedure	LOD ($\mu g\ l^{-1}$)	Precision (%)	Ref.
Triazine herbicides	Groundwater, surface water	CW–DVB	Direct immersion (manual)	GC–MS	3 ml stirred sample with 10% NaCl extracted for 30 min; desorption at 240°C for 5 min	0.02–0.06	3–13	[54]
Thiocarbamate herbicides	Ultrapure water	PA	Direct immersion (manual)	GC–FID GC–NPD GC–MS	4 ml stirred sample extracted for 50 min; desorption at 230°C for 5 min	0.8–2.0 (FID) 0.02–0.06 (NPD) 0.05–0.1 (MS)	7–13 (NPD) 10–14 (MS)	[35]
Thiocarbamate herbicides	Drinking water, surface water	CW–DVB	Direct immersion (automated)	GC–NPD	11 ml stirred sample (pH 7 and 4 *M* NaCl) extracted for 30 min; desorption at 280°C for 2 min	0.2–0.7	13–18	[56]
Thiocarbamate herbicides	Drinking water, surface water	PA	Direct immersion (manual)	GC–MS	3.5 ml stirred sample with 5 g l^{-1} NaCl extracted for 45 min at 55°C; desorption at 250°C for 2–5 min	0.08 (SCAN) 0.002 (SIM)	–	[52]
Thiocarbamate herbicides	Groundwater, surface water	PDMS 100 µm PA	Direct immersion (manual)	GC–MS	4 ml stirred sample extracted for 50 min; desorption at 250°C for 5 min	0.001–0.014 (PDMS) 0.001–0.019 (PA)	3–14 (PDMS) 7–19 (PA)	[34]
Thiocarbamate herbicides	Groundwater, surface water	PDMS 100 µm	Direct immersion (manual)	GC–NPD GC–MS	4 ml stirred sample saturated with NaCl at pH 7 extracted for 20 min; desorption at 220°C for 5 min	0.02–0.11 (NPD) 0.01–0.04 (MS)	10–25	[38]
Thiocarbamate herbicides	Surface water	PA	Direct immersion (manual)	HPLC–ECD	15 ml stirred sample with 270 g l^{-1} NaCl extracted for 180 min at 60°C; desorption time 30 min	0.1–0.5	7.1–9.0	[39]
Thiocarbamate herbicides	Groundwater, surface water	CW–DVB	Direct immersion (manual)	GC–MS	3 ml stirred sample with 10% NaCl extracted for 30 min; desorption at 240°C for 5 min	0.02	4–8	[54]
Substituted uracils herbicides	Ultrapure water	PA	Direct immersion (manual)	GC–FID GC–NPD GC–MS	4 ml stirred sample extracted for 50 min; desorption at 230°C for 5 min	15–19 (FID) 0.2–0.4 (NPD) 0.1–1.0 (MS)	10–22 (NPD) 10–13 (MS)	[35]
Substituted uracils herbicides	Groundwater, surface water	PDMS 100 µm PA	Direct immersion (manual)	GC–MS	4 ml stirred sample extracted for 50 min; desorption at 250°C for 5 min	9–10 (PDMS) 8–9 (PA)	8–17 (PDMS) 9–17 (PA)	[34]
Substituted uracils herbicides	Groundwater, surface water	CW–DVB	Direct immersion (manual)	GC–MS	3 ml stirred sample with 10% NaCl extracted for 30 min; desorption at 240°C for 5 min	0.01	5–21	[54]
Phenylurea herbicides	Distilled water	Omegawax250 SPB-5 SPB-1		HPLC–ECD	In-tube SPME; desorption with methanol	2.7–4.1	1.6–8.3	[61]
Dinitroaniline herbicides	Wastewater	PA	Direct immersion (manual)	GC–MS	5 ml stirred sample saturated with NaCl extracted for 30 min; desorption at 250°C for 2 min	0.11–2.6 (SCAN) 0.004–0.042 (SIM)	<8	[43]
Dinitroaniline herbicides	Groundwater	PA	Direct immersion (manual)	GC–NPD	3 ml stirred sample extracted for 25 min; desorption at 250°C for 5 min	0.005–0.06	2.5–8.2	[21]
Dinitroaniline herbicides	Groundwater, surface water	PDMS 100 µm PA	Direct immersion (manual)	GC–MS	4 ml stirred sample extracted for 50 min; desorption at 250°C for 5 min	0.001 (PDMS) 0.001 (PA)	6–7 (PDMS) 2–11 (PA)	[34]

Dinitroaniline herbicides	Surface water	PDMS 100 μm	Headspace (manual)	GC–ECD	1 ml stirred sample with 0.28 g Na_2SO_4 anhydrous extracted for 30 min at 70°C; desorption at 270°C for 5 min	0.1	6–10	[22]
Phenoxyacids herbicides	Ultrapure water	PDMS 100 μm PA	Direct immersion (manual)	GC–MS	25 ml stirred sample (pH 1, 5 *M* NaCl) extracted for 50 min; desorption at 250°C for 7 min; postderivatization of methylation on the fibre	0.03–1.5 (PDMS) 0.01–0.9 (PA)	<12	[25]
Phenoxyacids herbicides	Ultrapure water	PDMS–DVB 65 μm	Direct immersion (manual)	GC–MS	3 ml stirred sample (previously derivatised using benzyl bromide) extracted for 60 min; desorption at 250°C for 5 min	0.1–1	14–32	[36]
Herbicides	Wastewater	PA	Direct immersion (manual)	GC–MS	5 ml stirred sample saturated with NaCl extracted for 30 min; desorption at 250°C for 2 min	0.4–1.9 (SCAN) 0.013–0.055 (SIM)	<8	[43]
Herbicides	Groundwater, surface water	PDMS 100 μm PA	Direct immersion (manual)	GC–MS	4 ml stirred sample extracted for 50 min; desorption at 250°C for 5 min	0.001–0.013 (PDMS) 0.001–0.016 (PA)	4–9 (PDMS) 8–16 (PA)	[34]
Herbicides	Run-off water	PDMS 100 μm	Direct immersion (manual)	GC–ECD	30 ml stirred sample extracted for 15 min; desorption at 200°C for 2 min	0.002	<10	[62]
Herbicides	Ultrapure water	PA	Direct immersion (manual)	GC–FID GC–NPD GC–MS	4 ml stirred sample extracted for 50 min; desorption at 230°C for 5 min	0.2–6.0 (FID) 0.01–0.8 (NPD) 0.00001–0.015 (MS)	7–20 (NPD) 5–22 (MS)	[35]
Herbicides	Drinking water, river water	CW–DVB	Direct immersion (automated)	GC–NPD	11 ml stirred sample (pH 7, 4 *M* NaCl) extracted for 30 min; desorption at 280°C for 2 min	0.1–0.4	4–8	[56]
Herbicides	Groundwater, surface water	PDMS 100 μm	Direct immersion (manual)	GC–NPD GC–MS	4 ml stirred sample saturated with NaCl at pH 7 extracted for 20 min; desorption at 220°C for 5 min	0.13–27.25 (NPD) 0.01–2.5 (MS)	7–21	[38]
Fungicides	Groundwater, surface water	PDMS 100 μm	Direct immersion (manual)	GC–NPD GC–MS	4 ml stirred sample saturated with NaCl at pH 7 extracted for 20 min; desorption at 220°C for 5 min	0.12–950 (NPD) 0.01–3.5 (MS)	11–19	[38]
Fungicides	Wastewater	PA	Direct immersion (manual)	GC–MS	5 ml stirred sample saturated with NaCl extracted for 30 min; desorption at 250°C for 2 min	0.93–6.0 (SCAN) 0.005–0.2 (SIM)	<8	[43]
Fungicides	River water	PA	Direct immersion (automated)	GC–MS	4 ml stirred sample saturated with NaCl extracted for 45 min; desorption at 300°C for 10 min	0.05	4–18	[63]
Fungicides	River water, sea water	PA	Direct immersion (manual)	GC–MS	3 ml stirred sample with 180 g l^{-1} NaCl extracted for 60 min at 60°C; desorption at 250°C for 2 min	0.2–3.0 (SCAN) 0.05–0.08 (SIM)	12–24 (SCAN) 12–18 (SIM)	[37]
Fungicides	Surface water	PA	Direct immersion (manual)	HPLC–ECD	15 ml stirred sample with 270 g l^{-1} NaCl extracted for 180 min at 60°C; desorption time 30 min with acetonitrile	0.5–4.2	5.5–10.1	[39]

Table 3
Applications of SPME to determination of pesticides in soil samples

Pesticide group	Matrix	Fibre type	Mode of application	Determination nation	Procedure	LOD (µg kg^{-1})	Precision (%)	Ref.
Carbamate pesticides	Soil	CW–TPR	Direct immersion (manual)	HPLC–MS	Extraction over a slurry of 200 g of soil and 4 ml of water for 60 min; then desorption with 50 µl of methanol	10–1000	–	[31]
Fungicides	Soil	PA	Direct immersion (automated)	GC–MS	10 g of soil extracted with 20 ml of acetonitrile–water (70:30, v/v) for 30 min; 200 µl of supernatant diluted with 7 ml of water; 4 ml stirred sample saturated with NaCl extracted for 45 min; desorption at 300°C for 10 min	10	12–14	[63]
Herbicides, organochlorine and organophosphorus pesticides	Soil	PDMS	Direct immersion (manual)	GC–MS	0.5 g of soil with addition of 4 ml of water extracted with stirring for 50 min; desorption at 230°C for 5 min	–	–	[34]
Chloropehonol compounds	Soil	PA	Direct immersion (manual)	GC–MS	40 mg of soil dissolved to a final volume of 50 ml of pH 1 buffer solution with addition of 5 *M* KCl; 25 ml of stirred sample extracted for 40 min; desorption at 290°C for 2 min	–	5–9	[50]
Organophosphorus pesticides	Soil	PA	Headspace (manual)	GC–FID GC–MS	3.5 g of sample+3.5 ml distilled water extracted for 60 min at 80°C; desorption for 3 min at 250°C	29–143 (FID) 14–29 (MS)	5–20	[45]
Triazine herbicides	Soil	CW–TPR	Direct immersion (manual)	HPLC–MS	Extraction over a slurry of 200 g of soil and 4 ml of water for 60 min; then desorption with 50 µl of methanol	2–10	–	[31]
Herbicides	Soil	CW–DVB	Direct immersion (manual)	GC–MS	5 g of soil extracted with 5 ml of methanol using microwave heating for 1.5 min at 20% max. power; 2 ml of supernatant diluted with 18 ml of water; 3 ml stirred sample with 10% NaCl extracted for 30 min; desorption at 240°C for 5 min	1–60	3–20	[54]

tion and the analytical characteristics of the methods proposed by several authors.

Most applications are based on the preparation of a mixture of the soil with distilled water and subsequent immersion of the SPME fibre on this slurry [31,34,45,50]. Typically soil masses used in the SPME procedures are as low as 20 to 500 mg that are diluted with several millilitres of distilled water [31,34,50]. Main attention during method development is given to the negative effects of the soil matrix over the SPME efficiency and over chromatographic resolution.

On the other hand, two papers deal with the application of SPME over soil extracts in order to quantify the presence of fungicides [63] or herbicides [54] in soil samples. In this way, Crook [63] describes the application of SPME (using the polyacrylate fibre) for the determination of several fungicides in a soil extract obtained using acetonitrile and subsequent dilution of the organic extract with distilled water (35-fold dilution). Hernandez et al. [54] have applied SPME using a CW–DVB fibre to the determination of seven herbicides (triazines, molinate and bromacil) in soil samples by using a previous extraction of the sample using a microwave assisted methanol extraction and a subsequent dilution of the organic extract (10-fold dilution) with distilled water in order to decrease the organic solvent content that negatively affects to the absorption of pesticides on the fibre.

Although most applications are based on direct immersion of the fibre in the sample extract (or slurry), Ng et al. [45] have developed an SPME procedure that allows the quantitative determination of organophosphorus pesticides in soil samples by a headspace SPME technique. When the soil sample is wet with water in a 50% dilution extracted amount is increased for more than 14 times thus enhancing the sensitivity of the procedure.

Probably the slow development of SPME procedures for pesticide determination in soil samples is supported by two experimental drawbacks of the technique. Firstly, most authors [31,34,45,50,54] agree on considering that the presence of organic matter in the soil sample greatly influences the recovery of compounds from the soil. Secondly, the quantitative application of SPME to soil samples does not allow the direct use of external standard calibration curves, being necessary to use internal standard quantitation [45,50] or the standard addition procedure [31]. Anyway, the papers reviewed consider that SPME technique has great potential as a quick, simple and inexpensive screening technique for pesticide determination in soil samples.

3.3. Food samples

Table 4 presents the data corresponding to the applications of SPME for the determination of pesticides in food samples. As in other conventional procedures, SPME application requires, typically, a previous sample preparation step. Fruit samples are extracted with high speed blending using acetonitrile–water mixtures [63] or water [32,67]; liquid samples, including fruit juices (pear and orange) and wine are extracted directly as for water samples, sometimes after dilution with distilled water in order to reduce or eliminate matrix interferences [32,34,35,65,66]. Jimenez et al. [24] determine a number of organochlorine and organophosphorus pesticides in honey reducing the sample preparation step to a simple dilution with distilled water (five-times dilution). Batlle et al. [55] give data on the application of SPME to several mixtures of water–ethanol (from 0 to 95% ethanol) which are considered as food simulants in migration tests used to check the behaviour of plastic materials used for food protection.

In relation to the SPME conditions, the fibres used were mostly PDMS [24,32,34,55,65–67] and PA [35,63] carrying out the extraction manually by direct immersion of the fibre in the sample (or sample extract) at room temperature, except for honey samples which were extracted at 70°C [24].

An important point is the effect of sample matrix on the SPME efficiency, which is specially pronounced in the case of fruit (and juice fruit) samples leading to an important decrease in pesticide recovery [24,32,34,67]. Negative matrix effects can be reduced by diluting the sample with distilled water. Thus, Simplicio and Boas [32] showed that the pesticide recoveries can be much improved by diluting the samples up to a 100-fold dilution in the determination of organophosphorus pesticides in pear fruit and juice. Similar results are reported by Jimenez et al. [24] comparing the effect of five- and

Table 4
Applications of SPME to determination of pesticides in foodstuff samples

Pesticide group	Matrix	Fibre type	Mode of application	Chromatographic determination	Procedure	Detection limit ($\mu g\ l^{-1}$ or $\mu g\ kg^{-1}$)	Precision (%)	Ref.
Organochlorine pesticides	Food simulants (ethanol–water mixtures)	PDMS	Direct immersion (manual)	GC–MS		20–400	–	[55]
Organochlorine pesticides	Honey	PDMS	Direct immersion (manual)	GC–ECD	3 ml of honey–water solution (1:5) extracted under stirring for 60 min at 70°C; desorption at 260°C for 4 min	0.1–30	8–16	[24]
Organochlorine pesticides	Orange juice	PDMS	Direct immersion (manual)	GC–MS	4 ml sample extracted for 50 min with magnetic stirring; desorption for 5 min at 250°C	–	–	[34]
Organochlorine pesticides	Wine	PDMS	Direct immersion (manual)	GC–MS	30 ml stirred samples saturated with $MgSO_4$ extracted for 30 min; desorption at 250°C for 3 min	0.1–17	11–17	[65]
Organophosphorus pesticides	Food simulants (ethanol–water mixtures)	PDMS	Direct immersion (manual)	GC–MS		20–400	–	[55]
Organophosphorus pesticides	Pear fruits and juice	PDMS	Direct immersion (manual)	GC–FPD	3 ml stirred sample extracted for 20 min at room temperature; desorption for 2 min at 250°C	0.3–1.4	0.8–3.4	[32]
Organophosphorus pesticides	Honey	PDMS	Direct immersion (manual)	GC–ECD	3 ml of honey–water solution (1:5) extracted under stirring for 60 min at 70°C; desorption at 260°C for 4 min	0.1–30	8–16	[24]
Organophosphorus pesticides	Wine	PDMS	Direct immersion (manual)	GC–MS	30 ml stirred samples saturated with $MgSO_4$ extracted for 30 min; desorption at 250°C for 3 min	0.2–0.5	10–17	[65]
Triazine herbicides	Orange juice	PDMS	Direct immersion (manual)	GC–MS	4 ml sample extracted for 50 min with magnetic stirring; desorption for 5 min at 250°C	–	–	[34]
Herbicides	Wine	PA	Direct immersion (manual)	GC–MS	4 ml stirred sample extracted for 50 min; desorption at 280°C for 5 min	–	–	[35]
Herbicides	Wine	PDMS	Direct immersion (manual)	GC–MS	30 ml stirred samples saturated with $MgSO_4$ extracted for 30 min; desorption at 250°C for 3 min	0.15–0.55	11–16	[65]
Fungicides	Crops (sweet corn foilage)	PA	Direct immersion (automated)	GC–MS	5 g of prepared crop extracted with 25 ml of acetonitrile–water (35:65, v/v) by high-speed blender; 4 ml of centrifuged extract saturated with NaCl is extracted under stirring for 45 min; desorption for 10 min at 300°C	10	10–12	[63]
Fungicides	Wine	PDMS	Direct immersion (manual)	GC–MS	30 ml stirred samples saturated with $MgSO_4$ extracted for 30 min; desorption at 250°C for 3 min	0.1–5.5	9–18	[65]
Fungicides	Wine	PDMS	Direct immersion (manual)	GC–MS	3 ml stirred sample extracted for 30 min; desorption at 250°C for 3 min	0.1	3–6	[66]
Fungicides	Strawberries	PDMS	Direct immersion (manual)	GC–MS	25 g of sample extracted with 80 ml of water by high-speed blender; 4 ml of centrifuged extract is extracted under stirring for 45 min; desorption for 10 min at 270°C	0.5–50	4–89	[67]

Table 5
Applications of SPME to determination of pesticides in biological fluid samples

Pesticide group	Matrix	Fibre	Mode of application type	Chromatographic	Procedure determination	Detection limit (ng ml^{-1})	Precision (%)	Ref.
Organophosphorus pesticides	Blood, urine	PDMS	Headspace (manual)	GC–NPD	0.5 ml stirred sample with addition of 0.5 ml of water, 0.4 g NaCl, 0.4 g $(NH_4)_2SO_4$ and with pH adjusted to 3 with HCl extracted for 20 min at 100°C; desorption at 180°C for 5 min	1–50 (blood) 0.4–6 (urine)	6–10 (blood) 5–11 (urine)	[68]
Organophosphorus pesticides	Blood	PDMS	Headspace (manual)	GC–MS	0.2 g of blood with addition of 2 ml 0.1 N H_2SO_4 and 0.2 g $(NH_4)_2SO_4$ extracted for 5 min at 90°C; desorption at 250°C for 3 min	1000	4	[44]
Organochlorine pesticides	Blood	PA	Headspace (manual)	GC–ECD	0.5 ml sample with addition of 1 ml deionized water and 0.5 ml 2 *M* HCl extracted for 40 min at 100°C with stirring; desorption at 280°C for 10 min	0.08–1.6	–	[27]
Dinitroaniline herbicides	Blood, urine	PDMS	Headspace (manual)	GC–ECD	1 ml urine sample (0.5 ml blood+0.5 ml water) with addition of 0.28 g Na_2SO_4 anh. extracted with stirring for 30 min at 70°C; desorption at 270°C for 5 min	0.1 (urine) 1 (blood)	5–14 (urine) 4–9 (blood)	[22]
Organophosphorus and organochlorine pesticides	Serum	PDMS	Direct immersion (manual)	GC–NPD GC–ECD	3 ml stirred sample (serum diluted 50 times) with 15% NaCl extracted for 30 min (OPs) or 45 min (OCs); desorption at 270°C for 4 min (OPs) or at 250°C for 5 min (OCs)	2–100 (OPs) 1–23 (OCs)	2–22 (OPs) 2–11 (OCs)	[69]
Organophosphorus pesticides	Urine	PDMS	Direct immersion (manual)	GC–NPD	3 ml stirred sample (urine diluted 10 times) with 15% NaCl extracted for 30 min; desorption at 270°C for 4 min	0.06–15	4–24	[69]

50-fold dilution in the determination of organochlorine and organophosphorus pesticides in honey.

Finally, it should be stressed that when quantitative results have to be obtained the use of calibration by external standards prepared with ultrapure water (even after sample matrix dilution) is not always feasible [24,32,34,35,55]. Most authors recommend the use of either internal/surrogate standard quantitation or the standard addition method for the accurate quantitation of samples.

3.4. Biological fluid samples

Application of SPME to the determination of pesticides in biological samples (blood and urine) has not been fully implemented and only four references are reviewed in the present paper (Table 5). The most recent results obtained in our laboratory on the determination of 15 organochlorine and 10 organophosphorus pesticides in urine and serum are also discussed [69]. In the papers reviewed the mode of application selected for determining some organophosphorus [44,68] and organochlorine pesticides [27] and dinitroaniline herbicides [22] has been the headspace extraction, in order to avoid the interferences derived from these complex matrices of biological origin. However, Pitarch et al. [69] have studied the feasibility of determination of organophosphorus pesticides in urine by direct immersion of the fibre, showing the need for diluting the urine sample 10 times with distilled water in order to reduce matrix effects and achieve adequate quantitation by external standard. A similar procedure has been applied to organochlorine and organophosphorus pesticides in human serum, in this case, it was necessary to dilute the sample 50 times in order to get quantitative results by calibration using one (organophosphorus) or two surrogate standards (organochlorine) to correct peak responses [69]. Precision of the procedure applied over spiked samples (50 ng ml^{-1} for serum and 10 ng ml^{-1} for urine) were in the range of 2–11% for organochlorine in serum and 2–9% (serum) or 4–14% (urine) for organophosphorus, except for dichlorvos and azinphos methyl which showed the worst results. Even after diluting the samples, the limits of detection were in the range of 1–25 (with the exception of dichlorvos and azinphos methyl) and 2–11 ng ml^{-1} for organophosphorus and organochlorine in serum, respectively. Limits of detection (LODs) for organophosphorus in urine were in the range of 0.06 to 6 ng ml^{-1}.

Analysis of whole blood samples requires, as indicated by Guan et al. [22] and Lee et al. [68], the optimisation of the sample pre-treatment, which include the addition of distilled water (0.5 ml of blood+0.5 ml of water) in order to avoid problems of blood coagulation [22] and addition of quite high concentrations of ionic salts as 40% $(NH_4)_2SO_4$/40% NaCl [68] or 30% Na_2SO_4 anhydride [22]. Additionally, the sample pH is acidified using HCl [27,67] or H_2SO_4 [44].

The extraction of urine samples compared to that of blood samples is far more efficient leading to higher recoveries (up to 10-times higher) and, in consequence, to lower detection limits as indicated by Guan et al. [22] and Lee et al. [68], for several dinitroaniline herbicides and organophosphorus pesticides, respectively.

In these types of complex matrices the quantitation of pesticides found in real samples is carried out by using internal standard in order to obtain adequate linear responses and quantify properly taking into account the matrix interferences.

4. Conclusions

From the papers reviewed the main conclusion that can be drawn is that SPME is a recent technique that has received increasing attention since its commercial introduction in 1993, revealing itself as a powerful tool in pesticide residue analysis for both qualitative and quantitative determination.

The bulk of the efforts dedicated to method development in SPME on pesticides have been devoted to analysis of several chemical families in water samples due to its simplicity as sample matrix. Several papers can be found dealing with pesticide determination in more complex samples which include food samples (wine, fruit and juices), soil samples and biological fluids (urine, serum and blood). When samples other than water are analysed, most authors recognise the need for some sample pre-treatment in order to simplify sample matrix or reduce organic solvent content when a previous

solvent extraction is required, which are usually achieved by diluting sample extracts prior to SPME application. In SPME, as in other extraction techniques (SPE, liquid–liquid extraction, supercritical fluid extraction, etc.) dealing with complex matrix samples, accurate quantitative determination frequently requires the use of internal/surrogate standards or the application of standard additions procedure.

In relation to SPME fibres used the vast majority of work has been done using the PDMS and PA fibres, mainly due to the fact that they were the first commercially available. Nowadays, the trend is to use more polar fibres that have been recently commercialised as Carbowax–divinylbenzene, Carbowax–templated resin or Carboxen–PDMS. These fibres should allow the extraction of more polar compounds which is specially important in pesticide residue analysis for analytes different from most of organochlorine and organophosphorus pesticides. The commercialisation of new fibres is also enhancing the application of SPME to HPLC analysis by solvent elution of absorbed compounds and subsequent HPLC determination.

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