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Review

Solid-phase microextraction for herbicide determination in environmental samples

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Abstract

Liquid–liquid extraction or solid-phase extraction followed by gas chromatography (GC) or high-performance liquid chromatography are traditional herbicide residue determination methods for environmental samples. Solid-phase microextraction (SPME) is a solventless, fast, and sensitive alternative herbicide residue extraction method that can be applied to numerous environmental matrices. The objective of this paper was to review SPME literature regarding extraction theory, extraction modes, fiber types, and method optimization in conjunction with present and future SPME applications for herbicide determination in environmental samples.

Keywords: Reviews; Solid-phase microextraction; Environmental analysis; Soil; Water analysis; Pesticides

Contents

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1. Introduction

LLE and SPE have traditionally been used for herbicide residue determination in environmental samples. LLE methods require large solvent volumes and long preparation times. Conversely, SPE requires less solvent volume than LLE while offering a limited reduction in sample preparation time. The LLE and SPE restraints are minimized in SPME.

SPME was first reported by Pawliszyn and co-workers in 1990 [1,2]. It is a two-step process conducive to the simultaneous extraction and pre-concentration of analytes from sample matrices. In the first step, a fused-silica fiber coated with a polymeric stationary phase is exposed to the sample matrix where the analyte partitions between the matrix and the polymeric stationary phase. In the second step, the fiber/analyte is transferred to the analytical instrument for desorption, separation, and quantification.

The first application of SPME to herbicide residue analysis was reported in 1995 by Boyd-Boland and Pawliszyn [3] for the simultaneous determination of nitrogen-containing herbicides in soil, water, and wine samples. Since 1995, SPME methods have been used to determine 81 compounds from 15 herbicide families in numerous environmental (soil and water) and biological (blood, urine and serum) matrices. Robust SPME methods have been developed for the simultaneous determination of compounds from individual [4–11] and corporate herbicide families [3,12–17].

The advantages of SPME over traditional extraction techniques for herbicides have been documented: SPME is fast [10,11,18,19], simple [7,11,18,20], solvent-free [11,18], easily automated for both GC and HPLC instruments [16,19,21], and exhibits good linearity and sensitivity.

2. Extraction theory

SPME is based on the analyte's partitioning between an aqueous sample and a polymeric stationary phase. The absorption dynamics are described mathematically by Louch et al. [22]:

$$n = K_{fs}V_fC_0V_s/(K_{fs}V_f + V_s)$$

where n is the moles of analyte absorbed by the stationary phase, K_{fs} is the analyte partitioning coefficient between the stationary and the aqueous phase, V_f and V_s are the stationary phase and sample volumes, respectively, and C_0 is the initial analyte concentration in the aqueous phase. When $V_s \gg K_{fs}V_f$, the amount of analyte extracted by the stationary phase is independent of V_s and proportional to K_{fs} and V_f. This relationship is described as follows [22]:

$$n = K_{fs}V_fC_0$$

The quantitative basis for SPME is the linear relationship between the aqueous phase analyte concentration and the analyte amount absorbed by the fiber.

3. Extraction modes

There are currently three SPME modes that require either fused-silica fibers or GC capillary columns. Headspace (HS) and direct insertion (DI) SPME are the two fiber extraction modes, while the GC capillary column mode is referred to as in-tube SPME. Herbicides have been quantified with all three extraction modes.

Direct insertion SPME is the most common mode for herbicide analysis, and is conducted by directly inserting the fiber into the sample matrix. Sixty-seven compounds from 14 herbicide families have been quantified with DI-SPME. The mode is generally rugged and precise as demonstrated by Boyd-Boland et al. [13] who simultaneously quantified 22 compounds from eight herbicide families: chloroacetamides, diphenylether, nitroanilines, substituted uracils, substituted amides, thiocarbamates, triazines, and triazoles. The limit of detection (LOD) was between ng and sub-ng l^{-1}.

The HS-SPME mode is adapted for the analysis of volatile analytes. The primary advantage of HS-SPME is the prevention of direct fiber contact with the sample thus lowering background noise [23,24]. HS-SPME has been used to quantify herbicides in both biological and environmental matrices [7,19,25,26]. Oxadiazon in ground water, agricultural soil, must, wine and human urine samples was

quantified with HS-SPME at an LOD≥0.02 μg ml^{-1} [19]. Similarly, Namera et al. [26] analyzed butachlor, diphenamid and propanil in the headspace of human serum at an LOD≥0.25 μg ml^{-1}. Guan et al. [7] and Kumazawa et al. [25] determined six dinitroanilines and eight triazine herbicides in the headspace of human body fluids at an LOD≥18 ng ml^{-1}.

In-tube SPME is the latest mode to emerge. The method differs from fiber SPME in that analyte extraction is performed on the inner surface of a GC capillary column. The method is coupled in line with liquid chromatography. During the in-tube SPME absorption step, the aqueous sample is repeatedly aspirated and dispensed through the GC column. Desorption is achieved by flushing the capillary with a volume of organic solvent which is injected on-line into a HPLC system. The method was first developed for the identification of phenylurea herbicides in water samples [21], but has been expanded to the identification of phenoxy acid and carbamate herbicides [6].

In-tube SPME is well adapted for the determination of less volatile and/or thermally labile compounds [21], and there is a larger range of coatings available for the GC capillary columns than for the SPME fibers allowing for better analyte/coating optimization [6]. Several GC capillary columns have been evaluated for herbicide determination: DB-1, SPB-1, DB-50, SPB-5, PTE-5, Supelcowax, DB-WAX, and Omegawax 250. Phenylurea and carbamate herbicide extraction efficiencies were optimized using an Omegawax 250 GC capillary column [6,21], while the extraction efficiency of selected chlorinated phenoxy acid herbicides was maximized with a DB-WAX GC capillary column.

4. Polymeric stationary phases

Several polymeric stationary phases of varying film thicknesses and phase mixtures are commercially available (Table 1). Stationary phases are immobilized on fused-silica fibers by non-bonding, bonding, partial crosslinking, or highly crosslinking. Highly crosslinked phases differ from partially crosslinked phases in that some core bonding occurs. Non-bonded and partially crosslinked phases are more stable in water-miscible organic solvents than non-polar solvents, while bonded phases are stable in nearly all systems except for some non-polar solvents [23]. In mixed stationary phases where porous DVB microspheres are immobilized on the fiber with CW or PDMS, adsorption discrimination as a function of molecular mass is likely.

5. Solid-phase microextraction optimization

Several factors influence SPME efficiency and are evaluated during method development. Solid phase microextraction is optimized by adjusting parameters that impact analyte absorption and desorption. The primary parameters influencing analyte absorption into the stationary phase are fiber type, extraction time, ionic strength, pH, temperature, sample volume, and agitation. For SPME–GC, analyte desorption is a function of time vs. temperature. Conversely, solvent type vs. volume or time is critical for SPME–HPLC modes.

5.1. Fiber type

Nearly all reviewed articles evaluated the impact of polymeric stationary phases on SPME optimization [6–8,10,11,13,14,16,17,20,25,27–34]. Two general conclusions can be deduced from studies that optimized SPME as a function of fiber type: (i) match analyte and stationary phase polarity, (ii) sensitivity increases as stationary phase thickness increases.

Older literature indicates that PA extraction efficiency is greater than PDMS extraction efficiency for the triazine, dinitroaniline, substituted uracil, thiocarbamate, chloroacetamide, and oxadiazole herbicides [3,10,11]. With the advent of new commercially available stationary phases, this trend is less evident. Nilsson et al. [32] reported that the extraction efficiency of PDMS–DVB for phenoxy acid herbicides in aqueous matrices exceeded the extraction efficiency of PA, PDMS, and CW–DVB. The extraction efficiency of PDMS for triazines in human body fluids was greater than the extraction efficiency of CW–DVB, PA, or PDMS–DVB [25].

Table 1
Commercially available fibers and the herbicide families that have been evaluated with each fiber

SPME fiber	Film thickness (μm)	Description	Herbicide family
Polydimethylsiloxane (PDMS)	100	Nonbonded	Amides
	30	Nonbonded	Carbamates
	7	Bonded	Chloroacetamides
			Degradation products
			Dinitroanalines
			Diphenylethers
			Oxadiazole
			Phenoxy
			Pyridazinone
			Thiocarbamates
			Triazines
			Uracils
Polydimethylsiloxane–divinylbenzene (PDMS–DVB)	60	Partially crosslinked	Amides
	65	Partially crosslinked	Chloroacetamides
	65	Highly crosslinked	Atrazine metabolites
			Phenoxy
			Pyridazinone
			Thiocarbamates
			Triazines
Polyacrylate (PA)	85	Partially crosslinked	Amides
			Carbamates
			Chloroacetamides
			Degradation products
			Dinitroanalines
			Diphenylethers
			Oxadiazole
			Phenoxy
			Phenylurea
			Pyridazinone
			Thiocarbamates
			Triazines
			Uracils
Carboxen–polydimethylsiloxane (CAR–PDMS)	75	Partially crosslinked	Thiocarbamates
	85	Highly crosslinked	Triazines
			Uracils
Carbowax–divinylbenzene (CW–DVB)	65	Partially crosslinked	Amides
	70	Highly crosslinked	Chloroacetamides
			Degradation products
			Phenoxy
			Pyridazinone
			Thiocarbamates
			Triazines
Carbowax–templated resin (CW–TPR)	50	Partially crosslinked	Cyclohexene oxime
			Triazines
Divinylbenzene–Carboxen–polydimethylsiloxane (DVB–CAR–PDMS)	50/30	Highly crosslinked	Triazines

Current literature suggests that the extraction efficiency for chloroacetamides, amides, thiocarbamates, triazines, uracils, and triazine metabolites is optimized using CW–DVB [14,16,29–31]. Moder et al. [16] reported that CW–DVB has limitations including decreased extraction efficiency following 10 to 15 extraction cycles and carryover problems with some triazines/carbamates with high CW affinity.

5.2. Extraction time

Herbicide extraction time is optimized by determining the time required for an analyte to reach equilibrium between the sample matrix and the stationary phase. A graph representing the relationship between peak area and extraction time is typically reported. Generally, extraction yield increases even over relatively long exposure times. Consequently, extraction times are rarely set at equilibrium but rather at a point where sensitivity and precision are maximized over an acceptable experimental time. A broad range of extraction times are presented in the literature with values ranging from 15 to 180 min.

5.3. Ionic strength

SPME methods can be optimized by altering the ionic strength of the matrix. Typically, analyte solubility decreases as ionic strength increases. A decrease in analyte solubility improves sensitivity by promoting analyte partitioning into the stationary phase. This ‘‘salting-out’’ effect is compound-specific. Extraction efficiency decreases as ionic strength increases for phenoxy acid [8,27], dinitroanaline [3], oxadiazon [3,19], and oxyfluorofen herbicides [3]. Conversely, ionic strength either has no effect or increases extraction efficiency for triazine [3,24,26,28,29,32,34], substituted uracils [3,34], thiocarbamates [3,34,35], chloroacetamides [3,30], amides [3,30,34], profoxydim [36], bensulide [35], and bromacil herbicides [28]. Caution should be taken since high salt concentrations in the sample matrix facilitates salt deposition on the fiber which decreases extraction efficiency over time [30,36].

5.4. pH

Matrix pH can be adjusted to optimize the SPME of acidic and basic herbicides. Extraction efficiency for acidic herbicides increases as pH decreases. At low pH, the acid–base equilibria of acidic herbicides is shifted toward the neutral form and analyte partitioning into the stationary phase is enhanced. Conversely, basic herbicides shift towards the ionized form as pH decreases and extraction efficiency decreases. Varying the pH from 4 to 11 had no significant effect on extraction efficiency for triazine [26,32], nitroaniline, substituted uracil, thiocarbamate [12], chloroacetamide, diphenylether, amide, and oxadiazole herbicides [3]. However, at pH 2, extraction efficiency increased for diphenylethers and dinitroanilines [3].

5.5. Temperature

Equilibrium time and analyte partitioning into the stationary phase are inversely related to extraction temperature. Consequently, SPME methods can be optimized by selecting extraction temperatures where satisfactory sensitivity is achieved in an acceptable time period. The optimum DI-SPME extraction temperature is between 55 and 60 °C for oxadiazon [20], triazines [12], carbamates [36], and thiocarbamate herbicides [12,36,17]. For HS-SPME, the gaseous phase analyte concentration depends on the extraction temperature. The optimum extraction temperature is between 90 and 100 °C for acetamide, chloroacetamide, dinitroaniline, and triazine herbicides in blood, urine and serum samples [7,25,26].

5.6. Agitation

Extraction efficiency is associated with the analyte’s equilibration between the sample matrix and the stationary phase. Analyte equilibration time depends on the analytes mass transfer rate in the aqueous phase. Stirring and sonication enhances analyte transfer from the matrix to the stationary phase, thus reducing extraction time [3,5,8,18,20,27,30,33,36–38]. Although the equilibration time is inversely related to agitation rate, excessive agitation may adversely affect equilibration time and precision [20,23].

Table 2
Application of SPME to the determination of herbicides in soil matrices

Family	Herbicide	Fiber	Extraction	Detection	LOD (ppb)	Precision (%)	Ref.
Chloroacetamides	Metolachlor	PDMS PA	DI	GC–MS	8–9	5–16	[13]
Metabolites	DIA	PDMS PA	DI	GC–MS GC–ECD	10–15	3–10	[40]
	DEA	PDMS PA	DI	GC–MS GC–ECD	10–15	3–10	[40]
	DETB	PDMS PA	DI	GC–MS GC–ECD	10–15	3–10	[40]
Oxadiazole	Oxadiazon	PDMS PA	HS DI	GC–MS	1.00	≤13	[19,20]
Thiocarbamates	Molinate	PDMS PA CAR–PDMS CW–DVB	DI	GC–MS	10	≤10	[29]
Triazines	Ametryn	PDMS PA	DI	GC–MS GC–EDS	NA	≤20	[10,18]
	Asulam	CW–DVB CW–TPR PA	DI	HPLC–ESI-MS	1–2	≤10	[16]
	Atrazine	CW–DVB CW–TPR PA CB–PDMS PDMS	DI	HPLC–ESI-MS GC–MS GC–ECD	0.5–30	≤11	[16,18,29,40]
	Barban	CW–DVB CW–TPR PA	DI	HPLC–ESI-MS	50	≤10	[16]
	Chlorpropham	CW–DVB CW–TPR PA	DI	HPLC–ESI-MS	0.5	≤10	[16]
	Cyanazine	PDMS PA	DI	GC–MS GC–ECD	10–15	3–10	[40]
	Propazine	PDMS PA CW–DVB CW–TPR	DI	GC–MS HPLC–ESI-MS	0.3	≤20	[10,16]
	Prometryn	PDMS PA CW–DVB CW–TPR	DI	GC–MS HPLC–ESI-MS	0.1	3–20	[10,16]
	Propham	PA CW–DVB CW–TPR	DI	HPLC–ESI-MS	10	≤10	[16]
	Sebuthylazine	PDMS PA	DI	GC–MS	NA	≤12	[10]
	Simazine	PA CW–DVB CW–TPR CAR–PDMS	DI	HPLC–ESI-MS GC–MS GC–ECD	1–15	≤10	[16,29,40]

Table 2. Continued

Family	Herbicide	Fiber	Extraction	Detection	LOD (ppb)	Precision (%)	Ref.
	Terbuthylazine	PDMS PA CAR–PDMS CW–DVB	DI	GC–MS GC–ECD	NA	≤20	[10,29,40]
	Terbumeton	PDMS PA CAR–PDMS CW–DVB	DI	GC–MS	10	≤10	[29]
	Terbutryn	PDMS PA CAR–PDMS CW–DVB	DI	GC–MS	NA	≤18	[10,29]
Uracils	Bromacil	PDMS PA CAR–PDMS CW–DVB	DI	GC–MS	10	≤10	[29]

5.7. Sample volume

Solid-phase microextractions are optimized by assessing the response vs. volume-sampled relationship. Generally, the analyte amount absorbed into the stationary phase increases as sample volume increases. As a result, sensitivity increases as sample volume increases. Few studies report optimizing SPME by adjusting the sample volume. In studies where sample volume was optimized, the optimum sample volume was between 4 and 120 ml [20,38,39].

5.8. Desorption

Optimal desorption can be determined by evaluating herbicide amount desorbed following extraction of a solution with a known analyte concentration. Herbicide desorption methods differ for fiber SPME–GC, fiber SPME–HPLC, and in-tube SPME–HPLC.

Extraction time and temperature are the primary factors governing fiber-SPME–GC desorption. Gonzalez-Barreiro et al. [39] evaluated fiber SPME–GC desorption and concluded that desorption time was not statistically significant since the lower level for desorption time (15 min) was sufficient for complete alachlor desorption. Conversely, Boyd-Boland et al. [13] evaluated herbicide carryover across a range of desorption temperatures and times, concluding that optimal desorption conditions were 230 °C for 5 min. The reported range for optimal fiber SPME–GC temperatures and time periods is 200 to 300 °C and 2 to 15 min, respectively [4,5,7,11,12,14,18,25,28,30–32,38].

Three papers describe fiber SPME–HPLC desorption optimization [16,36,37]. For fiber SPME–HPLC, desorption occurs in a solvent-filled chamber where the fiber/absorbed analyte is exposed for a predetermined time period. Following desorption, the entire solvent content from the desorption chamber is flushed onto the HPLC column by means of the mobile phase. Jinno et al. [36] determined the optimal desorption time by plotting herbicide carryover vs. time. They concluded that 30 min in acetonitrile was optimal for propyzamide, thiobencarb, and bensulide desorption. Moder et al. [16] and Eisert et al. [37] reported an optimal desorption time of 5 min using methanol for several triazines and profoxydim, respectively. For in-tube SPME–HPLC, the sample is aspirated directly onto a GC capillary column, and the analyte partitions from the sample matrix into the column's stationary phase. The extracted analyte is directly desorbed from the stationary phase by mobile phase flow. The desorption step is optimized by evaluating the effect of solvent type and volume on herbicide retention

Table 3
Application of SPME to the identification of herbicides in aqueous samples

Family	Herbicide	Matrix	Fiber	Method	Detection	LOD (ppb)	Precision (%)	Ref.
Amides	Pronamide	Groundwater Surface water	PDMS	DI	GC–MS GC–NPD	0.02–0.65	12	[35]
	Propanil	Deionized-water	PA PDMS PDMS–DVB CW–DVB	DI	GC–MS GC–MS–MS	2	5–10	[31]
	Napropamide	Surface water Drinking water	PA PDMS PDMS–DVB CW–DVB	DI	GC–NPD	100–200	8	[14]
Carbamates	Barban	Deionized water	SPB-1 SPB-5 PTE-5 Supelcowax Omegawax 250	IT	HPLC–UV	7.5	1.7	[6]
	Propham	Deionized water	SPB-1 SPB-5 PTE-5 Supelcowax Omegawax 250 PA	IT DI	HPLC–UV	0.5–6	4–6	[6,36]
	Chlorpropham	Deionized water Surface water	SPB-1 SPB-5 PTE-5 Supelcowax Omegawax 250 PDMS	IT DI	HPLC–UV GC–MS GC–NPD	0.04–9	2–18	[6,35]
Chloroacetamides	Acetochlor	Deionized water Groundwater Surface water Sea water	CW–DVB PA PDMS PDMS–DVB	DI	GC–MS GC–MS–MS GC–ECD GC–FTD	0.01–18	3–12	[31,41,42]
	Alachlor	Deionized water Groundwater Surface water	DVB–CAR–PDMS PDMS–DVB CW–DVB	DI	GC–MS GC–NPD HPLC–UV GC–FTD GC–ECD	0.01–46	8–17	[15,30,35,39,41]

	Butachlor	Groundwater	CW–DVB	DI	GC–ECD	10	2	[41]
	Metolachlor	Deionized water	PDMS	HS	GC–MS	0.002–1000	2–19	[3,13–15,30,35,38,41,43]
		Groundwater	PA	DI	GC − NPD			
		Surface snow	DVB–CAR–PDMS		GC–FID			
		Ice core	PDMS–DVB		GC–ECD			
		Wine	CW–DVB		GC–FTD			
		Orange juice						
		Surface water						
	Pretilachlor	Groundwater	CW–DVB	DI	GC–ECD	0.015	3	[41]
	Propachlor	Drinking water	PDMS	HS	GC–MS	0.03–6000	5–14	[3,13,15,42]
		Groundwater	PA	DI	GC–NPD			
		Surface snow			GC–FID			
		Ice core			GC–FTD			
		Wine						
		Orange juice						
		Surface water						
		Sea water						
Cyclohexene oxime	Profoxydim	Surface water	CW–TPR	DI	HPLC–UV	<1.0	<10	[37]
Degradation products	CMP	Deionized water	PDMS	DI	GC–MS	0.2	4–7	[28]
	DCP	Deionized water	PDMS	DI	GC–MS	0.6	19–31	[28]
	DCPP	Deionized water	PDMS	DI	GC–MS	0.61	19–31	[28]
	DIA	Deionized water	DVB–CAR–PDMS	DI	GC–MS	20–44	6–34	[27,30]
		Groundwater	PDMS–DVB					
			CW–DVB					
			PA					
	DEA	Deionized water	DVB–CAR–PDMS	DI	GC–MS	0.01–40	6–19	[15,27,30]
		Groundwater	PDMS–DVB		GC–FTD			
			CW–DVB					
			PA					
	MCPA	Deionized water	PDMS	DI	GC–MS	2.3	25–56	[28]
Dinitroanilines	Benfluralin	Surface water	PDMS	HS	GC–ECD	0.1–300	4–14	[3,7,13]
		Drinking water	PA	DI	GC–MS			
		Groundwater			GC–NPD			
		Surface snow			GC–FID			
		Ice core						
		Wine						
		Orange juice						
	Ethalfluralin	Surface water	PDMS	HS	GC–ECD	0.1–120	4–7	[7]
	Fluchloralin	Surface water	PDMS	HS	GC–ECD	0.1–120	6–10	[7]
	Isopropalin	Surface water	PDMS	HS	GC–ECD	0.1–300	5–21	[3,7,13]

Table 3. Continued

Family	Herbicide	Matrix	Fiber	Method	Detection	LOD (ppb)	Precision (%)	Ref.
		Drinking water Groundwater Surface snow Ice core Wine Orange juice	PA	DI	GC–MS GC–NPD GC–FID			
	Pendimethalin	Surface water Drinking water Groundwater Surface snow Ice core Wine Orange juice	PDMS PA	HS DI	GC–ECD GC–MS GC–NPD GC–FID	0.1–200	2–17	[3,7,13]
	Prodiamine	Surface water	PDMS	HS	GC–ECD	0.1–120	14–62	[7]
	Profluralin	Drinking water Groundwater Surface snow Ice core Wine Orange juice	PDMS PA	HS DI	GC–MS GC–NPD GC–FID	0.1–200	4–7	[3,13]
	Trifluralin	Drinking water Wine Groundwater Surface snow Ice core Orange juice Surface water Sea water	PDMS PA CW–DVB PDMS–DVB	HS DI	GC–MS GC–NPD GC–FID GC–FTD GC–ECD	0.005–400	6–16	[3,13,15,41,42,44]
Diphenylethers	Oxyfluorofen	Drinking water Groundwater Surface snow Ice core Wine Orange juice	PDMS PA	HS	GC–MS GC–NPD GC–FID	6–300	8–14	[3,13]
Oxadiazole	Oxadiazon	Groundwater Drinking water Surface snow Ice core Wine Orange juice	PDMS PA	HS DI	GC–MS GC–NPD GC–FID	0.01–300	4–22	[3,13,19,20]

Phenoxy	Dicamba	Drinking water	PDMS PA	HS	GC–MS	10–110	<12	[8]
	Dichlorprop	Surface water	DB-WAX PA PDMS–DVB CW–DVB PDMS	IT HS	LC–ESI-MS GC–MS	0.01–0.2	3–18	[28,34]
	Dinoseb	Deionized water	PDMS	HS	GC–MS	150–900	<12	[27]
	MCPA	Surface water Deionized water	DB-WAX PDMS PA PDMS–DVB CW–DVB	IT HS DI	LC–ESI-MS GC–MS	0.01–750	3–12	[8,28,32,34]
	Mechlorprop	Deionized water	PDMS PA	HS DI	GC–MS	0.8–30	12–24	[8,28]
	Mecoprop	Deionized water	PDMS PA PDMS–DVB CW–DVB	HS	GC–MS	0.1	14	[32]
	2,4-D	Surface water Deionized water Drinking water	DB-WAX PDMS–DVB CW–DVB PDMS PA	IT HS	LC–ESI-MS GC–MS	0.005–1	2–32	[8,32,34]
	2,4-DB	Surface water	DB-WAX	IT	LC–ESI-MS	0.03	4–8	[34]
	2,4-DP	Drinking water	PDMS PA	HS	GC–MS	20–170	<12	[8]
	2,4,5-T	Surface water Drinking water	DB-WAX PDMS PA	IT HS	LC–ESI-MS GC–MS	0.02–1500	2–12	[8,34]
	2,4,5-TP	Surface water Drinking water	DB-WAX PDMS PA	IT HS	LC–ESI-MS GC–MS	0.02–40	3–12	[8,34]

Table 3. Continued

Family	Herbicide	Matrix	Fiber	Method	Detection	LOD (ppb)	Precision (%)	Ref.
Phenylurea	Chlorotoluron	Surface water Deionized water	PA	DI	GC–MS	0.5–1	12–30	[5]
	Diuron	Drinking water Surface water Deionized water	Omegawax 250 SPB-5 SPB-1 PA	IT DI	HPLC–UV GC–MS	0.3–2700	2–13	[5,21]
	Fluometuron	Drinking water	Omegawax 250 SPB-5 SPB-1	IT	HPLC–UV	3300	3–4	[21]
	Isoproturon	Deionized water Surface water	PA	HS DI	GC–MS	0.3	2–33	[5,45]
	Linuron	Drinking water	Omegawax 250 SPB-5 SPB-1	IT	HPLC–UV	2800	1–3	[21]
	Monuron	Drinking water	Omegawax 250 SPB-5 SPB-1	IT	HPLC–UV	3300	3–9	[21]
	Neburon	Drinking water	Omegawax 250 SPB-5 SPB-1	IT	HPLC–UV	2600	1–3	[21]
Pyridazinone	Norflurazon	Surface water Drinking water	PA PDMS PDMS–DVB CW–DVB	DI	GC–NPD	100–200	6	[14]
Pyridine	Fluroxypyr	Groundwater	CW–DVB	DI	GC–ECD	0.02	31	[41]
Thiocarbamates	Butylate	Tap water Groundwater Surface snow Ice core Surface water Wine Orange juice	PDMS PA	HS DI	GC–MS GC–NPD GC–FID	0.02–1000	3–25	[3,13,35]

	Cycloate	Deionized water Groundwater Surface snow Ice core Surface water Drinking water Wine Orange juice	PDMS PA PDMS–DVB CW–DVB	HS DI	GC–MS GC–NPD GC–FID	0.03–800	5–14	[3,13,14,35]
	EPTC	Drinking water Groundwater Surface snow Ice core Surface water Wine Orange juice Sea water	PDMS PA PDMS–DVB CW–DVB	HS DI	GC–MS GC–NPD GC–FID GC–FTD	0.01–2000	9–15	[3,13,15,35,42]
	Molinate	Groundwater Surface water Deionized water Surface snow Ice core Wine Orange juice Sea water	PDMS PA CAR–PDMS CW–DVB PDMS–DVB	DI HS	GC–MS GC–NPD GC–FID GC–FTD	0.02–2000	4–36	[3,12,13,29,35,42]
	Pebulate	Drinking water Groundwater Surface snow Ice core Wine Orange juice	PDMS PA	HS DI	GC–MS GC–NPD GC–FID	1–1000	7–13	[3,13]
	Thiobencarb	Deionized water	PA	DI	HPLC–ESI-MS HPLC–UV	0.1–161	7–12	[17,36]
	Vernolate	Drinking water Groundwater Surface snow Ice core Surface water Wine Orange juice	PDMS PA PDMS–DVB CW–DVB	HS DI	GC–MS GC–NPD GC–FID	0.02–1000	12–18	[3,13,35]
Triazines	Ametryn	Milli-Q water Groundwater Surface water Soil leachate	DVB–CAR–PDMS PDMS–DVB CW–DVB PDMS PA	DI	GC–MS GC–NPD	0.03–200	6–36	[11,12,27,30,35]

Table 3. Continued

Family	Herbicide	Matrix	Fiber	Method	Detection	LOD (ppb)	Precision (%)	Ref.
	Asulam	Soil leachate	CW–DVB CW–TPR PA	DI	HPLC–ESI-MS	1–2	1–10	[16]
	Atraton	Groundwater Surface water River water	PDMS	DI	GC–MS GC–NPD	0.04–0.4	8	[35]
	Atrazine	Groundwater Surface water Deionized water Surface snow Ice core Drinking water Wine Orange juice Beef kidney Sea water	PDMS PA CAR–PDMS CW–DVB CW–TPR DVB–CAR–PDMS PDMS–DVB	DI HS	GC–MS HPLC–ESI-MS GC–NPD GC–FID GC–TSD GC–FTD GC–ECD	0.005–7000	1–36	[3,4,12–16,27,29,30, 35,41,42,46,47]
	Barban	Soil leachate	CW–DVB CW–TPR PA	DI	HPLC–ESI-MS	50	1–10	[16]
	Cyanazine	Drinking water Groundwater	DVB–CAR–PDMS PDMS–DVB CW–DVB PA	DI	GC–MS GC–NPD	9–24	1–17	[19,27]
	Chlorpropham	Soil leachate	CW–DVB CW–TPR PA	DI	HPLC–ESI-MS	0.5	1–10	[16]
	Desmetryn	Drinking water Groundwater	DVB–CAR–PDMS PDMS–DVB CW–DVB	DI	GC–MS	9	1–9	[30]
	Hexazinone	Drinking water Groundwater Surface snow Ice core Wine Orange juice	PDMS PA	HS DI	GC–MS GC–NPD GC–FID	1–6000	4–31	[3,13]
	Metribuzin	Deionized water Groundwater Surface snow Ice core Wine Orange juice	PDMS PA DVB–CAR–PDMS PDMS–DVB CW–DVB	HS DI	GC–MS GC–NPD GC–FID GC–ECD	1–14 000	5–32	[3,13,30,33]

Prometon	Deionized water Groundwater Surface water Drinking water	DVB–CAR–PDMS PDMS–DVB CW–DVB PDMS PA	DI	GC–MS GC–NPD GC–FTD	0.005–100	1–36	[12,14,15,27,30,35]
Prometryn	Soil leachate Deionized water Groundwater Surface water Sea water	CW–DVB CW–TPR PA DVB–CAR–PDMS PDMS–DVB PDMS	DI	HPLC–ESI-MS GC–MS GC–NPD GC–FTD	0.01–17	<1–12	[11,14,16,30,35,42]
Propazine	Soil leachate Deionized water Groundwater Surface snow Ice core Surface water Wine Orange juice Sea water	CW–DVB CW–TPR PA PDMS DVB–CAR–PDMS PDMS–DVB	DI HS	HPLC–ESI-MS GC–MS GC–NPD GC–FID GC–TSD GC–FTD	0.1–10 000	1–14	[3,4,11,13,16,20,27 30,46]
Propham	Soil leachate	CW–DVB CW–TPR PA	DI	HPLC–ESI-MS	10	1–10	[16]
Sebuthylazine	Drinking water Soil leachate	PA PDMS	DI	GC–FID GC–MS	NR	<1–5	[11,46]
Simazine	Groundwater Surface water Surface snow Ice core Soil leachate Deionized water Wine Orange juice Sea water	PDMS PA CX–PDMS CW–DVB CW–TPR DVB–CAR–PDMS PDMS–DVB	DI HS	GC–MS HPLC–ESI-MS GC–NPD GC–FID GC–TSD HPLC–DAD GC–FTD	0.01–1000	1–37	[3,4,13,15–17,27,29, 30,35,42]
Simetryn	Groundwater Surface water	PDMS	DI	GC–MS GC–NPD	0.02–0.18	9	[35]

Table 3. Continued

Family	Herbicide	Matrix	Fiber	Method	Detection	LOD (ppb)	Precision (%)	Ref.
	Terbumeton	Groundwater Surface water Drinking water	PDMS PA CAR–PDMS CW–DVB DVB–CAR–PDMS PDMS–DVB	DI	GC–MS GC–ECD GC–NPD	0.04–7.2	1–14	[29,30,33]
	Terbuthylazine	Groundwater Surface water Soil leachate Wine Sea water	PDMS PA CAR–PDMS CW–DVB DVB–CAR–PDMS PDMS–DVB	DI	GC–MS GC–FID GC–FTD	0.005–5	1–20	[11,15,27,29,30,42,44,46]
	Terbutryn	Groundwater Surface water Deionized water Soil leachate	PDMS PA CAR–PDMS CW–DVB PDMS–DVB DVB–CAR–PDMS	DI	GC–MS GC–NPD	0.01–20	3–36	[11,12,29,30,35]
	Trietazine	Deionized water	PDMS	DI	GC–NPD	<0.1	5–20	[4]
Uracils	Bromacil	Drinking water Groundwater Surface water Surface snow Ice core Wine Orange juice	PDMS PA CAR–PDMS CW–DVB	HS DI	GC–MS GC–NPD GC–FID	0.1–19 000	8–22	[3,13,29]
	Terbacil	Deionized water Groundwater Surface snow Ice core Wine Orange juice	PDMS PA	HS DI	GC–MS GC–NPD GC–FID	1–15 000	10–17	[3,13]
Non-classified	Bensulide	Deionized water	PA	DI	HPLC–ESI-MS HPLC–UV	2–141	5–11	[17,36]

[6,34]. Takino et al. [34] reported that the desorption of chlorinated phenoxy acid herbicide was optimized with 10 μl of acetonitrile. Gou et al. [6] screened nine solvents for their ability to desorb carbamates. They concluded that non-polar solvents were less efficient than polar solvents at promoting herbicide desorption, and that the elution power of methanol was similar to acetonitrile.

6. Current analytical applications

6.1. Soil samples

Since 1995, the soil concentration of 21 compounds from five herbicide families has been determined using SPME methods (Table 2). Three basic methods are reported in the literature. Originally, researchers used a soil/water suspension that was sampled either by DI- or HS-SPME [3,13,16,19]. A similar method was employed by Zambonin et al. [10] where a soil/water suspension was centrifuged, and the herbicide concentration in the aqueous phase was determined by DI-SPME. Currently, the literature suggests that DI-SPME of a diluted organic extract obtained by a conventional solid–liquid extraction method is the most reliable soil SPME method [20,29].

6.2. Aqueous samples

Numerous SPME methods have been developed for herbicide determination for aqueous samples. To date, 36 articles described the quantification of 81 compounds from 14 herbicide families (Table 3). Herbicide extraction from numerous aqueous matrices including groundwater, surface water, deionized water, Milli-Q water, surface snow, ice cores, wine, orange juice, and tap water are reported. Robust SPME methods enabling the simultaneous determination of phenylurea [5], triazine [4,10,11], phenoxy [8,32], carbamate [6], and dinitroaniline herbicides [7] have been developed. Similarly, methods describing the simultaneous determination of compounds from several different herbicide families are reported [3,12–17].

7. Future analytical applications

The advantages of SPME to traditional extraction methods should facilitate advances in the field of herbicide chemistry. Researchers have reported SPME to be fast [10,11,18,19], simple [7,11,18,20], solvent-free [11,18], easily automated for both GC and HPLC instruments [16,19,20], and to exhibit good linearity and sensitivity. Conversely, SPME limitations include analyte carryover [16], fiber damage at extreme pH [33], and salt-related problems [31,37]. Furthermore, SPME sensitivity is limited in complex matrices such as blood, urine, and soil samples [7,19,25,29]. Despite these limitations, SPME will likely be adopted by applied herbicide chemists. Application areas include the following: (i) HS-SPME applied to herbicide drift, (ii) in-tube SPME–HPLC for herbicide metabolite determination in aqueous samples, (iii) DI-SPME for herbicide K_d determination. Currently, SPME has not been adopted by applied herbicide chemists as evident from the lack of SPME publications in the *Journal of Environmental Quality*, *Journal of Soil Science*, and *Weed Science*. Perhaps, this trend will be reversed in the next few years.

8. Nomenclature

CAR	Carboxen
CMP	4-chloro-2-methylphenol
CW	Carbowax
2,4-D	(2,4-dichlorophenoxy)acetic acid
DAD	diode array detection
2,4-DB	4-(2,4-dichlorophenoxy)butyric acid
2,4-DP	2-(2,4-dichlorophenoxy)propanoic acid
DCP	2,4-dichlorophenol
DCPP	dichlorprop
DEA	deethylatrazine
DETB	deethyltertbutyl
DI	direct insertion
DIA	deisopropylatrazine
DVB	divinylbenzene
ECD	electron-capture detection
EPTC	S-ethyl dipropyl carbamothiate
ESI	electrospray ionization
FID	flame ionization detection

FTD	flame thermonic detection
GC	gas chromatography
HPLC	high-performance liquid chromatography
HS	headspace
IT	inter tubular
LC	liquid chromatography
LLE	liquid–liquid extraction
MCPA	(2-methyl-4-chlorophenoxy)acetic acid
MS	mass spectrometry
NPD	nitrogen–phosphorus detection
NR	not reported
PA	polyacrylate
PDMS	polydimethylsiloxane
SPE	solid-phase extraction
SPME	solid-phase microextraction
2,4,5-T	(2,4,5-trichlorophenoxy)acetic acid
2,4,5-TP	2-(2,4,5-trichlorophenoxyl-propionic acid
TPR	templated resin
TSD	thermonic specific detection
UV	ultraviolet

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