Solid-Phase Microextraction

Khaled Murtada and Janusz Pawliszyn

Abstract Sample preparation represents a pivotal stage within the analytical workflow. This chapter delves into the latest advancements in solid-phase microextraction (SPME), a technology renowned for its ability to facilitate uncomplicated, highly sensitive, swift, and solvent-free extraction of analytes from gaseous, liquid, and solid samples. This versatile approach extends its utility to trace-level analysis of compounds even within intricate matrices. Consequently, SPME has emerged as a preeminent sample preparation technique in the past decade, frequently employed in the form of an automated fiber-injection system in conjunction with chromatographic separation modules. Its primary application pertains to the extraction of volatile and semi-volatile organic compounds.

Keywords Solid-phase microextraction · Fiber · Membrane · Headspace · Sample preparation · Solvent free

Abbreviations

SPME	Solid-phase microextraction
GC	Gas chromatography
LC	Liquid chromatography
MS	Mass spectrometry
FID	Flame ionization detector
HS	Headspace
DI	Direct immersion
LOD	Limit of detection
MOF	Metal organic framework

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COF	Covalent organic framework
PDMS	Polydimethylsiloxane
PAN	Polyacrylonitrile
DVB	divinylbenzene
MWCNTs	Multiwalled carbon nanotubes
Car	Carboxen
GO	Graphene oxide
HLB	Hydrophilic-lipophilic balance
NPs	Nanoparticles
OPPs	Organophosphorous pesticides
PAHs	Polycyclic aromatic hydrocarbons
PAEs	Phthalate esters
PCBs	Polychlorinated biphenyls
PFASs	Per- and polyfluorinated alkyl substances
PPY	Polypyrrole
PANI	Polyaniline
PAN	Polyacrylonitrile
PEG	Polyethylene glycol
PA	Polyacrylate
TF-SPME	Thin-film solid-phase microextraction
VOCs	Volatile organic compounds

1 Introduction

In recent decades, researchers in chemistry and technology communities have achieved significant advances in separation science and sample-preparation technologies. However, an efficient universal sample-pretreatment method capable of isolating target compounds from a sample matrix for instrumental analysis, irrespective of sample type and complexity or the chromatographic technique used for quantitative and qualitative analysis, remains elusive. Sample preparation is a critical component in all analytical workflows, as the clean extracts produced via such methods enable effective separation and seamless analysis, and help ensure the analytical instrument is operating under optimum working conditions [1–3].

Liquid-liquid extraction (LLE) and solid-phase extraction (SPE) are classical exhaustive sample-preparation techniques that have been successfully applied for the analysis of various samples [4–7]. Unfortunately, LLE techniques are characterized by numerous limitations, such as inadequate selectivity for target compounds, the need for large amounts of toxic organic solvents, unwanted emulsion formation, and long preparation times due to solvent evaporation and sample reconstitution. Conversely, SPE is a time-consuming, multi-step procedure that requires clean, particle-free samples, and often involves solvent evaporation and sample reconstitution in solvents, which can result in analyte loss. Moreover, the application of SPE for the isolation of polar compounds and metabolites, especially in biological samples, is limited by the availability of only a handful of suitable sorbents. Solid-phase microextraction (SPME) is an innovative sample-preparation technology that addresses many of the limitations of SPE and LLE, particularly the ability to offer high sensitivity without the use of solvent, which has led to its wide application in analytical chemistry [8–11]. SPME is an equilibrium-based extraction technique based on the migration of analytes from the sample to a sorbent material applied to a substrate via a free radical cross-linking reaction. The most widely employed sorbents in SPME devices include polydimethylsiloxane (PDMS), polyethylene glycol (PEG), polyacrylate (PA), carboxen/polydimethylsiloxane (Car/PDMS), and carboxen/divinylbenzene/polydimethylsiloxane (Car/DVB/PDMS). In SPME, sampling continues until the sorbent has reached its maximum capacity (equilibrium), at which point the device is removed and subjected to direct or indirect instrumental desorption.

The literature contains a large (and continuously growing) number of reports of novel SPME workflows developed for a wide variety of applications, including the analysis of environmental, biological, and pharmaceutical samples; the analysis of foods, beverages, flavors, and fragrances; forensic and toxicology studies; and product testing [12–19]. In recent years, several authors have published reviews/articles surveying the application of SPME in areas such as the analysis of wine volatiles, in vivo analysis of pollutants, on-site soil analysis, water sample analysis, food analysis, in vitro and in vivo metabolomics studies, and pharmaceutical and biomedical analysis [8, 9, 20–25].

This chapter provides an overview of recent, innovative work focusing on SPME. The remainder of this chapter can be divided into four primary sections. Firstly, we will introduce the core principles of SPME. Next, we will delve into recent research that has led to innovative advancements in SPME geometries and coating materials. Following that, we will provide a recap of noteworthy recent applications of SPME in the realms of food, environmental, and bioanalytical studies. Lastly, we will engage in a discourse on the prospective paths for future research and developments in the field of SPME.

2 Fundamentals

SPME operates by establishing equilibrium between the target compounds within the sample matrix and the extraction phase adhered to the SPME device's surface (as depicted in Fig. 1). In this regard, SPME shares foundational principles with electrochemical methods like potentiometry and amperometry, albeit with key distinctions, primarily in terms of capacity. This distinction is crucial because it permits SPME to be seamlessly integrated with various readout techniques such as GC or LC-MS, facilitating qualitative and quantitative analysis, particularly when employing coatings compatible with the sample matrix. Analogous to biosensors, matrix-compatible coatings adopt a membrane protection strategy, enabling their application in highly intricate samples. The comprehension and optimization of coating extraction kinetics

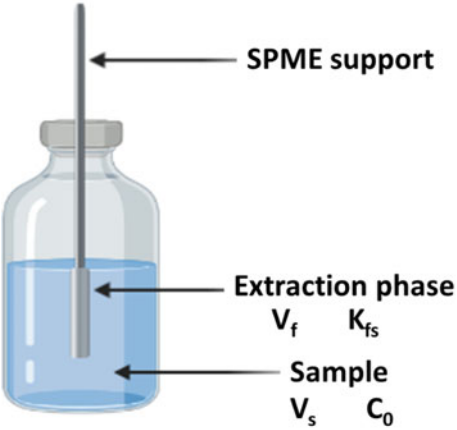

Fig. 1 V_f represents the volume of the fiber coating, K_{fs} denotes the distribution coefficient between the fiber coating and the sample, V_s represents the sample volume, and C_0 signifies the initial analyte concentration within the sample

and thermodynamics are of paramount importance, ensuring the swift accumulation of analytes and prompt pre-equilibrium determinations with the requisite sensitivity. The mass transfer of analytes from the matrix to the extraction phase can be elucidated employing Fick's second law, a second-order partial differential equation solvable via the initial and boundary conditions of the specific system under investigation [26–28].

In addition to its applicability in the analysis of organic compounds across various disciplines, SPME also enables researchers to compute the distribution coefficients of analytes between the coating material and the sample matrix. Several studies have made efforts to estimate the SPME distribution constant (K_{SPME}) and correlate it with the partition coefficient (log K_{ow}) [29–32]. However, predictions regarding the quantity of extracted compounds display variability, and as of now, there is no clear-cut relationship established between the partition coefficients and the characteristics of the analytes [33, 34].

In the context of SPME, the process is typically deemed finished when distribution equilibrium is attained between the sample matrix and the fiber coating, as described by Eq. 1. Adhering to the principles of mass conservation, particularly when only two phases are under consideration (for example, the sample matrix and the fiber coating), then

$$C_0 V_s = C_s^{\infty} V_s + C_f^{\infty} V_f \tag{1}$$

where C_0. represents the initial analyte concentration within the sample, V_s denotes the sample volume, C_s^{∞} stands for the equilibrium concentration within the sample, C_f^{∞} represents the equilibrium concentration on the coating, and V_f signifies the volume of the coating.

The distribution coefficient (K_{fs}). between the coating and the sample matrix is formally defined as:

$$K_{fs} = \frac{C_f^{\infty} V_f}{C_s^{\infty} V_s} \tag{2}$$

The quantity of analyte moles absorbed (n) by the coating when it reaches equilibrium can be succinctly expressed using Eq. (3), which results from the amalgamation of Eqs. (1) and (2):

$$n = C_f^{\infty} V_f = \frac{K_{fs} V_f V_s C_0}{K_{fs} V_f + V_s} \tag{3}$$

Here, K_{fs} represents the distribution coefficient governing the interaction between the coating and the sample matrix. Equation (4) proves useful in establishing the equilibrium state for a three-phase system, encompassing scenarios that include the headspace,

$$n = C_f^{\infty} V_f = \frac{K_{fs} V_f V_s C_0}{K_{fs} V_f + K_{hs} V_h + V_s}. \tag{4}$$

where K_{hs}. represents the distribution coefficient between the coating and the headspace. Equation (4) stipulates that the quantity of analyte extracted remains unaffected by the positioning of the fiber within the system. Therefore, the fiber can be positioned either in the headspace or directly within the sample, provided that the volumes of the fiber coating, headspace, and sample are maintained at a constant level.

The fiber constant serves as a useful metric for assessing the fiber's performance, particularly in situations involving coatings with solid particles. What makes it particularly valuable is that it doesn't necessitate data regarding the active surface area or adsorption distribution constant. For assessing mass transfer within the coating, it's advantageous to treat the entire extraction phase as a liquid phase, even when it contains particles. In this context, we use the extraction phase diffusion coefficient as the effective diffusion coefficient (D_{eff}) [35]. Equation (5), derived and adapted from theories related to mass transfer in porous media and chromatography [36], elucidates the concept of this effective diffusion coefficient.

$$D_{eff} = \frac{D_E}{1 + k} \tag{5}$$

where D_E represents the diffusion coefficient ($m^2 s^{-1}$) within a single binder material (e.g., PDMS, PAN, etc.) and k stands for the phase capacity, which denotes the extraction ratio between the composite mixed-phase sorbent (e.g., HLB/PDMS, HLB/PAN, etc.) and the extraction phase composed solely of PDMS or PAN. In the case of mixed-phase sorbents (e.g., HLB/PDMS, HLB/PAN, C_{18}/PAN, etc.), the majority of analytes tend to accumulate on the sorbent material (e.g., HLB, C_{18}, etc.), as evidenced by variations in their respective distribution constants (K).

3 Novel Developments

SPME has been studied extensively, producing a variety of different configurations. Currently, there are a variety of available SPME geometries, including: (A) fibers [14], (B) in-tube [37], (C) in-tip [38], (D) vessel wall, (E) arrow [39], (F) suspended particles [40], (G) stirrer, (H) disk, (I) thin-film [41], and (J) 96-blade configuration [42]. Figure 2 illustrates the different forms of SPME considered in this chapter.

Among the above-listed techniques, fibers can be sequenced prior to being introduced to the GC instrument, while in-tube SPME can be used for liquid chromatography. SPME arrows are an evolution of SPME fibers and can be applied for headspace analysis or direct immersion in liquid matrices [39, 43]. Thin-film solid-phase microextraction (TF-SPME) is a new geometry that has emerged as an attractive sample-preparation technique, as its high surface area-to-volume ratio—and thus, its greater volume of extraction phase—enables enhanced sensitivity without sacrificing sampling time [10, 11, 44, 45]. On the other hand, the use of 96-well plates has also received much attention due to their potential to provide high-throughput when performing multiple microextractions in parallel [46, 47]. As the above examples show, the variety of available SPME geometries allows researchers to select the

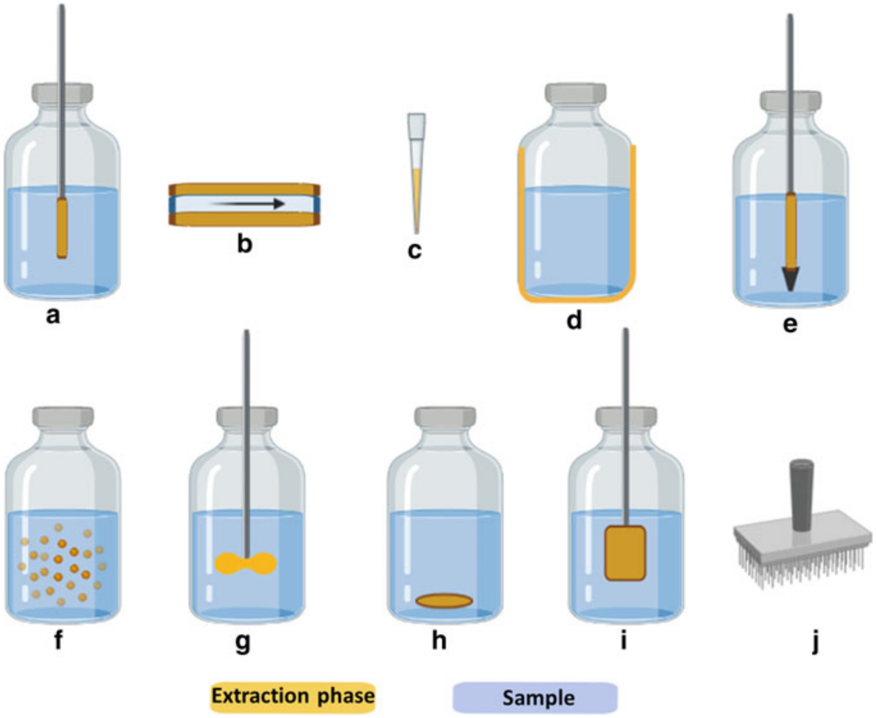

Fig. 2 Different SPME geometries

most optimal configuration for a given application. Currently, SPME fibers are the most widely used geometry due to their small size, high portability, and easy automation. Due to these advantages, the preparation of SPME fibers has been studied more extensively compared to other SPME geometries; however, these strategies can be adapted to prepare SPME devices with other configurations.

The coating's properties determine the method's analyte enrichment efficiency, and consequently, its sensitivity and reliability. Typically, extraction phases are constructed using either polymeric absorbents with liquid-like properties or solid adsorbents [48]. The extraction capabilities of liquid-like absorbents are determined by the distribution coefficient of the target analytes between the coating and the sample. In recent times, there has been a growing prevalence of solid-phase adsorbents characterized by their substantial surface areas, extensive porosities, and a profusion of interaction sites in research pertaining to SPME..

In the case of solid sorbents, analytes engage in interactions with the adsorbent surface through mechanisms such as hydrogen bonding, π-π interactions, dipole-dipole forces, electrostatic attractions, or hydrophobic/hydrophilic interactions. These various interaction types collectively exert a significant influence on both the quantity and the rate at which analyte adsorption occurs [49]. Two principles should be considered when designing an SPME coating. Firstly, there should be strong interaction between the coating materials and target analytes, as this will ensure excellent analyte enrichment. Secondly, it should be easy to firmly immobilize the coating material onto the supporting substrate. Table 1 presents an overview of recent developments in different SPME coating materials.

4 Main Applications

SPME has been applied successfully for the analysis of analytes in various samples, including organic analytes in environmental [8, 19, 112], food [113, 114], biological matrices [115–117], particularly whole blood, pharmaceuticals, and air. To date, researchers and separation experts have published several thorough reviews detailing the use of SPME for the analysis of different sample matrices and gaps that need to be addressed.

4.1 Environmental Applications

The development of effective SPME methods in the environmental field has been critical in enabling the extraction and analysis of several analytes. Various traditional SPME methods have been employed to analyze certain analytes in environmental samples, despite possessing notable limitations such as the need for a post-treatment step, higher costs, and limited efficiency [19, 112, 114]. However, despite these challenges, SPME remains the prevailing microextraction technique,

Table 1 Recent developments in SPME coating materials

Coating material	Analytes	LOD (ng L^{-1} or ng g^{-1})	Instrument	Sample matrix	Refs.
Silver	PAEs and PAHs	20–100 for PAHs; 20–50 for PAEs	GC-FID	Disposable paper cup and instant noodle barrel	[50]
Palladium	PAEs and PAHs	50–100 for PAHs; 30 for PAEs	GC-FID	Various aqueous samples	[51]
Etched stainless-steel wire	PAHs	240–630	GC-FID	River water and wastewater samples	[52]
PPY-Ag NP nanocomposite	Parabens	10	LC-UV	Water, fruit juice, and beer	[53]
Octanedithiol-functionalized Au nanoparticles	UV filters	25–56	LC-UV	River water, wastewater, and rainwater	[54]
Tungsten	Antimalarial drug	8 for pyrimethamine	High-resolution MS	Fish and paramecium	[55]
Silver nanoparticles	Monounsaturated fatty acid methyl esters	5.2	HPLC	Food	[56]
Silver nanoparticles	PAHs	60	GC-FID	Underground water	[57]
Gold nanoparticles	PAHs	10–200 (μg L^{-1})	GC-FID	Sea water	[58]
Gold nanoparticles	Aromatic hydrocarbons	8–37 for PAHs	LC-UV	Water	[59]
Anodized aluminum	Alcohols, benzene homologues, and alkanes	30–300 for alcohols	GC-FID	Gaseous samples	[60]
Anodized aluminum	Volatile compounds	–	GC-MS	Medicinal plants	[61]
Ordered nanoporous anodic alumina	VOCs	0.7–3.4	GC-MS	Human exhaled breath	[62]

(continued)

Table 1 (continued)

Coating material	Analytes	LOD (ng L^{-1} or ng g^{-1})	Instrument	Sample matrix	Refs.
Titanium dioxide nanowires	Phosphopeptides and phospholipids	≤ 25	High-resolution MS	Biological matrices	[63]
Zinc-zinc oxide	UV filters	52–84	LC-UV	Environmental water samples	[64]
Titanium dioxide@Carbon	PAHs	0.4–7.1	GC-MS	River water	[65]
Zirconium dioxide	Halophenols	201–300	GC-ECD	Wastewater	[66]
Lead (IV) oxide nanoparticles	Volatile organoselenium	11–16	GC-MS	Beverages, urine, and plasma	[67]
Nanostructured cobalt tetraoxide	Benzene homologues	1–11 (μg L^{-1})	GC-MS	Water and fruit juice	[68]
Oxidized MWCNTs	Amphetamine-type stimulants	200–1300	GC-MS	Human urine	[69]
MWCNTs/PANI-PPy@PDMS	Pesticide residues	0.39–2.49	GC-MS	Garlic	[70]
Tetraethylene-pentamine-functionalized MWCNTs	BPAs	450	UV-Vis	Water	[71]
Functionalized and carboxylated carbon nanotubes	Morphine	150	HPLC	Urine	[72]
MWCNTs/MnO_2 nanocomposite-based polythiophene	PAHs	0.1–0.8	GC	Soil	[73]
MIL-88(Fe)/GO composite	PAEs	0.5–2.0	GC	Vegetable oil	[74]
(PANI/PPy/GO) composite	VOCs	1.0–12	GC-MS	Water	[75]
Molybdenum disulfide/reduced GO	PCBs	50–90	GC-MS	Food	[76]
Hollow carbon nanobubbles	PCBs	0.0017–0.0042	GC-MS	Water	[77]
Nitrogen-doped porous biochar	Chlorobenzenes	0.007–0.079	GC	Water	[78]

(continued)

Table 1 (continued)

Coating material	Analytes	LOD (ng L^{-1} or ng g^{-1})	Instrument	Sample matrix	Refs.
Carboxylation modified mesoporous carbon aerogel	Tetracyclines	0.36–0.71	LC	Water	[79]
Large-pore ordered mesoporous carbon	PAHs	1.6–10	GC	Water	[80]
Polydopamine modified ordered mesoporous carbon	Phenols	0.08–0.38	GC-MS	Water	[81]
Nitrogen-doped porous carbon derived from g-C_3N_4 templated MOF	OPPs	0.23–7.5	GC-MS	Food	[82]
Porous carbon derived from MOF-74-C	Odorous organic contaminants	0.01–0.9	GC-MS	Water	[83]
Ni-Zn MOF	PAHs	0.1–3.0	GC-MS	Water and soil	[84]
Cd-MOF	BTEX	1–10	GC-FID	Seawater	[85]
HKUST-1	PAHs	0.12–0.99	GC-MS	Water	[86]
MOF	UV filters	0.6–2.1	GC-MS	Aqueous samples	[87]
ZIF-8, UiO-66, MIL-88, $Tb_2(BDC)_3$	PFOA	11(ZIF-8)	MS	Water	[88]
Zn-FMOF	VOCs	150–900	GC-FID	Wastewater	
	[89]				
MOF-5 and MIL-101 (Fe)	PAHs	0.0.2–0.30 for MIL-101@MON	GC-MS	Water, particulate, and food	[90]
MOFs/PANI	Chlorobenzenes	0.1–0.2	GC-MS	Water	[91]
ZIF-8	PAHs, NPAHs	0.3–27.0	GC-MS	Water	[92]
UiO-66	Polycyclic musks	0.015–0.010	GC-MS	Fortified river water	[93]

(continued)

Table 1 (continued)

Coating material	Analytes	LOD (ng L^{-1} or ng g^{-1})	Instrument	Sample matrix	Refs.
MOF-5	Volatile organic sulfur compounds	200–1700; 6000–23,800	GC-MS	Chinese chive and garlic sprouts	[94]
HKUST-1	PAHs	0.12–9.9	GC-MS	Water	[95]
(Cu-DAT) MOFs	PAHs	1.3–6.7	GC-MS	River water and living fish	[96]
TFPB-BD COF	PCBs	0.07–0.35	GC-MS/MS	Aquatic products	[97]
$TpPaBD_{50}$ COF	Tetrabromobisphenol A derivatives	0.5–12	CFDI-MS	Water	[98]
CF_3-COF	PFASs	0.0001–0.0008	UHPLC-MS/MS	Milk products	[99]
Dioxin-linked COF	PFASs	0.002–0.0045	UPLC-MS/MS	Water	[100]
$TpPaNO_2$-COF	Pesticides	0.04–0.25	GC-ECD	Fruit	[101]
TPB-DMTP-COF	Phenols	0.0048–0.015	GC-MS	Water	[102]
TpPa-1-COF	Synthetic musks	0.04–0.31	GC-MS/MS	Water	[103]
TpPa-1-COF	Polybrominated diphenyl ethers	0.0058–0.022	GC-MS	Water	[104]
TpBD-COF	PAHs	0.02–1.66	GC-MS	Grilled meat	[105]
SNW-1-COF	Phenols	0.06–0.2	GC-MS	Honey	[106]
TpBD-COF	Chlorophenols	0.3–0.7 and 0.8–1.8	GC-MS	Honey and canned yellow peaches	[107]
Hydrazine-COF	Pyrethroids	0.11–0.23	GC-ECD	Vegetable and fruit	[108]
GO/SNW-1	PAEs	10–500	GC-MS	Water and picked cucumber solution	[109]

(continued)

Table 1 (continued)

Coating material	Analytes	LOD (ng L^{-1} or ng g^{-1})	Instrument	Sample matrix	Refs.
TPT-COF	PAEs	5–95	GC-FID	Juice	[110]
COF-SCU1	Benzene homologues	0.03–0.15	GC-MS	Indoor air	[111]

and researchers are consistently exploring ways to address the mentioned limitations. The conventional commercially available SPME device comprises a fused silica or stainless-steel fiber, either coated or uncoated, with a thin sorbent layer. This fiber is typically affixed to a syringe-like device. In pursuit of enhanced extraction efficiency for environmental applications, researchers have delved into diverse strategies, encompassing the adoption of varied coating materials and alternative device configurations [118, 119]. As a result, SPME techniques have received great attention in the analytical and environmental fields due to their enhanced properties and high selectivity for certain target analytes. Commercial SPME fibers featuring non-polar or semipolar coatings fabricated from conventional and newly synthesized materials (e.g., PDMS, DVB, or Car) have been successfully employed to extract selected analytes from environmental samples. For instance, Wu et al. [120] developed and deployed two novel monolith-based electrodes for electric field assisted SPME (EFA-SPME) aimed at the simultaneous detection of phenylurea and sulfonylurea herbicides. In this work, the authors applied poly(vinylimidazole-co-ethylene dimethacrylate) and poly(methylacrylic acid co-ethylene dimethacrylate/divinylbenzene) monolith onto the surfaces of stainless steel wires, which were then respectively used as the anode and cathode for EFA-SPME. Figure 3 shows the preparation of the poly(vinylimidazole-co-ethylene dimethacrylate)-monolith-based anode and the poly(methylacrylic acid co-ethylene dimethacrylate/divinylbenzene)-monolith-based cathode, as well as the electric field assisted SPME protocol applied for the simultaneously extraction of sulfonylureas and phenylureas.

Grandy et al. [121] developed a drone-equipped TF-SPME sampler featuring HLB/PDMS membranes, enabling the remote assessment of environmental water pollutants (see Fig. 4). In order to enhance mobility, this drone-assisted sampling method was integrated with portable hand-held GC-MS instrumentation, thereby bolstering the method’s suitability for on-site sampling, extraction, and analyte identification.

In 2020 [44], our research team introduced an innovative in-vial standard gas generation system that employed thin-film membranes supported by mixed-sorbent carbon mesh as carriers for analytes. These vials were designed with carbon mesh membranes loaded with various sorbents such as pure PDMS, DVB/PDMS, HLB/PDMS, and Car/PDMS, which were subsequently spiked with modified McReynolds standards. The results obtained indicated that the TF-SPME gas generation vial exhibited comparable, and in certain instances, superior performance when compared to the PS/DVB silicone-oil-based vial (as illustrated in Fig. 5). Additionally, the TF-SPME vial boasted a much cleaner, reusable, and user-friendly design. Moreover, the outcomes also confirmed the suitability of these novel TF-SPME-based standard gas generation vials for the consistent generation of gaseous standards essential for GC-MS analysis and quality control purposes.

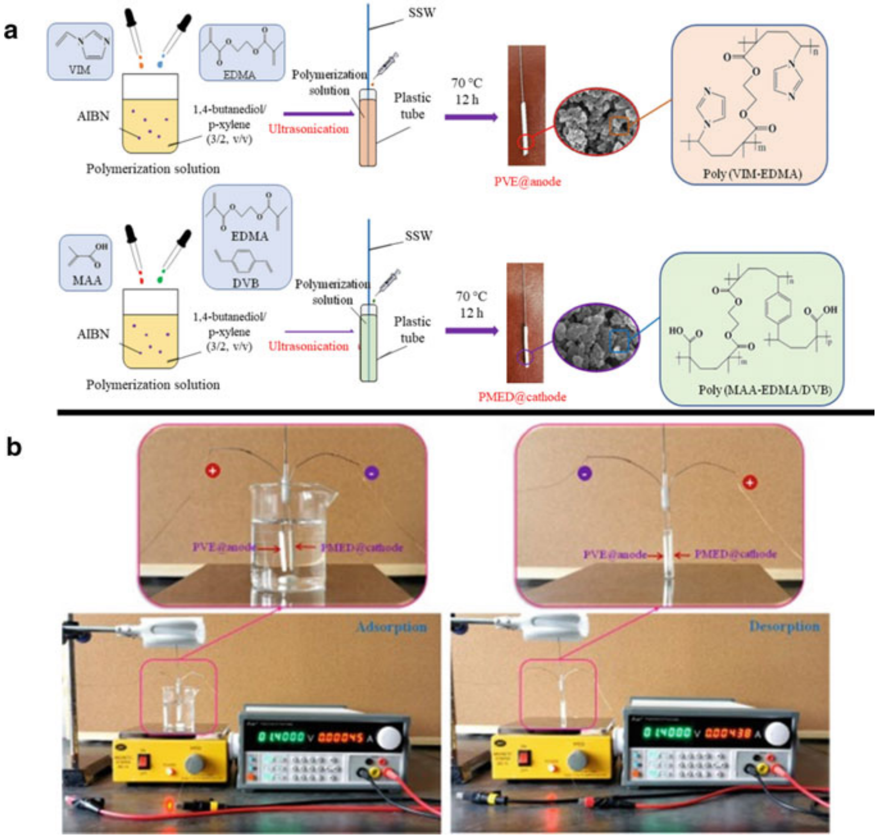

Fig. 3 **a** Synthesis of the monolithic anode using poly(vinylimidazole-co-ethylene dimethacrylate) and the cathode using poly(methylacrylic acid co-ethylene dimethacrylate/divinylbenzene). **b** Operation of the developed monolith-based electrodes/electric field assisted-SPME protocol in the adsorption and desorption steps. Reprinted with permission from [120] with permission from Elsevier

4.2 *Food Applications*

SPME has become one of the most popular methods for the pretreatment of food samples, having been applied for a range of matrices including liquids, such as milks, wines, and oils; semifluids, such as honey; and solids, such as meats, vegetables, and fruits. One reason for SPME's popularity with such samples is that it can be applied for targeted or untargeted analysis. Researchers have fabricated various SPME devices (fibers, thin films, in tube, and coated blades) using a range of functional materials and extraction models to satisfy the wide range of extraction requirements when using food samples [122–126]. Food matrices are inherently intricate, often comprising proteins, fats, salts, acids, bases, and a multitude of food additives with diverse chemical properties. Among the various coating materials studied, PDMS,

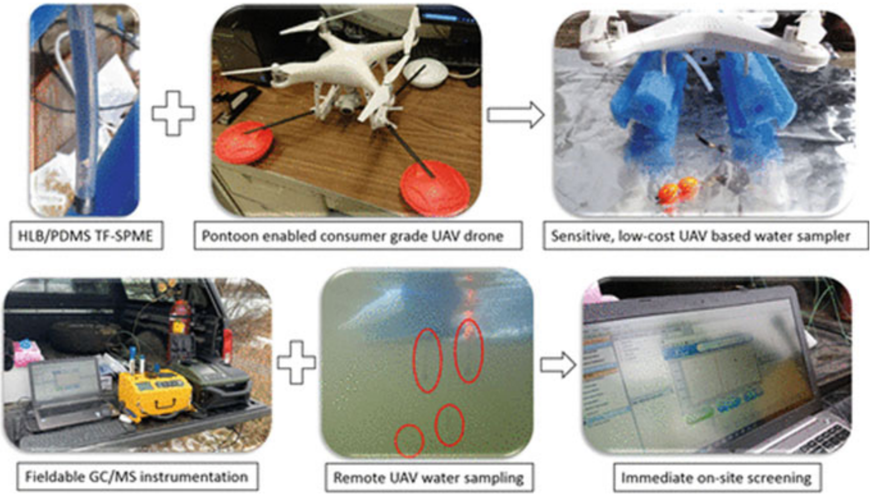

Fig. 4 Utilizing a drone-based TF-SPME system for water sampling. Reprinted from [121] with permission from American Chemical Society

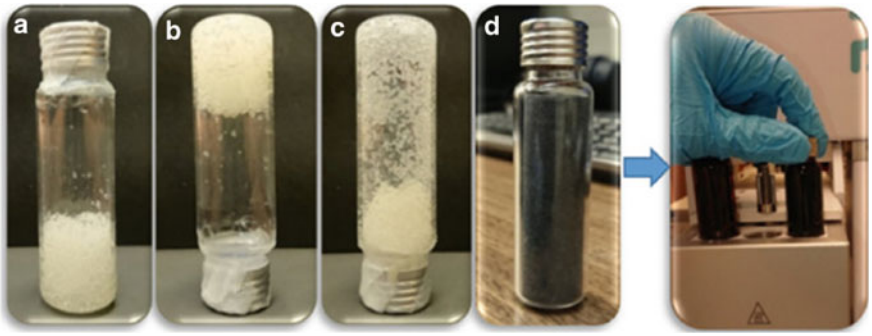

Fig. 5 Concept and rationale behind the development of dual-phase in-vial standard gas generation vials: **a** Utilization of a recently prepared silicone oil, PS/DVB vial. **b** Assessment of vial stability suitable for laboratory applications. **c** Evaluation of vial contents following agitation or transportation. **d** Deployment of DVB/PDMS-coated carbon fiber fabric as a sorbent, along with the integration of new vials into an autosampler unit. Reprinted from [44] with permission from Elsevier

characterized by its liquid nature and smooth, uniform surface, stands out for its remarkable resilience to irreversible fouling effects triggered by matrix components (as compared to solid coatings) [127], Consequently, it emerges as the most robust choice for the direct analysis of food samples. Nevertheless, PDMS's susceptibility to analytes of interest has posed a significant challenge. To address this limitation, researchers have explored the enhancement of conventional commercial SPME fiber coatings by incorporating a thin PDMS layer, thus creating a novel matrix-compatible coating that preserves the original coating's sensitivity to the target analytes [128]. As depicted in Fig. 6, these modified SPME fiber coatings, such as PDMS/DVB, DVB/Car/PDMS, and PDMS/DVB/PDMS, exhibit exceptional extraction efficiency and durability, rendering them highly effective for the direct analysis of complex matrices [128]. As a result, these PDMS-modified coatings have risen to prominence as the preferred choices for SPME in food analysis. Moreover, researchers have also devised innovative SPME fiber coatings, which we will delve into further in the subsequent section.

Chen et al. drew upon sampling rate correction theory to develop a non-invasive *in-vivo* sampling-rate-calibrated SPME-GC/MS method for the accurate quantification of target analytes [129]. The researchers employed their methodology directly on-site to observe and analyze the environmental dynamics, encompassing absorption, enrichment, migration, and elimination processes, of three insecticides (hexachlorobenzene, fipronil, and chlorfenapyr) within edible plants, specifically garlic bulbs and leaf sheaths. Additionally, they investigated the kinetics of these insecticides' elimination within living garlic plants. Figure 7 illustrates a schematic representation of Chen et al.'s in vivo SPME procedure. In this in vivo SPME

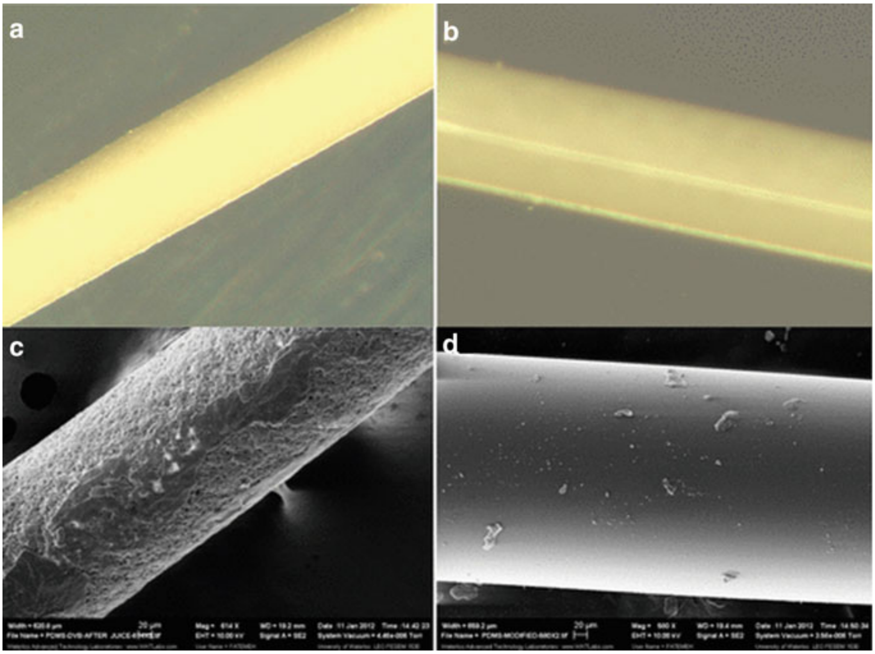

Fig. 6 **a** Microscopic image depicting a commercial PDMS/DVB coating in its pre-extraction state. **b** Microscopic image showing a PDMS/DVB/PDMS coating before any extraction. **c** Scanning Electron Microscope (SEM) image revealing the surface of a PDMS/DVB coating after undergoing 20 extraction cycles within grape juice. **d** SEM image depicting the surface morphology of a PDMS/DVB/PDMS coating after enduring more than 130 extraction cycles in grape juice, observed at 580× magnification. Reprinted from [128] with permission from the American Chemical Society

sampling method, an SPME fiber was inserted directly into the garlic bulbs or leaf sheaths, reaching a depth of approximately 1.5 cm while being shielded by an external cannula. Following a static extraction period of 25 min at a temperature of 25 °C, the probe was carefully withdrawn, washed with deionized water, wiped clean with Kimwipes, and promptly prepared for analysis using GC/MS.

The ability to detect spoilage and nutrient content in salmon is critical for ensuring it is safe to consume and determining its market value. To this end, Yu et al. [39] developed and fabricated an innovative SPME arrow coated with HLB/PDMS, which was subsequently integrated with GC-MS for the untargeted assessment of volatile metabolites and unsaturated fatty acids within fresh salmon samples. This newly developed device was effectively employed in two distinct operational modes, specifically headspace (HS) and direct immersion (DI) (as depicted in Fig. 8). As a result, it emerged as an excellent solution for real-time monitoring of salmon spoilage mechanisms and the comprehensive analysis of essential nutrients present in salmon fillets.

The application of ambient mass spectrometry techniques for pesticide analysis in produce, along with the validation of these techniques through chromatographic separation, has not received extensive exploration. In one of the few existing studies, Kasperkiewicz and Pawliszyn developed a coated blade spray (CBS) protocol to quantitate multiresidue pesticide levels in various fruit matrices [130]. In CBS, sampling, sample preparation, and introduction to analytical instrumentation is consolidated into a single device consisting of a polymeric sorbent coated onto a conductive support [131, 132]. The use of CBS allowed the authors to couple

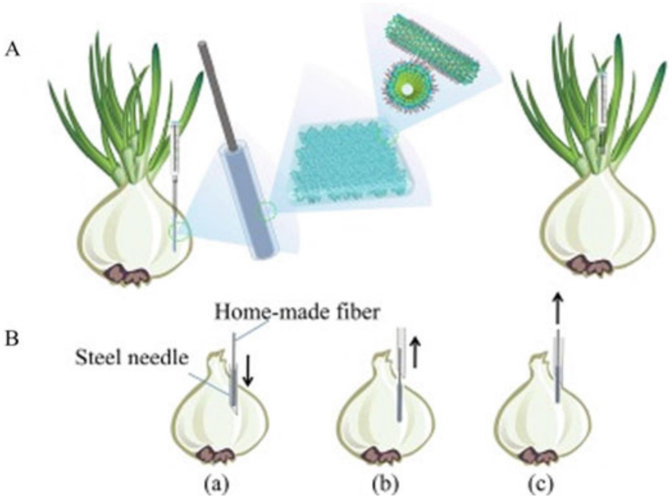

Fig. 7 **A** Real-time sampling within garlic bulbs and leaf sheaths. **B** In vivo SPME procedure: (*a*) Gently introduce the custom-made fiber into the garlic with the safeguard of a steel needle, (*b*) Extract analytes in vivo by carefully withdrawing the steel needle, (*c*) Retrieve the extracted fiber afterward. Reprinted from [129] with permission from Elsevier

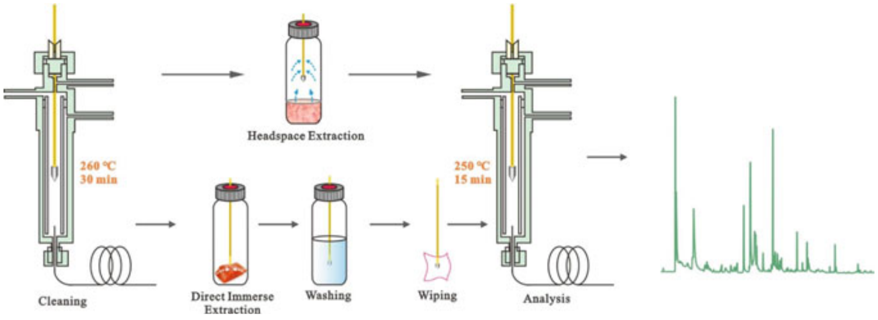

Fig. 8 Headspace and direct immersion SPME protocols. Reprinted from [39] with permission from Elsevier

the devices directly to mass spectrometry (MS) and liquid chromatography (LC) to perform multiresidue (e.g., organophosphates, organonitrogen, carbamates, neonicotinoids, strobilurins, triazines, spinosyns) analysis for a panel of pesticides in apple, blueberry, grape, and strawberry samples. Figure 9 shows the CBS-MS/MS and SPME-LC–MS/MS workflows to quantitatively assess 126 pesticides in apples, 139 pesticides in blueberries, 136 pesticides in grapes, and 135 pesticides in strawberries, as well as their analytical figures of merit, analytical properties (e.g., solvent usage, analysis time), and real-world sample quantification.

4.3 Biological Applications

Conducting direct-immersion SPME within complex matrices can be challenging. Generally, some form of sample pre-treatment is required to safeguard the coating and avert extraction phase fouling, which can result from the irreversible adsorption of large molecules present in the intricate matrix. This irreversible adsorption not only significantly shortens the fiber's operational lifespan (often limiting it to just a few samplings) but also alters the coating's extraction characteristics. Consequently, researchers are persistently exploring novel SPME coatings with enhanced performance capabilities for direct extractions from complex matrices.

The development of biocompatible coatings was a major breakthrough with respect to biological applications coupling SPME and LC/MS analysis. Within SPME, a biocompatible coating is characterized by its ability to (i) avoid eliciting toxic responses within the studied system and (ii) prevent the attachment of macromolecules, such as proteins, onto its surface [133]. To address the aforementioned biocompatibility issues, researchers have investigated coatings based on polyethylene glycol (PEG) [134], polypyrrole (PPY) [134, 135], restricted access materials (RAM) [136], and mixtures of SPE sorbents (coated silica particles) and biocompatible polymers [137]. As an illustration, Musteata et al. [135] utilized SPME fibers

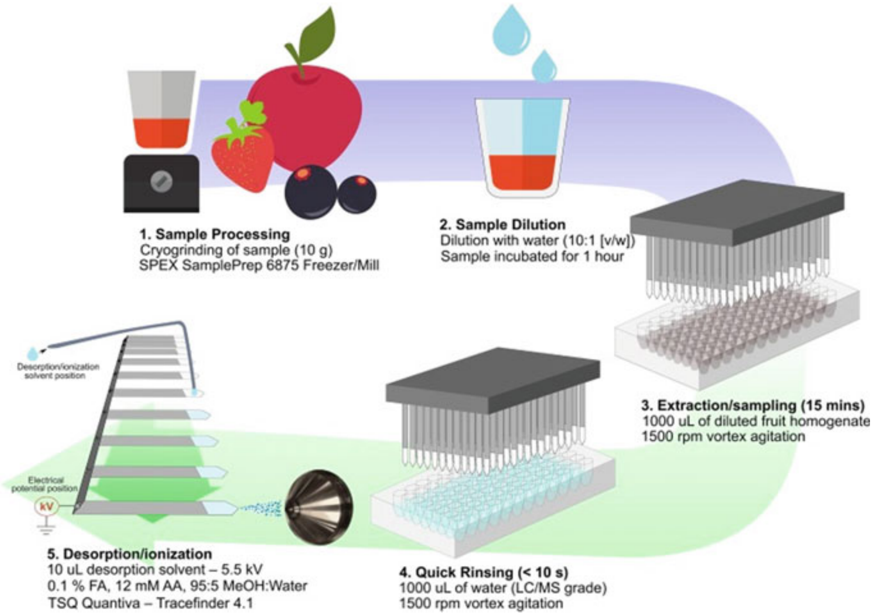

Fig. 9 The process for analyzing pesticides in fruit matrices (steps 1–4) was also utilized for CBS-MS/MS analysis (step 5). The LC-MS/MS protocol followed the identical sample-preparation workflow (steps 1–4). Reprinted from [130] with permission from Elsevier

featuring PPY/PEG and PEG/C_{18}-bonded coatings to directly extract diazepam and its metabolite from the circulating blood of beagle dogs.

In other work, scientists created novel biocompatible SPME fiber coatings through the amalgamation of polyacrylonitrile (PAN) with diverse extraction particles (including C_{18}, RP-amide-silica, HS-F5-silica, 5 μm). They subsequently assessed the efficiency of these coatings in extracting five distinct drugs from human plasma. [137]. In addition to biocompatibility and improved durability, the developed fibers offered significantly better extraction efficiency for the targeted drugs compared to PPY, RAM, and commercial CW/TPR coatings. Similarly, Mirnaghi et al. developed a method for preparing biocompatible C_{18}-PAN (polyacrylonitrile) thin-film coatings ("blades") for the direct extraction of small molecules from biological fluids [138]. Elsewhere, Sinha Roy et al. [42] developed a protocol enabling the high-throughput analysis of free concentrations of a panel of drugs in plasma, as well as the protein binding of a selection of substances with wide-ranging properties in order to elucidate the underlying principles of SPME technology. The chosen microsampling preparation device supported by plastic comprised 96 pins (as depicted in Fig. 10), each coated with a minimal quantity of matrix-compatible C_{18} extraction phase. This coating was employed to facilitate the extraction of small analytes of interest, even in the presence of macromolecules.

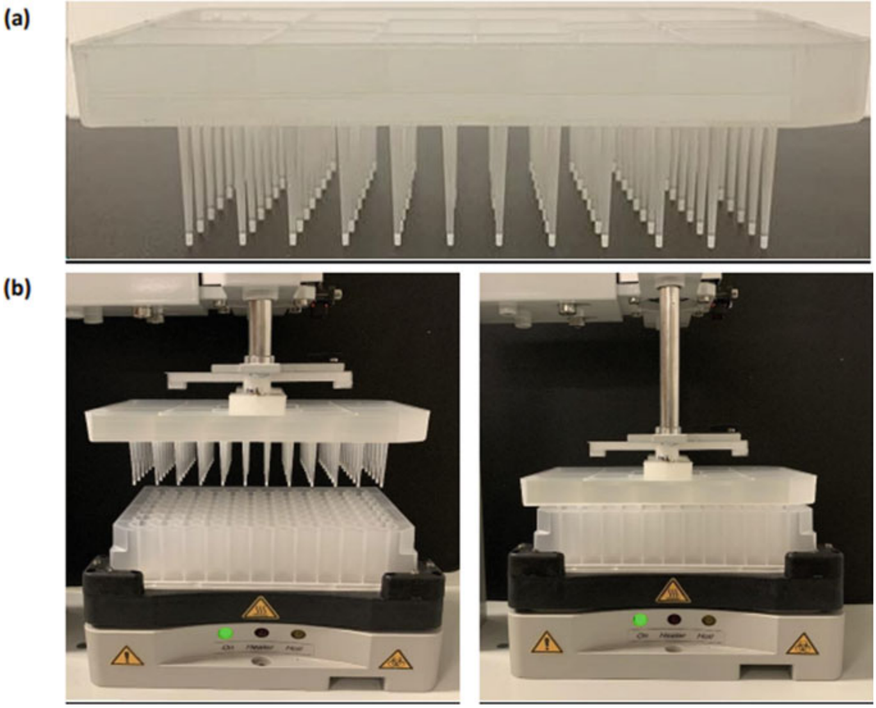

Fig. 10 **a** Supel™ BioSPME 96-Pin device. **b** BioSPME device coupled with a Concept96 automated system (PAS Technologies GmbH, Germany). Reprinted from [42] with permission from the American Chemical Society

Rocío-Bautista et al. directly coupled BioSPME to liquid electron ionization-tandem mass spectrometry (LEI-MS/MS) via a microfluidic open interface (MOI) to create a sensitive technique that eliminates matrix effects (ME) and enables the direct analysis of biological samples without necessitating sample purification or chromatographic separations [139]. In this protocol, the authors used C_{18} Bio-SPME fibers for direct immersion analysis of fentanyl compounds in urine and plasma. A schematic of the modified MOI-LEI-MS/MS system is shown in Fig. 11.

4.4 *In vivo Applications*

The application of in vivo SPME has found extensive use in numerous research investigations aiming to analyze organic analytes within intricate matrices [140–142]. Substances such as persistent organic pollutants (POPs), endocrine-disrupting compounds (EDCs), pesticides, disinfection byproducts (DBPs), and heavy metals have the potential to leach into environmental matrices like soil, air, water, and

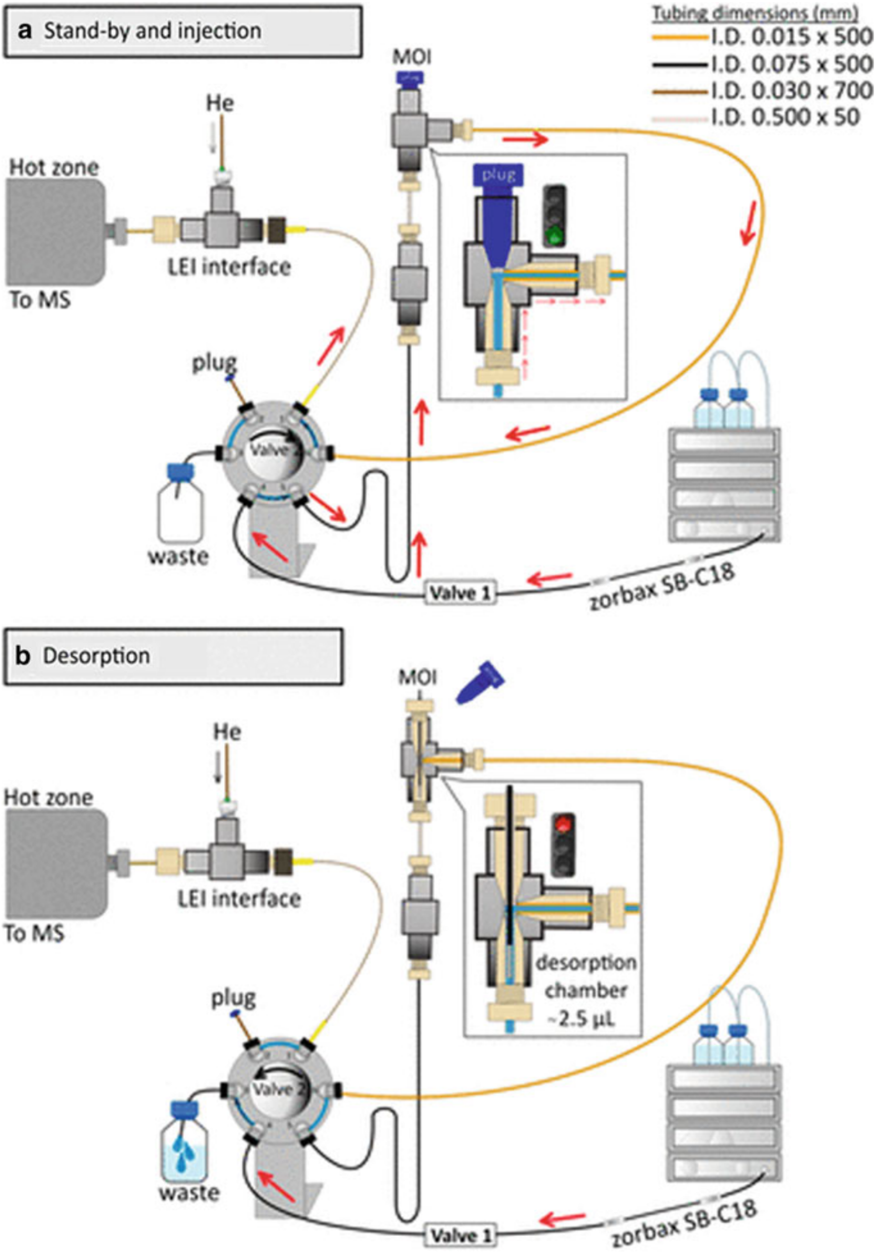

Fig. 11 Diagram illustrating the fluid dynamics of the MOI-LEI-MS/MS system. **a** Standby and injection configuration; **b** Desorption configuration. Reprinted from [139] with permission the from American Chemical Society

sediments, which can lead to their accumulation in plants, animals, and humans, either through direct contact with the matrices or via the food chain. This poses a risk to living organisms, as the accumulation of such compounds can lead to toxicity impairing different cellular processes at the genomic, proteomic, and metabolomic levels.

Napylov et al. [143] employed in vivo SPME sampling to assess oxylipin profiles within the brains of live, conscious rats. This groundbreaking and inventive technique circumvented alterations in oxylipin concentrations post-mortem, allowed for the real-time tracking of oxylipin levels with exceptional spatial precision, and could be executed using the identical experimental apparatus as in vivo microdialysis, a well-regarded standard in neuroscience research. Elsewhere, Musteata et al. [144] developed a fast in vivo microextraction technique with the potential to replace (at least in part) current sampling techniques based on blood drawing, especially in the case of small animals (Fig. 12). In this method, the sampling process does not require the animal to be handled once the interface has been installed, thus reducing its exposure to stress. This is a significant improvement, as lower levels of stress result in more relevant pharmacokinetic data, thus reducing the number of animals required to obtain reproducible data. In this study, Musteata et al. effectively utilized sampling devices founded on hypodermic tubes coupled with SPME fibers for the in vivo analysis of both free and total concentrations of diazepam and its metabolites within whole blood in rats.

Yuan et al. [145] developed a breath collection device utilizing a daily wearable face mask. In this approach, one or more SPME fibers are integrated into the face mask, leading to substantial selectivity and analyte enrichment through both specific and nonspecific adsorption mechanisms. Consequently, the proposed SPME-in-mask device proves well-suited for the ongoing collection of analytes from exhaled breath aerosols over extended periods, even in real-world settings, spanning multiple hours. After the exhaled breath samples were acquired, they were directly desorbed and

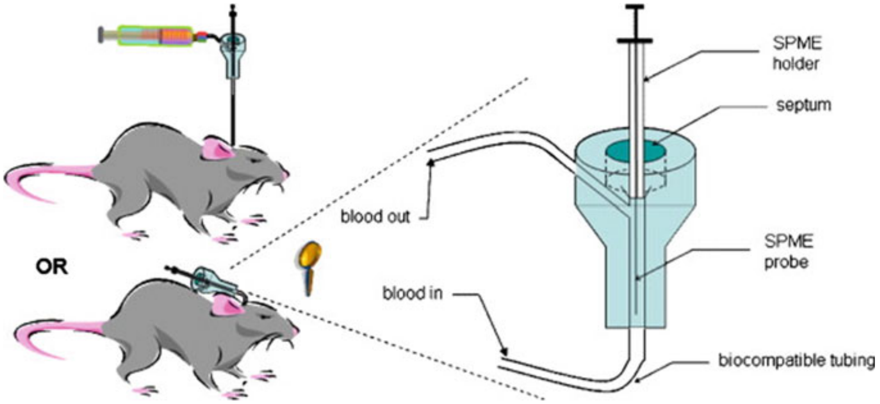

Fig. 12 In vivo SPME investigation involving rats: positioning of SPME devices and their connection interface to the carotid artery. Reprinted from [144] with permission from Elsevier

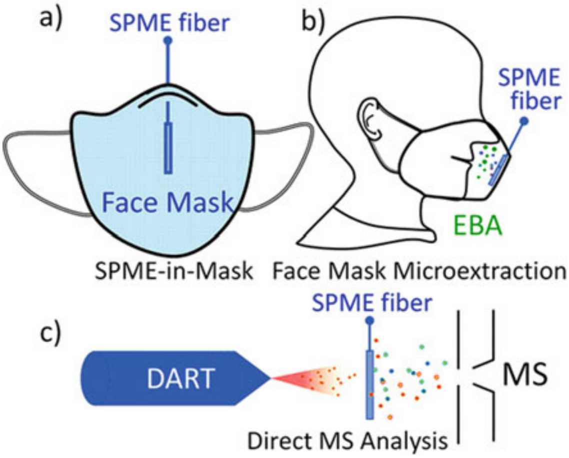

Fig. 13 Illustration depicting SPME-in-mask sampling and the subsequent direct mass spectrometry analysis of exhaled breath aerosol. **a** Insertion of the SPME fiber into a KN95 face mask; **b** Wearing of the SPME-in-mask for the collection of exhaled breath aerosol; **c** Direct linkage of SPME with DART-MS. Reprinted from [145] with permission from the American Chemical Society

ionized from the fibers via direct analysis in real time mass spectrometry (DART-MS) without further sample pretreatment. The SPME-in-mask concept is illustrated in Fig. 13.

5 Conclusions and Future Trends

Since its introduction in 1990, solid-phase microextraction has established itself as a highly popular microextraction approach for the analysis of a wide range of compounds in biological, food, and environmental samples. Indeed, SPME's numerous benefits endow it with great potential for several analytical applications. As an example, SPME proves highly advantageous for the analysis of volatile compounds found in exceedingly low concentrations within diverse food and environmental samples. In addition, SPME's status as a reliable and high-quality sample-preparation tool has further contributed to its widespread application for the identification and quantitation of myriad chemical compounds and biological substances. SPME's competitive edge over other extraction methods is primarily rooted in the large selection of available coating sorbents including polar, medium polar, non-polar, ion-exchange, and mixed-mode sorbents. Despite this variety, selecting an appropriate SPME fiber still requires detailed knowledge of the properties of the sample matrix under study. Finally, in addition to the large variety of fiber coatings, the availability of many different extraction and desorption techniques and derivatization procedures has also enabled the development of selective, sensitive, and repeatable SPME methods, especially for the analysis of food and environmental matrices.

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Conflict of Interest
The authors have declared no conflict of interest.

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