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Review

Miniaturized Solid Phase Extraction Techniques Applied to Natural Products

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Abstract: Natural products are increasingly becoming part of our daily lives through their use in industry, food, as therapeutic agents, etc. To evaluate their possible applications, it is essential to characterize them chemically to explore their potential. Different techniques may be used to characterize natural products, including microextraction techniques. These techniques have been gaining popularity due to the advantages associated with their low use of organic solvents and the small amount of sample used relative to more classical sample preparation techniques. Their application in the extraction of compounds from natural products is still scarce. This manuscript intends to review the most used solid-based miniaturized sample preparation techniques applied to determining compounds in natural products. The main applications of these methodologies will be discussed, with a particular focus on natural product analysis, as well as their advantages and disadvantages over traditionally used sample preparation techniques.

Keywords: miniaturised solid phase extraction; natural products; trends

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1. Introduction

There is a growing interest in the development of new analytical methods. This trend is partly due to concerns related to the environmental impact of chemicals used in human activities; for instance, industry and clinical and analytical laboratories. Developing greener methods usually implies techniques involving reduced amounts of samples and solvents, consequently producing fewer residues [1]. The implementation of green methods has also contributed to developing more sensible and selective analytical instruments, presenting higher energetic efficiencies; these instruments are compatible with ecological solvents and preparation methods dedicated to analysing microsamples [2]. Concerning sample preparation techniques, methods involving microextraction have definitely contributed to these principles of green chemistry. Those microextraction procedures can be categorized into two main branches: solid-phase microextraction and liquid-phase microextraction [3]. Several variations of solid-phase approaches exist, all involving the adsorption or absorption of the analytes onto a solid sorbent or film. Liquid-phase microextraction is also

divided into several categories, all of them involving analyte partitioning between the sample and a liquid. Multiple applications of these microextraction techniques have been published involving different areas; for instance, in extracting natural compounds.

This review will deal with the most used miniaturized sample preparation techniques based on solid-phase microextraction applied to the determination of compounds in natural products. The main developments that these methodologies present and their advantages and disadvantages will be presented, with a particular focus on natural product analysis. Furthermore, extraction conditions and linearity data for each of the sample preparation technique will be critically discussed and future challenges will be highlighted. To date, research has yet to be published that is entirely dedicated to solid-phase microextraction procedures applied to natural products. From our perspective, once we factor in a laboratory routine with these products, we have carried out a critical and valuable review for all scientists working in the field of natural products.

Three electronic databases were used for the systematic literature search: Medline, ISI Web of Knowledge, and Google Scholar. Search strings were "solid-phase microextraction", "microextraction by packed sorbent", "stir bar sorptive extraction", "micro solid phase extraction", "matrix solid-phase extraction", "dispersive micro solid phase extraction", "MSPD", "molecularly imprinted polymers", "MIP", "MISPE" and "natural products", all fields), and only papers from 2015 to present were selected. However, concerning matrix solid-phase extraction and molecularly imprinted polymers, only the last five years were included due to the high number of papers available. A similar situation occurred with solid-phase microextraction; only results from the past three years were included. In the case of microextraction by packed sorbent, the criteria for the search were extended to 2011 due to the low number of publications. Three authors independently selected the articles for each class of microextraction technique to determine their relevance in the current review; only articles selected by at least two authors were included.

Information in books was also important, especially concerning general aspects.

2. Classification

Solid-phase microextraction techniques can be divided into static batch equilibria microextraction and dynamic flow through equilibrium microextraction methods. There is no doubt that the most widely used solid-phase microextraction technique is conventional solid-phase microextraction (SPME) or fiber SPME. Still, other approaches can be efficiently used, namely in-tube SPME (or capillary microextraction), micro-solid phase extraction, microextraction in a packed syringe, matrix solid-phase dispersion, molecularly imprinted polymers, and stir sorptive bar extraction. All of those approaches have been used for natural product analysis. In the following section, a brief introduction to these techniques, advantages and drawbacks, as well as their applications in determining the composition of natural products, will be pointed out.

2.1. Solid-Phase Microextraction

Developed by Arthur and Pawliszyn [4], SPME is an innovative solvent-free extraction method that combines sampling, extraction, and sample injection into an analytical instrument in just one step. Due to its popularity, this technique has been used in different applications, such as pharmaceutical, food, flavour, forensic, and environmental applications [5,6].

There are different methods of SPME implementation, such as in-tube, agitation mechanism disks, and coated fibres or vessels. The classical approach uses fused silica fibres coated with a stationary phase immobilized in a syringe that is exposed to a sample matrix for a certain period. During that time, the distribution equilibrium is established between the sample matrix and the coated fibre, and the analytes are retained. When combined with analytical instrumentation (e.g., gas chromatography (GC), capillary electrophoresis (CE), and liquid chromatography (LC)), the analytes are desorbed and analysed [6,7].

Due to the higher impact of these types of extraction on the laboratories, a large variety of coating fibres are being designed for the different applications of this technique [8,9]. However, the fibre dimensions should be lower than 300 µm for a good column injection [4].

SPME is applicable in gaseous, liquid, and solid matrices. The complexity of sample matrices and the nature of the analytes can compromise the success of the SPME extraction. Three different approaches can be performed with coated fibre: direct extraction, membrane protection, and headspace extraction (Figure 1) [8].

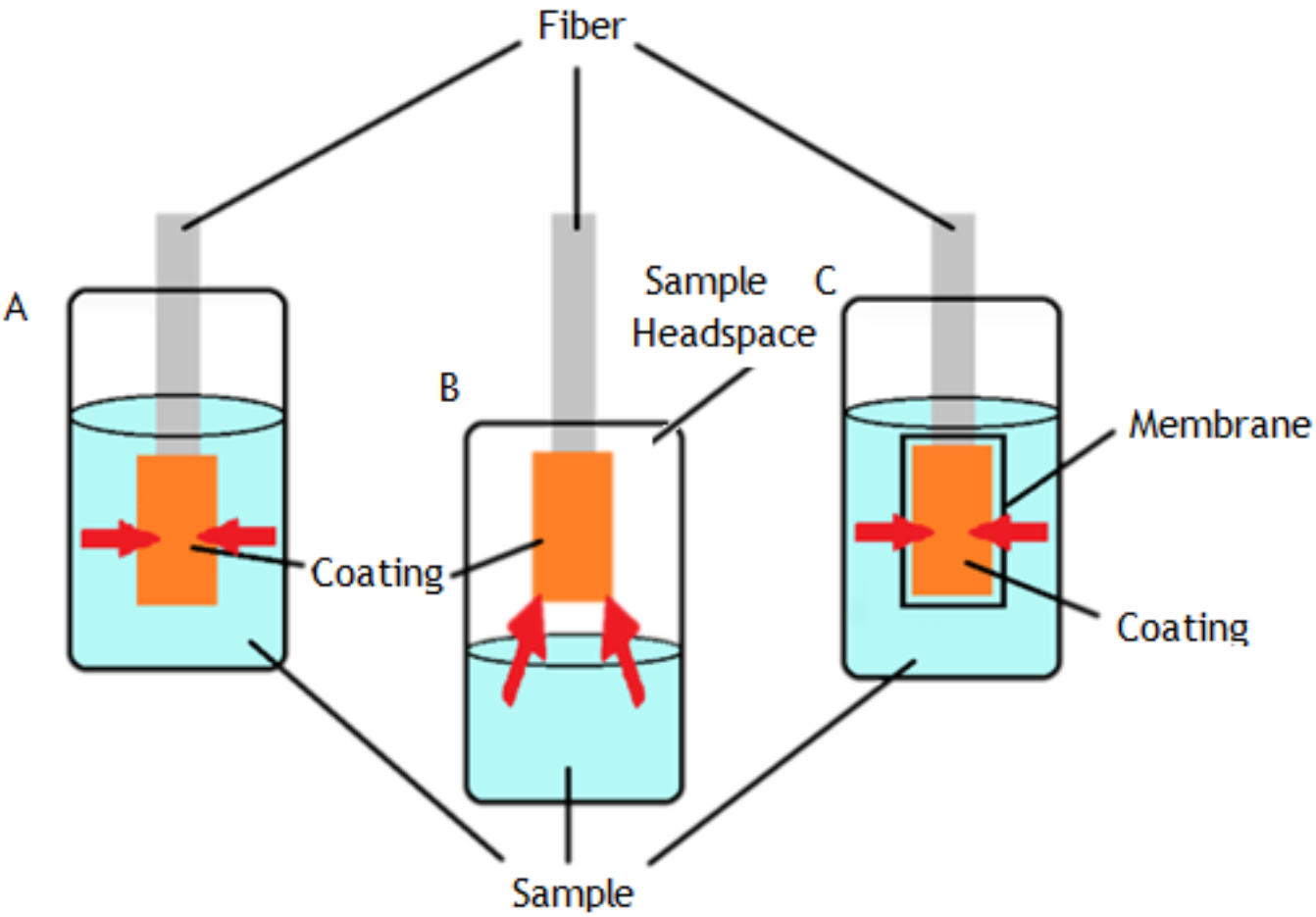

Figure 1. SPME extraction modes: (**A**) Direct immersion; (**B**) headspace mode; (**C**) membrane protection.

This technique is based on principles of thermodynamics and mass transfer, and, in opposition to other extraction methods, the whole of the extracted analyte is introduced in the chromatographic system [10,11]. It consists of a fused-silica capillary fibre of approximately 1 cm long, coated by a stationary phase, which can be liquid (usually a polymer) or solid (adsorbent substance). The fibre is connected to a stainless steel needle, which allows it to move freely and offers protection throughout the extraction and desorption processes as well.

In direct extraction, the coated fibre is immersed into the sample, transporting the analytes directly from the sample matrix to the stationary phase (Figure 1A). Depending on the nature of the sample matrices, the agitation could facilitate the diffusion of analytes to the coated fibre [8].

In the headspace mode, the analytes are extracted from the gas phase of the sample (Figure 1B). This approach permits the adjustment of matrix conditions without affecting the coating fibre. The headspace also protects the fibre from possible damages caused by high molecular weight and non-volatile substances present in the sample. The sensitivity of

this extraction mode will depend on the volume ratio between the sample and the gaseous headspace, temperature, pressure, and agitation [8,12].

In the membrane protection approach, the fibre and the sample are separated by a selective membrane (Figure 1C). The analytes diffuse through the selective membrane and reach the coated fibre while the interferences stay on the sample matrix. That way, the chemical nature of the membrane could increase the selectivity of this type of extraction. As an advantage, this extraction reduces fibre damage caused by dirty samples. The membrane protection is slower than the direct extraction, but the use of thin membranes and the increase in temperature may reduce the extraction time [8].

As a solvent-free extraction method, SPME is a sensitive method that reduces solvent consumption and time extraction, simplifying the sample preparation either in the laboratory or on-site. SPME is also a non-exhaustive method, i.e., only a small portion of analytes is extracted from the sample matrix. As a non-exhaustive method, SPME permits better characterization and accurate information about the system in the study. This also allows a better parameter monitorization (e.g., chemical changes, distribution equilibrium, speciation) of the investigated system, minimizing system perturbations [3,6,8].

Depending on the complexity of the sample matrices, a good knowledge of the sample properties is required for an appropriate selection of the coated fibre. SPME has, as a limitation, the chemical nature of the stationary phase on the market that could compromise the selectivity and efficiency of the extraction [3,6]. However, its popularity promotes the creation of a large variety of coated fibres [6]. The method's precision may vary depending on the number of conditions implemented. As fibres are fragile material, some issues, such as fibre breakage and coating stripping, can occur, limiting its lifetime [6,8].

Table 1 shows that the most commonly used fibre is a divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fibre with 50/30 µm. The fabricant recommends that the DVB/CAR/PDMS fibres be applied to extract flavours (volatiles and semivolatile, C3-20) with a molecular weight (MW) between 40 and 275. DVB/CAR/PDMS coating reveals a better extraction performance for medium and high MW analytes [13–16]. Although not reported for volatile compounds in natural products, CAR/PDMS coating appears to be the most suitable for low MW analytes [13–16]. Lindsay et al. [17] screened volatile profiles from food-grade agro-industrial by-products, such as apple, orange, carrot pomace, onion pulp, and kiwifruit peels. All extractions were carried out using HS-SPME with a 1 cm 50/30 µm DVB/CAR/PDMS (Supelco) fibre coupled with GC-MS. Samples were incubated for extraction for 10 min at 60 °C. Afterwards, desorption in the GC was performed under splitless mode (1 min at 250 °C). Yuan et al. [18] developed a feasible method of fabricating a meat replacement and to create high-added-value products using edible mushroom and soybean protein isolate through thermoextrusion. An extruded mushroom-based meat analogue (MMSA) was developed with different formulations in fabricating sausage analogues. HS-SPME coupled with GC-MS was used to characterize and compare the flavour profile of post-processing MMSA, with 64 volatile compounds being identified. Xiaofen Du et al. [19] used solid-phase microextraction coupled with gas chromatography−mass spectrometry (SPME-GC-MS) to analyse Cucumber Fruit volatiles. With this method, they identified 155 volatiles across eight samples, aldehydes and alcohols being the most dominant. Only 86 out of the 155 volatiles occurred in all eight samples.

Table 1 contains all the results mentioned above and others found in our research regarding SPME techniques for natural products.

Table 1. Application of SPME techniques for the extraction of several compounds in natural products.

Compounds	Sample	Amount	Mode	Type of Fiber	Limit of Detection	Conditions	Instrumentation	Relative Recovery (%)	Ref.
Volatile organic compounds	*Citrus*-based fruits (*C. reticulata*, *C. sinensis*, and *C. limon*)	1.0 g	HS-SPME	PDMS (100 µm)	n.s.	Equilibration: 30 min at room temperature; Extraction: 5 s to 5 min (n.s.); Desorption: time n.s., 220 °C.	GC-MS	n.s.	[20]
Volatile compounds	*Phaeodactylum* sp.	n.s.	HS-SPME	DVB/CWR/PDMS (1.1 mm)	n.s.	Equilibration: 15 min at 60 °C; Extraction: 15 min at 60 °C; Desorption: 2 min at 250 °C.	GC-MS	n.s.	[21]
Volatile compounds	Fruit (*Passiflora alata* Ait)	5.0 g	HS-SPME	DVB (n.s.)	n.s.	Equilibration: n.s. Extraction: 30 min at 50 °C; Desorption: 5 min at 250 °C	GC-MS	n.s.	[22]
Volatile compounds	Brewing malt	5.0 mL	HS-SPME	DVB/CAR/PDMS (50/30 µm)	n.s.	Equilibration: 20 min at 60 °C; Extraction: 40 min at 60 °C; Desorption: 5 min at 250 °C.	GC-MS	n.s.	[23]
Volatile compounds	Microalgal/ cyanobacterial biomass	0.3 g	HS-SPME	DVB/CAR/PDMS (50/30 µm)	n.s.	Equilibration: 15 min (T n.s.) Extraction: 30 min at 30 °C; Desorption: 15 min at 240 °C	GC-MS	n.s.	[24]
Volatile compounds	*Prunus avium* L. stems, leaves, and flowers	0.1 g	HS-SPME	DVB/CAR/PDMS (50/30 µm)	n.s.	Equilibration: 5 min (T n.s.) Extraction: 10 min at 45 °C; Desorption: 20 min at 250 °C	GC-MS	n.s.	[25]
Volatile compounds	Wheat protein and rice protein hydrolysates	2.0 g	HS-SPME	DVB/CAR/PDMS (50/30 µm)	n.s.	Equilibration: 15 min (T n.s.) Extraction: 30 min at 60 °C; Desorption: 5 min at 240 °C	GC-MS	100%	[26]
Volatile compounds	*Chrysanthemum* genus Leaves	n.s.	HS-SPME	DVB/CAR/PDMS (50/30 µm)	n.s.	Equilibration: (n.s.) Extraction: 30 min at 40 °C; Desorption: 5 min at 250 °C	GC-MS	n.s.	[27]
Volatile compounds	Orange Juice	5.0 mL	HS-SPME	DVB/CAR/PDMS (50/30 µm)	n.s.	Equilibration: 20 min at 40 °C; Extraction: 30 min at 40 °C; Desorption: 5 min at 250 °C.	GC-MS	n.s.	[28]

Table 1. *Cont.*

Compounds	Sample	Amount	Mode	Type of Fiber	Limit of Detection	Conditions	Instrumentation	Relative Recovery (%)	Ref.
Volatile compounds	Black rice (*Oryza sativa* L.)	2.0 g	HS-SPME	DVB/CAR/PDMS (n.s.)	n.s.	Extraction time: 18 min; Extraction temperature: 80 °C.	GC-MS	n.s.	[29]
Volatile compounds	Leaves of *Solidago altíssima*	n.s.	SPME	PDMS-DVB (65 μm)	n.s.	Stir rate: 400 rpm; Desorption time: 3–5 min; Desorption temperature: 200–230 °C	GC-FID	56.3–98.3	[30]
Volatile compounds	Fruits of *Eugenia stipitata*	n.s.	HS-SPME	DVB/CAR/PDMS (n.s)	n.s.	Extraction time: 15 min; Extraction temperature: 50 °C; Sampling rate: 1.0 mL/min; Desorption solvent: mixture of ethanol–water; Desorption time: 5 min; Desorption temperature: 270 °C	GC-MS	n.s.	[31]
Volatile compounds	Mango fruit	2 g	HS-SPME	DVB/CAR/PDMS (50/30 μm)	n.s.	Extraction time: 30 min; Extraction temperature: 60 °C; Desorption time: 5 min; Desorption temperature: 260 °C	GC-MS	n.s.	[32]
Volatiles compounds	Sesame oils	5 g	HS-SPME	DVB/CAR/PDMS (50/30 μm)	n.s.	Stir rate: 100 rpm; Desorption time: 3 min; Desorption temperature: 250 °C	GC-MS	16–89	[33]
Essential oils	Cowpea bean	5 g	HS-SPME	DVB/CAR/PDMS (50/30 μm)	0.0057 μg/kg	Extraction time: 3–10 min; Extraction temperature: 30/60 °C; Desorption time: 3 min	GC-FID	99.26–104.85	[34]
Volatile compounds	Leaf samples from *C. aromaticum*, *C. nankingense*, and hybrids	n.s.	HS-SPME	DVD/CAR/PDMS (50/30 μm)	n.s.	Extraction time: 30 min; Extraction temperature: 40 °C; Desorption time: 5 min; desorption temperature: 250 °C	GC-MS	n.s.	[27]
Volatile compounds	Leaves and flowers *Rosmarinus officinalis* L. and bread	1 g	HS-SPME	DVD/CAR/PDMS (50/30 μm)	n.s.	Extraction time: 30 min; Extraction temperature: 50 °C; Desorption time: 0.50 min; Desorption temperature: 270 °C	GC-MS	n.s.	[35]

Table 1. *Cont.*

Compounds	Sample	Amount	Mode	Type of Fiber	Limit of Detection	Conditions	Instrumentation	Relative Recovery (%)	Ref.
Volatile compounds	Kiwi peels	2 g	HS-SPME	DVD/CAR/PDMS (50/30 µm)	n.s.	Extraction time: 30 min; Extraction temperature: 40 °C; Desorption temperature: 250 °C	GC-MS	n.s.	[36]
Volatile compounds	Fruit and vegetables fermented	2 g	HS-SPME	DVD/CAR/PDMS (50/30 µm)	n.s.	Extraction time: 10 min; Extraction temperature: 60 °C; Desorption time: 1 min; Desorption temperature: 250 °C	GC-MS	n.s.	[17]
Volatile compounds	Strawberry	2 g	HS-SPME	DVD/CAR/PDMS (50/30 µm)	n.s.	Extraction time: 15 min; Extraction temperature: 50 °C; Desorption time: 2 min; Desorption temperature: 220 °C	GC-MS	n.s.	[37]
Volatile compounds	Soybean Oil	3 g	HS-SPME	DVD/CAR/PDMS (50/30 µm)	n.s.	Extraction time: 40 min; Extraction temperature: 100 °C; Desorption time: 5 min; Desorption temperature: 240 °C	GC-MS	n.s.	[38]
Volatile compounds	Sausage Analogue Elaborated with Edible Mushrooms and Soy Protein Isolate	6 g	HS-SPME	DVB/CAR/PDMS (50/30 mm)	ns	Extraction time: 20 min; Extraction temperature: 60 °C; Desorption time: 30 min	GC-MS	n.s.	[18]
Linalool	Essential Oils	1 g	HS-SPME	DVB/CAR/PDMS (n.s)	ns	Extraction time: 5 min; Desorption time: 30 min Desorption temperature: 270 °C	GC-MS	n.s.	[39]
Volatile Compounds	Fermented *Tetragonula pagdeni Schwarz* honey	n.s.	HS-SPME	n.s.	n.s.	n.s.	CG-MS	n.s.	[40]
Volatile aroma substances	Gracilaria lemaneiformis	6 mL	HS-SPME	n.s.	n.s.	Sodium chloride (3.0 g); Preincubation Time: 10 min; Preincubation Temperature: 60 °C; Extraction time: 35 min with stirring	CG-MS	n.s.	[41]

Table 1. *Cont.*

Compounds	Sample	Amount	Mode	Type of Fiber	Limit of Detection	Conditions	Instrumentation	Relative Recovery (%)	Ref.
Volatile Metabolites	*Brettanomyces bruxellensis* fermentation of apple pomace, carrot pomace, and orange pomace	2 mL	HS-SPME	DVB/CAR/PDMS (50/30 µm)	n.s.	Preincubation Time: 10 min; Preincubation Temperature: 60 °C; Extraction time: 10 min; Desorption time: 1 min; Desorption Temperature: 250 °C.	CG-MS	n.s.	[42]
Volatile components	Soybean paste	4.0 g	HS-SPME	n.s.	n.s.	water bath at 50 °C for 60 min	CG-MS	n.s.	[43]
Volatile compounds	Pét-Nat ciders	5 mL	SPME-ARROW	DVB/CWR/PDMS (120 µm/20 mm)	n.s.	NaCl (2.0 g); Preincubation Time: 20 min; Preincubation Temperature: Extraction time: 49 min; Desorption time: 10 min; Desorption Temperature: 250 °C	CG-MS	n.s.	[44]
Volatile Aroma	Cucumber	3.0 g	SPME	DVB/CAR/PDMS, (50/30 µm)	n.s.	Preincubation Time: 3 min; Preincubation Temperature: 200 °C; NaCl (1 g); sample incubated to reach equilibrium at 40 °C for 15 min; Extraction time: 20 min; Agitation: 250 rpm; Desorption time: 3 min; Desorption temperature: 250 °C	CG-MS	n.s.	[19]
Volatile constituents	*Clinopodium Candidissimum* (Munby) Kuntze (Lamiaceae)	n.s.	HS-SPME	PDMS (100 µm)	n.s.	Preincubation time: 1 h; Preincubation Temperature: 25 °C; Extraction time: 30 min	CG-MS	n.s.	[45]

Legend: DVB/CWR/PDMS: Divinylbenzene/carboxen/polydimethylsiloxane; DVB: Divinylbenzene; DVD/CAR/PDMS: Divinylbenzene/carboxen/polydimethylsiloxane; GC-MS: Gas chromatography–mass spectrometry; HS: Headspace; n.s.: Not specified; PDMS: Polydimethylsiloxane; SPME: Solid-phase microextraction; Ref.: Reference.

2.2. Microextraction by Packed Sorbent

Microextraction by packed sorbent, more commonly known as MEPS, is a miniaturized version of the solid-phase extraction technique (SPE) that is simpler, faster, greener, and user-friendly [46]. This method combines sample extraction, pre-concentration, and clean-up in a single device. It was developed in order to create a high-throughput technique that would be able to reduce handling time, lower sample and solvent volumes, and, at the same time, can allow direct injection of the eluate into chromatographic devices (GC/LC) without compromising the extraction efficiency [47–49]. In MEPS, a small amount of solid sorbent (around 1–4 mg) is either inserted into the barrel of a gas-tight syringe (BIN—barrel insert and needle) or between the needle and the barrel as a cartridge [47,48]. Once the BIN is exhausted, or another sorbent is required, it can easily be exchanged by simply unscrewing the locking nut and replacing the BIN, making the process extremely simple [49]. Many sorbents are used in MEPS, each bearing different particle sizes and adsorptive qualities. These sorbents can be traditional silica matrices (unmodified silica, C_2, C_8 and C_{18}), strong and weak cation/anion exchange C_{18} (SCX, SAX), mixed sorbents (C_8/SCX), carbon, polystyrene–divinylbenzene copolymers (PV-DVB), restricted access material (RAM), molecularly imprinted polymers, and organic monolithic sorbents [47,48]. The MEPS procedure usually follows a four-step protocol (Figure 2) consisting of conditioning of the sorbent, sample loading, washing, and elution. All these steps consist of an up-and-down motion of the solutions through the sorbent and are optimized for each extraction, providing the best efficiency and recoveries possible. Due to this extract/discard technique, the washing step is critical because it removes most of the interfering compounds in our sample while minimizing the loss of any of our target analytes in the process. Other conditions such as sorbent selection, pH, ionic strength and elution solvent must also be optimized to reduce matrix effects, interferents and carry-over [47,48].

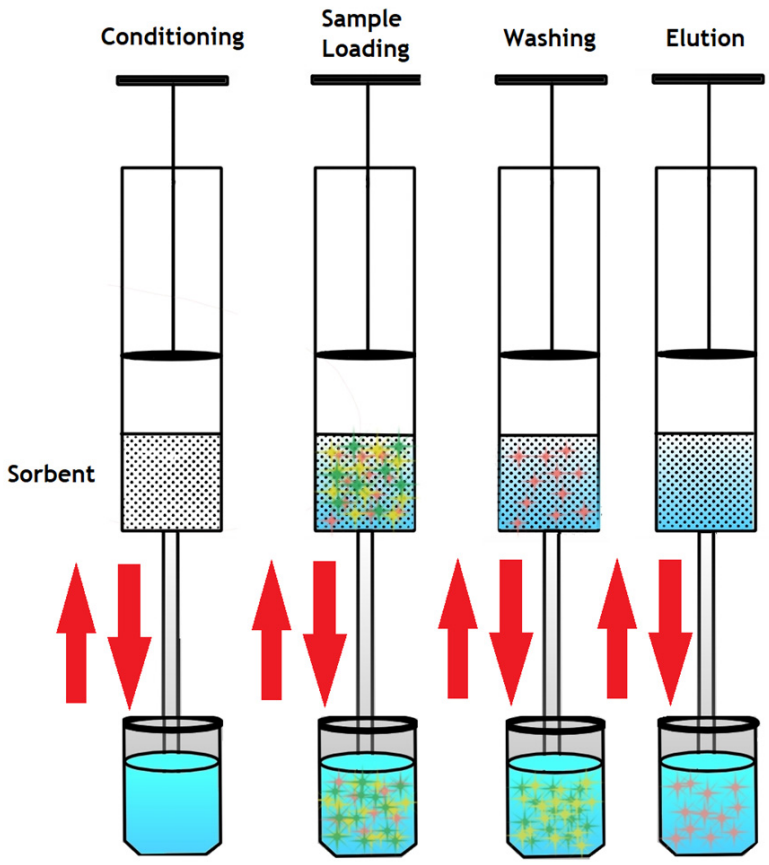

Figure 2. Representation of the MEPS protocol.

MEPS has several advantages in comparison to other extraction techniques. For starters, it is one of the simplest and broadest techniques, working with several ranges of analytes and matrixes while improving their analytical performance [49]. Due to the miniaturization of the sorbent amount and solvent volume, MEPS is much more environmentally friendly. Because it uses small sample volumes, it is instrumental in cases where said samples are precious, rare or of hard collection. Since MEPS sorbents can be re-used several times (up to 100 or more), the cost per analysis is much lower than other extraction techniques such as SPE [49,50]. Although this technique retains several advantages compared with others, it is not perfect; therefore, it carries some disadvantages too. Clogging of the sorbent is a real problem and can easily happen when highly viscous or highly concentrated samples are used. Once a sorbent has been clogged, it cannot be used or re-used, so sample dilutions and deproteinizations are imperative when working with complex matrixes to reduce the risk of clogging. In addition, MEPS cannot process large sample volumes, making the procedure too long and laborious to use with volumes above 500 µL. Carry-over is also a problem in MEPS; it can be minimized through the realization of carry-over studies and effects, with consequent addition/alteration of washing steps before the sorbent is re-used [49,50].

A wide variety of new and specific sorbents have appeared recently in MEPS protocols, presenting excellent efficiency and recoveries when applied to natural products. Mercolini et al. [51] tested classic C_2, C_8, C_{18}, and M1 (C_8+SCX mixed mode) sorbents to extract phenolic compounds from a sample of *Argania spinosa* leaves. The M1 sorbent was later chosen for having the best extraction results and presenting relative recoveries above 95%. Protti et al. [52] developed and optimized a MEPS protocol to analyse the artemisinin content in different plant extracts. Artemisinin is the main antimalarial compound of *Artemisia annua* L., and it has become popular due to its antiproliferative properties. Different commercially available sorbents, such as C_2, C_8, C_{18}, and M1, were tested for extraction efficiency, the C_8 sorbent being the best in terms of extraction yields and clean-up. The relative recoveries were in the 88–93% range, while extraction yields were over 85%. Their results revealed that the molecularly imprinted polymer sorbent was highly selective for estrogen-like structures and presented relative recoveries in the 81–103% range. The C_{18} sorbent was best suited for a multicomponent extraction and could attain relative recoveries broader than molecularly imprinted polymers in the 75–109% range. All these results are some of the standouts in our research that utilize newly synthesized and commercially available sorbents.

Perestrelo et al. [53] developed an analytical strategy based on MEPS and UHPLC-PDA to analyse major furanic derivates in fortified wines successfully. Furanic derivates are formed during the ageing procedures that the wines are submitted to and are of deep concern to humans due to their potential toxic effects. C_2, C_8, C_{18}, SIL (unmodified silica), M1, R-AX (polystyrene divinylbenzene partially functionalized with sulfonic acid groups), R-CX (polystyrene-divinylbenzene partially functionalized with quaternary amine groups), and PGC (porous graphitic carbon) sorbents were tested. C_8 presented the best analytical results, with relative recoveries ranging from 74–99%. Rahimi et al. [54] synthesized a carbon-based nanoporous material (CMK-3) as a MEPS sorbent to extract rosmarinic acid in rosemary samples. The CMK-3 sorbent was tested alongside ordinary activated carbon sorbents. Due to its high porosity, it was considered a much better sorbent, presenting a superior adsorption efficiency for rosmarinic acid than ordinary activated carbon sorbents (about 17 times). Relative recoveries for this MEPS protocol ranged between 94–105%.

Table 2 contains all the results mentioned above and some more found in our research regarding MEPS techniques for natural products.

Table 2. Application of MEPS techniques for extraction of several compounds in natural products.

Compounds	Sample	Amount	Life-Time	Type of Sorbent	Limit of Detection	Conditions	Instrumentation	Relative Recovery (%)	Ref.
Artemisinin	*Artemisia annua* L.	5 g	up to 200	C_8	1500 ng/L	Extraction cycles: 10 draw/discharge; Sampling rate: 2 µL/s; Washing: 100 µL ultrapure water, 100 µL methanol/water 95:5; Washing rate: 10 µL/s; Elution cycles: 5 × 100 µL; Elution solvent: methanol; Elution rate: 2 µL/s.	LC-DAD-MS/MS	88–93	[52]
Phenolic compounds	*Argania spinosa* leaves	25 g	up to 200	M1	100 ng/L	Extraction cycles: 10 draw/discharge; Sampling rate: 5 µL/s; Washing: 100 µL of ultrapure water, 100 µL methanol/water 90:10 (*v/v*); Washing rate: 10 µL/s; Elution Cycles: 2 × 250 µL; Elution solvent: methanol; Elution rate: 5 µL/s.	LC-DAD-MS/MS	>95	[51]
Major furanic derivatives	dry/medium dry fortified wine sweet/medium sweet, fortified wine	0.2 mL	100	C_8	4.5–129.3 ng/L 6.9–285.2 ng/L	Extraction cycles: 3 × 200 µL draw–eject; Washing: 100 µL water containing 0.1% formic acid; Elution solvent: 200 µL methanol: water (95:5, *v/v*).	UHPLC–PDA	74 to 97 83 to 99	[53]
Polyphenols	Wine	250 µL	100	C_8	0.01–0.2 µg/mL	Extraction time: 1 min; Sampling rate: 17.4–22.6 µL/s; Extraction cycles: 5; Ionic strength: 20% strong cationic exchange; Elution solvent: 50 µL methanol:water (95:5 *v/v*)	UHPLC- PDA	77-100	[55]
Prenylflavors	Beer	500 µL	>100	C_{18}	0.4–0.9 ng/mL	Extraction time: 5 min; Sampling rate: 20 µL/s; pH: 5; Ionic strength: 20% strong cationic exchange; Elution solvent: 250 µL acetonitrile	UHPLC-PDA	67.1–99.9	[56]
Polyphenols	Rosemary	50 mg	80	CMK-3 nanoporous carbon	0.059 µg/mL	Sapling rate: 1.0 mL/s; Extraction cycles: 14; pH: 2; Elution time: 20 min	HPLC-UV/VIS	94–105	[54]
(E)–Reveratrol	Wine	250 µL	n.s.	C_8	0.21 µg/mL	Extraction time: 3 min; Sampling rate: 20 µL/s; Extraction cycles: 1; pH: 2.7; Elution solvent: 0.1% formic acid and methanol; Elution time: 10 min	UHPLC-PDA	89.2–100.8	[57]

Legend: HPLC: High-performance liquid chromatography; LC-DAD-MS/MS: Liquid chromatography with diode array detection and tandem mass spectrometry; n.s.: Not specified; UHPLC–PDA: Ultrahigh-performance liquid chromatographic–photodiode array; UV/VIS: Ultraviolet-visible detector; Ref.: Reference.

2.3. Stir Bar Sorptive Extraction

Baltussen et al. [58] originally introduced stir bar sorptive extraction (SBSE) in 1999. This sample pre-treatment technology relies on the equilibrium distribution of target analytes between the sample and stir bar coating, representing the extraction phase [59]. SBSE is based on the same principles as SPME, but stir bars are coated instead of polymer-coated fibre [60]. The SBSE device is usually introduced into an aqueous sample for sampling. However, the SBSE rod can also be exposed to the HS of a vial containing a gaseous, liquid, or solid sample, even though this method is less popular. The bar adsorbs the analytes to be extracted while stirring (Figure 3). After being removed from the sample, the bar is dried and rinsed with deionized water. The analytes are then desorbed from the enrichment sorbent phase by thermal desorption (TD) in the GC or LC injection port. The analytes are desorbed when disintegrated at low temperatures by liquid desorption (LD) [60].

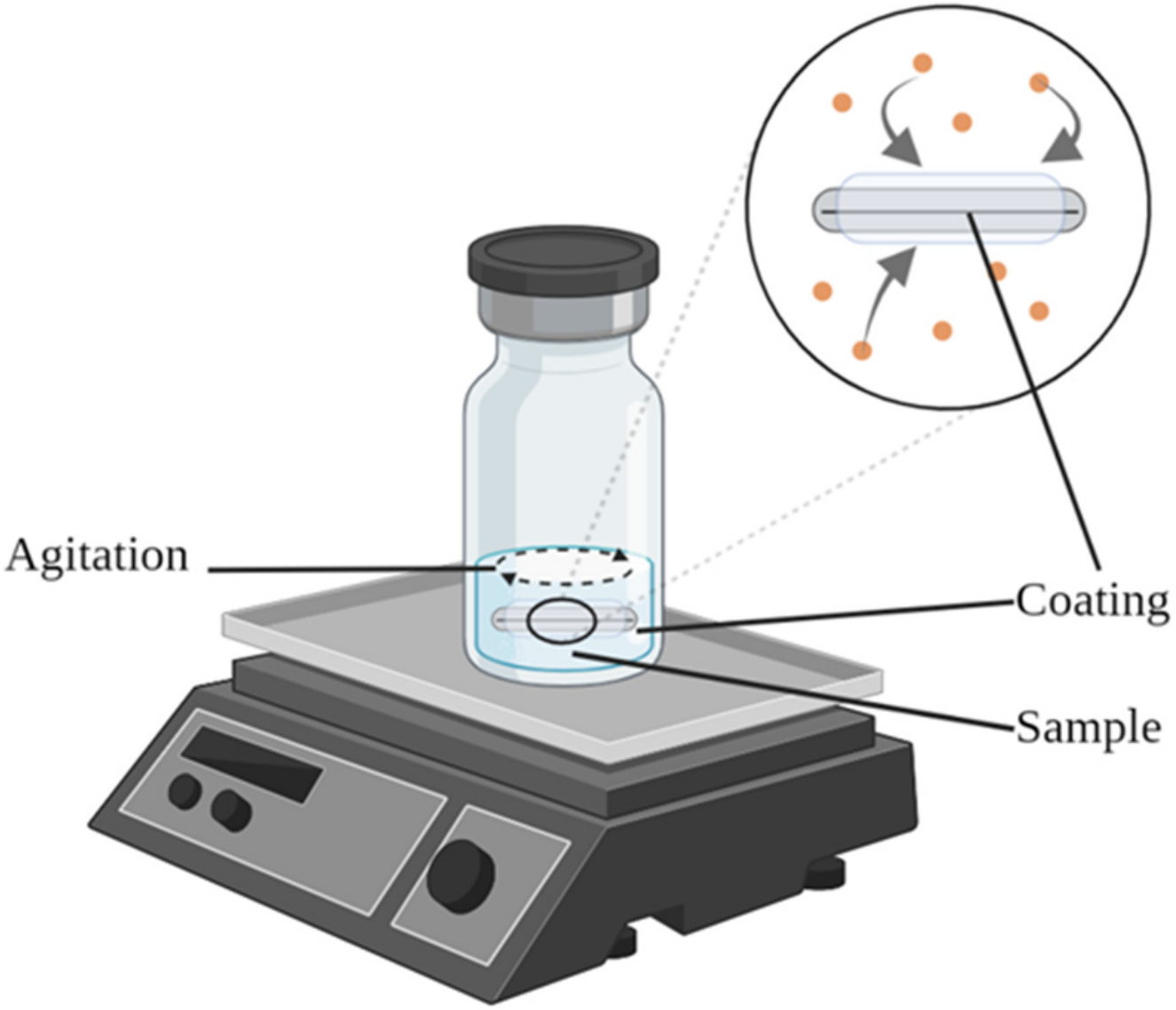

Figure 3. A system design demonstrating the SBSE.

SBSE has several advantages: it has a simple operation; it presents a high sorption capacity, increased robustness, excellent extraction efficiency, high selectivity (coating adapted for each particular type of target compound), and low limits of detection, down to sub-nanogram per litre concentrations [59–62]. Other benefits of this technique rely on the

possibility of automation and compatibility with different systems of analyte separation and detection [60]. As a result, all analytical domains, including environmental, clinical, and food analysis, as well as a wide range of matrices, including soils, environmental water and wastewater, solid and liquid foods, gaseous samples, and biological fluids, have efficiently resorted to this extraction technique [59,60,62,63].

The extraction time is higher than other miniaturized techniques (Table 3). However, SBSE compensates with an improved extraction efficiency and low carry-over [60,64]. Sample volume and stirring speed greatly influence extraction efficiency [3].

Table 3. Comparing with other miniaturized techniques, adapted from [60,64].

	SBSE	**SPME**	**MEPS**
Type of matrices	Liquid	Gaseous, liquid, and solid	Liquid
Sorbent amount	Coated 0.5–1 mm	Thickness 150 µm	1–4 mg
Sample volume (mL)	1–100	0.5–20	0.01–0.1
Handling time (min)	10–240	5–120	1–4
Cartridge re-use (extractions)	6–80, depending on the material used for coating	50–100	100
Recovery	Good	Low	Good
Sensitivity	Good	Low	Good
Carry-over	Low	High	Low
Main Advantages	Sample volume and stirring speed greatly influence extraction efficiency	No organic solvents are required; all the extracted material can be directly analysed; extracting device is portable and allows field sampling	Reduced sample preparation time, organic solvent consumption and cost of analysis
Main Drawbacks	It requires a particular desorption unit	Competition between drug and endogenous compounds for the fibre; the extraction is not exhaustive	Sorbent clogging

Nonetheless, manual stir-bar removal from the sample, rinsing, drying, and, in some cases, the additional back extraction step in proper solvent, are also drawbacks to be considered [60,62]. Because a single apolar polymer covers the stir bar, it can only be utilized with semivolatile and thermo-stable substances when TD is employed as a back-extraction mode. However, this restriction can be overcome, and the use of SBSE expanded, to include polar and thermally labile molecules by combining SBSE with a derivatization procedure [60]. The main disadvantage of this technique is the limited range of commercial coatings, consequently limiting the spectrum of analyte polarities (highly polar or hydrophilic solutes) [61–63]. Upton that, this technique is well-known for analytical methods with a high enrichment factor for a wide range of non-polar species (the most common) [62].

The most common coatings commercially available are polydimethylsiloxane (PDMS), polyethylene (PEG), and polyacrylate (PA) [62]. Conventional SBSE involves using PDMS polymer to coat the glass stir bar, which provides hydrophobic interactions with the target compounds. However, due to the hydrophobic nature of the polymer, it fails to achieve good performance for the extraction of polar and slightly polar compounds [65]. For this reason, developing new coating materials has become an important issue in improving SBSE versatility and expanding the applications of this technique [65]. Stable coatings can be prepared using: (1) adhesion; (2) molecularly imprinted polymers; (3) sol-gel; and (4) monolith. The development of new coatings for stir bars affects the selectivity, dynamics, and recovery of the SBSE-based method [59]. These new coatings have higher selectivity, including nanocarbon materials, functional monomers, metal–organic frameworks (MOFs), template-imprinted polymers, and inorganic particles [62].

The most commonly used conventional coating in SBSE is PDMS, widely reported in the literature for detecting analytes in natural products. Leite et al. [66] employed a PDMS twister (10 mm) to extract volatile compounds as phenolic compounds and flavonoids from soursop pulp. In contrast, the extracted compounds were desorbed on a thermal desorption unit and identified by GC-MS. It is also the target coating for comparison with novel coatings [66]. Liu et al. [67] developed an electrochemical polymerization of luminol molecularly imprinted polymers on carboxyl graphene (MIP/CG) to identify estrogens in milk. When compared to a commercial coating PDSMS/PA using the SBSE-HPLC-UV method, the authors concluded that the molecularly imprinted polymer coating increased selectivity, allowing recoveries that ranged from 83–96% [67]. However, Cheng et al. [68] used linear graphene nanocomposites (aLGN) as a novel coating in SBSE, combining with GC-MS to detect seventeen kinds of amino acids of *Camellia nitidissima* Chi seeds. The new coating produced higher TD performance and improved amino acid discrimination compared to traditional PDMS coating, resulting in a practical and highly distinct approach for amino acid analysis [68].

Furthermore, this miniaturized technique is carried out to analyse different analytes, and it is conducted by chromatography instruments, including high-performance liquid chromatography (HPLC), GC, CE, and mass spectrometry (MS). Ghani [69] used reversed-phase high-performance liquid chromatography–diode array detection (HPLC-DAD) to quantify phenolic acids (gallic acid, 3,4-dihydroxy benzoic acid, p-hydroxy benzoic acid), obtaining limits of detection between 0.06 and 0.26 μg/L. For this method, the author used in situ preparation and application of layered double-hydroxide-coated anodized aluminium (Zn-Al) stir bar [69]. Through MOFs (ZIF-67) and HPLC-UV, Ghani et al. [70] determined caffeine in beverages, such as tea and soda, among others. The relative recoveries obtained varied between 91–97%, whereas the spiking recovery varied between 91–102% [70].

Considering the alternative coatings mentioned above, there are a variety of analytical approaches for detecting and quantifying various substances employing SBSE and analysis systems. Table 4 summarises the published research on detecting and quantifying analytes under investigation in natural products with extraction by SBSE techniques.

Table 4. Application of SBSE techniques for extraction of several compounds in natural products.

Compounds	Sample	Amount	Type of Sorbent	Limit of Quantitation	Conditions of Extraction	Instrumentation	Recovery (%)	Ref.
Volatile compounds	Soursop pulp and rehydrated dried powder	10 g	PDMS (10 mm)	n.s.	Salts: 3 g of NaCl; Extraction time: 30 min; Extraction temperature: room temperature; Desorption temperature: 40 °C to 230 °C at a rate of 60 °C/min; Desorption time: 10 min	GC-MS	n.s.	[66]
Estrogens	Milk	2 g	MIP/GC and PDMS/PA	1.2–3.5 ng/mL	Stir rate: 500 rpm; Extraction time: 20 min; Desorption solvent: 5 mL methanol: Hac (99:1, *v/v*); Desorption time: 20 min	HPLC-UV	83–96	[67]
Amino acids	*Camellia nitidissima* Chi seeds	6 g	aLGN (100 nm × 100–300 µm) and PDMS (10 mm × 3.2 mm)	n.s.	Stir time: 120 min; Desorption solvent: 8 mL DMF; Desorption temperature: 150–300 °C during 10 min	GC-MS	n.s.	[68]
Phenolic acids	Grape juice	10 mL	Magnetic Zn-Al LDH	0.18–0.92 ng/mL	Stirred rate: 200 rpm; Stir time: 20 min (25 °C); Desorption time: 2 min	HPLC-UV	90–105	[69]
Caffeine	Coca-Cola, 7up, Pepsi, ZamZam, Diet Coca-Cola, black tea	10 mL	ZIF-67	0.16 ng/mL	Stirred rate: 700 rpm; Stir time: 20 min at room temperature; Desorption solvent: 100 µL of methanol; Desorption time: 4 min	HPLC-UV	91–104	[70]
Phytohormones	Apple and pears	10 mL	ZIF-8/poly (MMA-EGDMA)	n.s.	Stir rate: 800 rpm; Stir time: 50 min; Desorption solvent: 120 µL of 30 mM NaOH (methanol); Desorption time: 15 min	HPLC-UV	12–46	[71]
Estrogens	Chicken and pork	10 mL	PANi- PDMS	n.s.	Stir rate: 400 rpm; Extraction time: 40 min; Extraction temperature: 25 °C; Desorption solvent: 50 µL methanol; Desorption time: 15 min	HPLC-UV	82–106	[72]
Aroma compounds	Six different sake	10 mL	PDMS (10 mm length × 1.0 mm thickness, capacity 63 µL)	n.s.	Stir rate: 800 rpm; Extraction time: 1h; Extraction temperature: 25 °C; Desorption solvent: 500 µL acetone; Desorption time: 30 min	GC-MS	n.s.	[73]

Table 4. *Cont.*

Compounds	Sample	Amount	Type of Sorbent	Limit of Quantitation	Conditions of Extraction	Instrumentation	Recovery (%)	Ref.
Polychlorinated biphenyls	Fish	n.s.	Apt-MOF	0.011–0.015 ng/mL	Stir rate: 500 rpm; Extraction time: 50 min; Extraction temperature: 50 °C; Desorption solvent: 5 mL of methylene chloride–pH 3 glycine–HCl buffer (1:10, *v/v*); Desorption time: 20 min, pH = 3	GC-MS	89–97	[74]
Aflatoxins	Soy milk	0.1 L	GO	7.5–25 pg/mL	Stir time: 40 min; Extraction time: 40 min; Desorption solvent: 1.5 mL methanol; Desorption time: 10 min	HPLC-LIF	80–102	[75]
Volatile aroma compounds	Apple juice	20.0 mL	PDMS (length 10 mm, thickness 1.0 mm)	n.s.	Stir rate: 800 rpm; Extraction time: 120 min; DHE: incubation temperature: 30 °C; Incubation time: 30 min; Agitator on time: 10 s; Agitator off time: 1 s; Agitator speed: 500 rpm; Transfer heater temp: 70 °C; Trapping volume: 200 mL; Flow: 10 mL/min; Trap temp: 30 °C; Incubation temp: 30 °C; Drying phase volume: 10 mL; Drying flow: 10 mL/min and drying temperature of 30 °C	GC-FID	n.s.	[76]
Volatile compounds	Longjing tea	0.6 g	PDMS (10 mm length, 0.5 mm thickness, 24 µL capacity)	n.s.	Salt: 500 mg NaCl; Extraction time: 90 min; Extraction temperature: room temperature; Stir rate: 1250 rpm	GC-MS	112	[77]
Volatile compounds	Dark tea	0.6 g	PDMS twister (10 mm length, 1.0 mm thickness, 24 µL capacity)	n.s.	Salt: 500 mg NaCl; Extraction time: 90min; Extraction temperature 80 °C; Stir rate: 1200 rpm; Thermal desorption: 80 °C, held at 30 °C for 1 min, and then increased to 240 °C at a rate of 100 °C/min and held for 5 min	GC-MS	n.s.	[78]

Table 4. *Cont.*

Compounds	Sample	Amount	Type of Sorbent	Limit of Quantitation	Conditions of Extraction	Instrumentation	Recovery (%)	Ref.
Volatile compounds	Green tea	1.0 g	PDMS	n.s.	Stirred at 1000 rpm for 60 min at 60 °C (a control experiment was carried out at room temperature, about 28–30)	Es-GC-O/MS	n.s.	[79]
Volatile compounds	Beer	50.0 mL	PDMS (10 mm long and 0.5 mm thick)	0.01–45.71 ppb	Salt: 25% (*w*/*v*); Stir rate: 1000 rpm; Extraction time: 180 min; Thermal desorption: the desorption temperature was set up to climb from 40 °C to 300 °C with 0.5 min delay time and 10 min holding time	GC-MS	80–120	[80]

Legend: aLGN: Amino-modified linear graphene nanocomposites; Apt-MOF: Aptamer-functionalized-metal–organic framework; DHe: Dynamic headspace extraction; Es-GC-O/MS: Enantioselective Gas chromatography–olfactometry/mass spectrometry; FID: Flame ionization detection; GC: Carboxyl graphene; GC-MS: gas chromatography–mass spectrometry; GO: graphene oxide; HPLC: High-performance liquid chromatography; LIF: Laser-induced fluorescence; MIP: Molecularly imprinted polymer; MMA-EGDMA: Methyl methacrylate–ethyleneglycol dimethacrylate; n.s.: Not specified; PA: Polyacrylate; PANi: Polyaniline; PDMS: Polydimethylsiloxane; UV: Ultraviolet detection; ZIF-67: Zeolitic imidazole framework-67; ZIF-8/poly: Zeolitic imidazolate framework-8; Zn-Al LDH: Layered double-hydroxide-coated anodized aluminium; Ref.: Reference.

2.4. Matrix Solid-Phase Dispersion

Matrix solid-phase dispersion (MSPD) was first introduced by Barker et al. [81]. For solid, semi-solid, and viscous materials, this technique offers an alternate method for reducing solvent use and analysis time [82].

To create a uniform mixture, samples and sorbent are often blended together during an MSPD technique. The resultant mixture is moved into an extraction column, where it will be packed. The washing and elution processes are then carried out on the column in order to extract and isolate the analytes from the matrix (Figure 4). To further clean the eluent, an extra sorbent may occasionally be loaded at the bottom of the column. Analytical methods based on chromatography can typically be used to analyse the final extract [82].

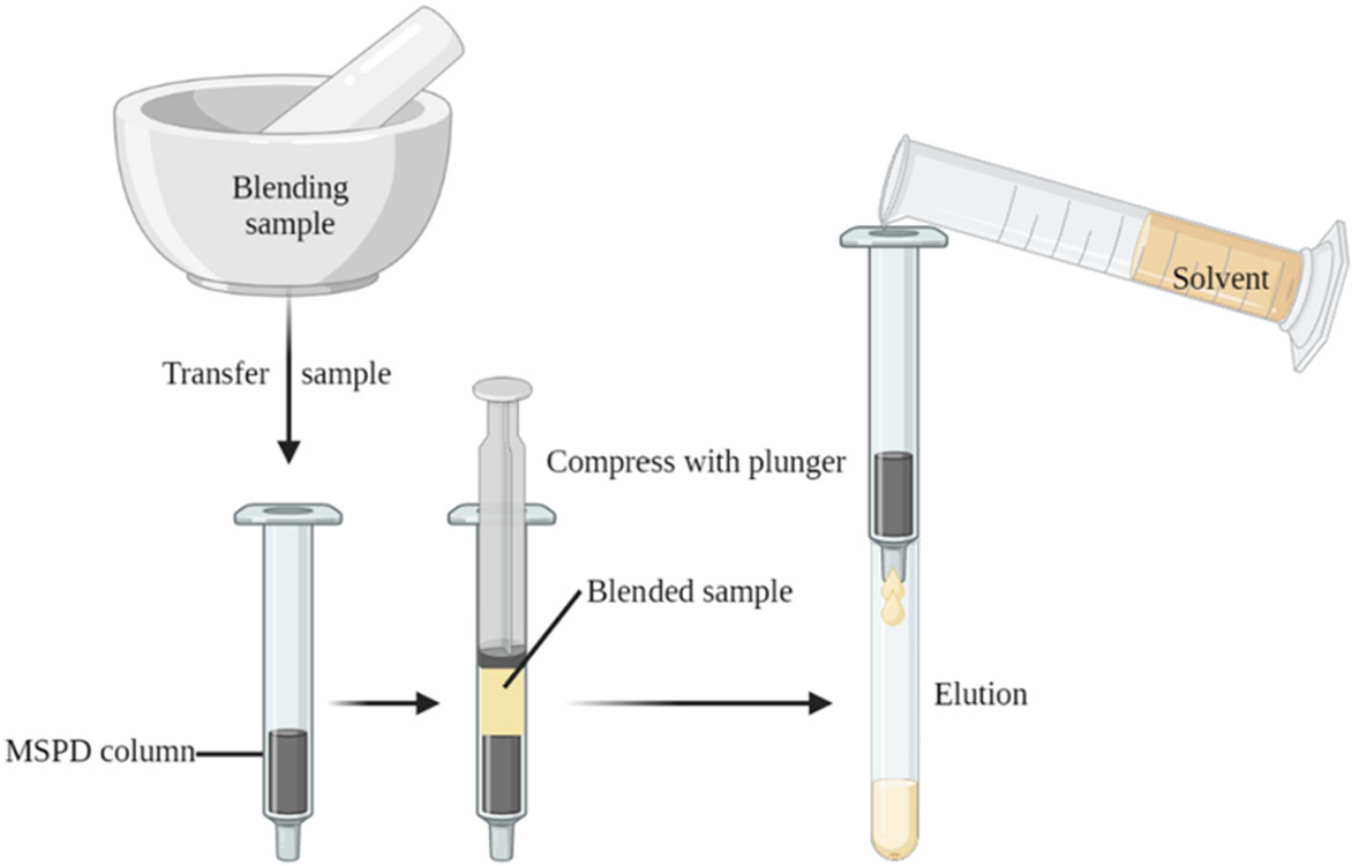

Figure 4. Schematic diagram of a typical MSPD extraction process.

One advantage of using MSPD is that, when compared to traditional solvent extraction, it does not require repetitive centrifugation, filtration, or extraction stages. With MSPD, the solvent extraction step is skipped. This significantly reduces the solvent and time needed for preparation-related manipulation [82]. Compared to other sample-preparation techniques, MSPD is more flexible, robust, and simple to use (no special equipment or instrumentation is needed).

The mild extraction conditions (i.e., room temperature and atmospheric pressure) preserve analytes from degradation and denaturation [82,83]. Moreover, MSPD has occasionally been used in combination with pressurized liquid extraction to enhance the recoveries of compounds that have significant interactions with the solid matrix [83,84]. The process's effectiveness and selectivity are determined by choice of solid support and elution solvent. Overall, MSPD requires a minimal consumption of organic solvents, particularly when miniaturized [83,85]. Although this extraction method is relatively quick, it cannot be fully automated, which is a problem when large sample sets are required for routine

analyses. The majority of the time, materials that have been processed or extracted using MSPD are subsequently analysed using GC-MS or LC-MS [83].

In MSPD, a variety of dispersing substances have been used. Materials frequently employed as SPE phases can improve the technique's selectivity and combine the extraction and clean-up steps. Most works use reversed-phase (RP) materials such as C_{18}- and C_8-silica bonded phases, but normal-phase (NP) materials, including alumina, silica, and florisil, are frequently used. New MSPD systems have recently been proposed, including molecularly imprinted polymers and carbon-based materials [83]. Deng et al. used a C_{18}-silica sorbent in MSPD combined with UPLC-MS/MS to determine eight gibberellins in *Arabidopsis thaliana* leaves. The recoveries ranged between 83–104% and LOQs of 0.87–4.37 pg/mL [86]. Gómez-Mejía et al. [87] created a novel with a straightforward MSPD extraction process that relied on titanium dioxide nanoparticles and capillary liquid chromatography connected to a diode array detector and mass analyser (cLC-DAD-MS) for the extraction and identification of polyphenols from grape residues [87]. Wei et al. [88] proposed a method for determining the five sesquiterpenoids of *Curcuma wenyujin* by MSPD extraction coupled with microemulsion electrokinetic capillary chromatography (MEEKC). This study investigated four conventional dispersants (silica gel, florisil, neutral alumina, and C_{18}) and three molecular sieves (TS-1, SBa-15, SAPO-11). The results demonstrated that C_{18} and silica gel exhibited a relatively higher extraction efficiency for curcumenol. However, the molecular sieves resulted in higher recoveries for all target sesquiterpenoids than conventional sorbents [88].

Table 5 includes all data described above and some additional findings from our investigation regarding MSPD techniques for natural products.

Table 5. Application of MSPD techniques for extraction of several compounds in natural products.

Compounds	Sample	Amount	Mode	Type of Sorbent	Limit of Quantitation	Conditions of extraction	Instrumentation	Recovery (%)	Ref.
Gibberellins	*Arabidopsis thaliana* leaves	0.30−0.80 mg	MSPD	silica	0.87–4.37 pg/mL	Stir time: 10 min; Stir rate: 10,000 rpm; Extraction solvent: methanol (10 mL/g); Extraction temperature: 4 °C	UPLC-MS/MS	83–104	[86]
Polyphenols	Grape residues	0.1 g	MSPD	titanium dioxide nanoparticles and diatomaceous earth	0.2–207 µg/g	Stir time: 1 min; Stir rate: 3000 rpm; Extraction solvent: 2 mL ethanol: water (20:80, *v/v*); Extraction temperature: room temperature; Other extraction time: 3 min	cLC-DAD-MS	ns	[87]
Sesquiterpenes	*Curcuma wenyujin*	2.0 g	MSPD	polypropylene	0.005–0.034 mg/mL	200 mg dispersant; Extraction solvent: 1 mL of methanol	MEEKC	99–102	[88]
5-HMF and glycosides	*Fructus Corni*	20.0 mg	MSPD	silica	0.07–0.24 µg/mL	Stir time: 3 min; Extraction solvent: 6 mL [Domim]HSO_4; Extraction time: 6 min	UHPLC-UV	95–103	[89]
Caffeic acid; Forsythoside A; Philyrin; Quercetin; Isorhamnetic; Arctigenin	*Forsythiae Fructus*	20.0 mg	MSPD	Surfactant T114-based vortex-synchronized	0.08–0.25 µg/mL	Extraction solvent: 2 mL 10% surfactant T114; Extraction time: 5 min	UHPLC-DAD	95–104	[90]
Polyphenols	Pomegranate peel	26.0 mg	µ-MSPD	Carbon molecular sieve	0.76–11.00 ng/mL	Extraction solvent; 200 µL methanol; Extraction time: 1.5 min	UHPLC-Q-TOF-MS	88–106	[91]
Lignans	Aerial parts of *Saururus chinensis*	0.2 g	MSPD	Silica gel	0.26–2.63 µg/mL	Extraction solvent: 5 mL of methanol; Extraction time: 15 min	HPLC-DAD	93–103	[92]
Anthraquinones	*Cassieae Semen*	0.02 g	MSPD	C_{18} and silica gel	2.20–13.20 µg/mL	Extraction solvent: 1 mL of 250 mM [Domim]HSO_4; Extraction time: 10 min	HPLC	91–106	[93]
Terpenoids, crocins, quinic acid flavonoids	*Gardeniae fructus*	10.0 mg	MSPD	2,6-dimethyl-β-cyclodextrin	0.06–1.25 µg/mL	Extraction solvent: 0.5 mL of 100 mM [C12mim]HSO_4;	UHPLC-DAD	96–100	[94]

Legend: [C12mim]HSO_4: 1-dodecyl-3-methylimidazolium hydrogen sulfate; [Domim]HSO4: 1-do- decyl-3-Methyl-1H-Imidazolium hydrogensulfate; µ-MSPD: Micro matrix solid-phase dispersion; cLC-DAD-MS: Capillary liquid chromatography coupled to a diode array detection and a mass spectrometry; DAD: Diode array detection; HPLC: High-performance liquid chromatography; MEEKC: Microemulsion electrokinetic capillary chromatography; MS: Mass spectrometry; MSPD: matrix solid-phase dispersion; UHPLC-Q-TOF-MS: ultrahigh-performance liquid chromatography coupled with quadrupole time-of-flight tandem mass spectrometry; UV: ultraviolet detection; Ref.: Reference.

2.5. Micro-Solid Phase Extraction

Modern SPE-modified techniques can be categorized into three groups: micro-SPE (μ-SPE), dispersive micro-SPE (D-μ-SPE), and magnetic dispersive SPE (M-D-μ-SPE) method [95].

Micro-SPE (μ-SPE) has been used in many studies in reference to the trend towards miniaturization, with the "μ" designation intended to imply a reduction in device dimensions, amount of sorbents, and/or use of microsized or nanosized materials (particularly the latter with their advantageously large surface area and exceptional physicochemical properties) [96]. In comparison to standard SPE, μ-SPE provided substantial insight into sample preparation that reduces the solvents' operating time and chemical consumption. As a result, μ-SPE became quite well-known as a solvent-free method [95]. Therefore, μ-SPE has several benefits, including low solvent consumption, a higher enrichment factor than SPME, extremely high selectivity and sensitivity, simplicity of application, being less time consuming, a relatively low cost, compatibility with various systems of analyte separation and detection, and also enabling headspace and immersion modes. Despite all of this, there are drawbacks to the implementation of μ-SPE, including analyte carry-over, fragile fibres, and a stationary phase with a restricted range [60,95,96].

μ-SPE extraction is conducted using a device that comprises a porous membrane envelope containing a small amount of sorbent (Figure 5). A wide variety of commercial and in-house-synthesized sorbent materials can be utilized in μ-SPE, with the choice of sorbent being predominantly dictated by the nature of the target analytes. There are several commercially available sorbents: activated alumina, Haye-Sep B, Haye-Sep A, Porapak R, ethylsilane (C_2), octylsilane (C_8), octadecylsilane (C_{18}), activated carbon (CA), carbograph (GC), and multi-walled carbon nanotubes (MWCNTs) [64]. Khayoon et al. [97] used μ-SPE in combination with LC-MS/MS for the extraction and determination of aflatoxins (B1, B2, G1, G2) from food samples (coffee and malt beverage). The authors resorted to C_8, with only 350 μL of solvent volume. The detection limits ranged from 0.12–0.76 ng/g [97]. In another example, Oasis μ-SPE was used to extract and determine phenolic compounds in four sea algae samples. Sorbents of μ-SPE plate mixed-mode cation exchange sorbent (MCX) and mixed-mode anion exchange sorbent (WAX) with MCX and WAX sorbent SPE cartridges were compared. The authors concluded that using the MAX cartridge in μ-SPE plate was more efficient than conventional SPE columns [98].

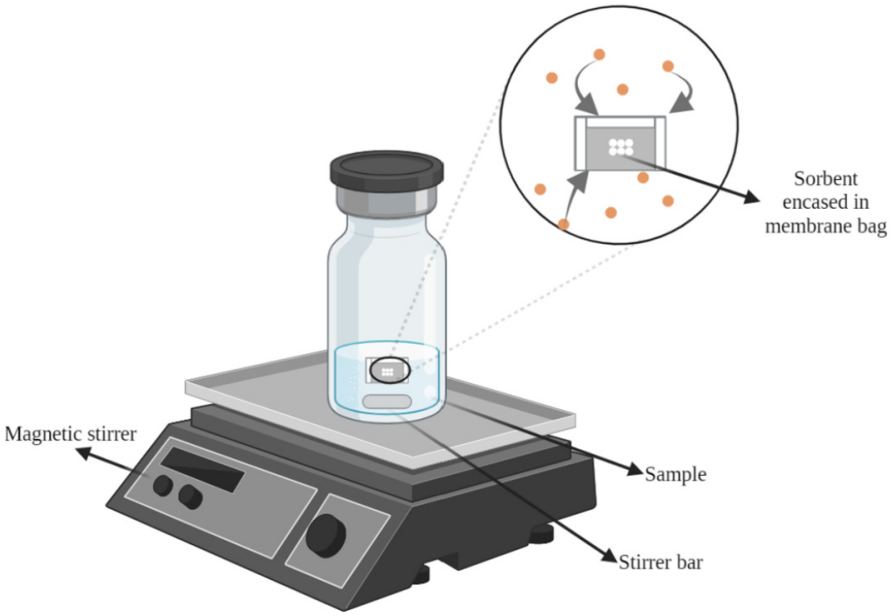

Figure 5. Illustration of μ-SPE system.

Some of the most used novel sorbents are zeolite, silica, molecularly imprinted polymers, and MOFs [96]. MOFs are among the most significant μ-SPE materials [95]. However,

there are few reports on applying this technique to determine natural products, since investigations with D-μ-SPE are more common. Nonetheless, the studies that implement μ-SPE use molecularly imprinted polymer sorbents. Lee et al. [99] used molecularly imprinted polymers combined with HPLC and coupled with a fluorescence detector (FD) for the determination of ochratoxin A (OTA) from coffee and grape juice samples. The method was applied in 24 samples, where 18 were positive for OTA. Furthermore, compared to other methods that employed LC-MS/MS, the proposed method achieved a lower LOQ [99].

Concerning D-μ-SPE, Anastassiades et al. [100] worked on the first article that introduced the D-μ-SPE method. This miniaturized technique has superior advantages over the conventional SPE method, such as a convenient conduction process (once it does not involve the passage of the sample solution or extraction solvent through an SPE column), being cost-effective, fast, requiring lower volumes of solvent, can be applied to different analyte–matrix combinations, and can avoid column-blocking problems [60,95].

This method leads to a higher interaction between the sorbent and analyte, consequently improving extraction efficiency since the sorbent is directly mixed with the sample through methods such as sonication or vortexing (Figure 6) [95,96]. Extensive types of sorbents have been investigated for their maximum adsorption capability and reusability. Hence, the development of novel materials such as RP-C_{18}, mesoporous hybrid materials, carbon nanotubes, graphene, and functionalized silica. Furthermore, MOFs have been used as extraction sorbents in the D-μ-SPE method [95].

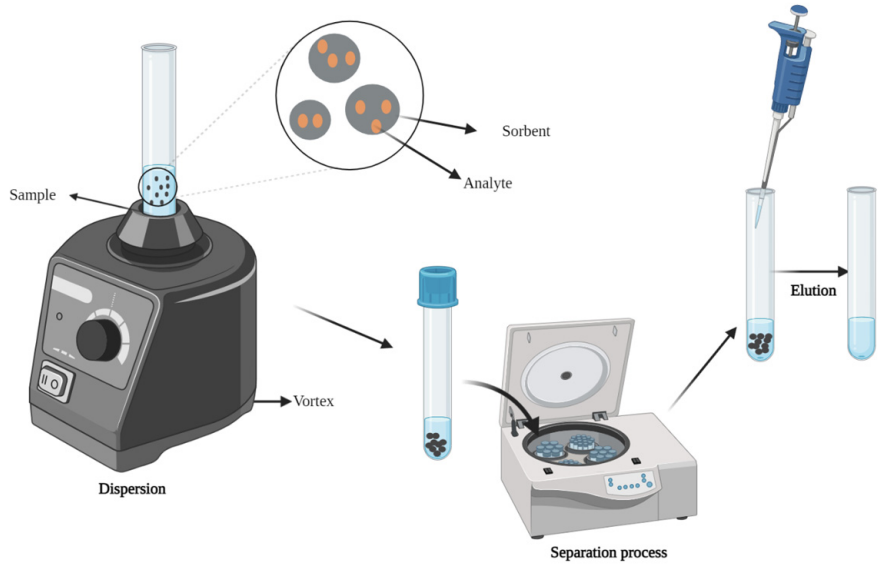

Figure 6. Representation of D-μ-SPE methodology.

Asfaram et al. [101] created a method of D-μ-SPE combined with UV-Vis spectrometry via ultrasound to determine quercetin concentrations in extracts of *Nasturium officinale* and fruit juice. For this method, the sorbent was synthesized by doping copper and sulfide into the tetragonal structure of SnO_2-nanoparticles (Cu- and S- @SnO_2-NPs) and subsequently loading it on activated carbon (AC). Recoveries ranging from 90–97% were achieved [101]. More recently, Bakhytkyzy et al. [102] extracted a diverse range of lipids from a total of 30 commercially available oilseeds using dispersive sorbent hybrid SPE-Phospholipid and C_{18} (50/50, *w/w*) and LC-Q-TOF-MS. The identified lipid classes included lysophosphatidylcholines (LPC), lysophosphatidylethanolamine (LPE), glycerol phosphatidylcholines (PC), glycerophosphatidylethanolamines (PE), diacylglycerols (DG), and triacylglycerols (TG) [102].

In addition to the facts mentioned above, Table 6 encompasses other research results from our research.

Table 6. Application of μ-SPE/D-μ-SPE techniques for extraction of several compounds in natural products.

Compounds	Sample	Amount	Mode	Type of Sorbent	Limit of Quantitation	Conditions of Extraction	Instrumentation	Recovery (%)	Ref.
Aflatoxins	Coffee and malt beverage	10.0 mL	μ-SPE	C_8	0.40–1.94 ng/g	Stir rate: 1000 rpm; Extraction time: 90 min; Desorption solvent: 350 μL acetonitrile; Desorption time: 25 min	LC-MS/MS	86–109	[97]
Phenolics	Sea algae	50.0 mg	μ-SPE	MCX, MAX, WAX, WCX,	0.23–1.68 ng/mL	Conditioning: 50 μL methanol and 50 μL water; Washing: 2% acetic acid in methanol; Elution: 2% ammonium hydroxide in methanol	RRLC-MS/MS	n.s.	[98]
Ochratoxin A	Coffee and grape juice	10.0 g of coffee and 10 mL of juice	μ-SPE	MIP	0.06–0.19 ng/g	Stir rate: 1000 rpm; Extraction time: 30 min; pH sample: 1.5; Desorption solvent: 250 μL methanol: acetic acid (98:2, *v/v*); Desorption time: 20 min	HPLC-FD	90–101	[99]
Quercetin	*Nasturtium officinale* extract and fruit juice	0.01 g	D-μ-SPE	Cu- and S-@SnO_2-NPs-AC	14.49 ng/mL	pH sample: 3.5; Stir rate: 4000 rpm; Extraction time: 4 min; Desorption solvent: 200 μL methanol; Desorption time: 2 min	UV-Vis	90–97	[101]
Lipids	Oilseed	1.0 mL	D-μ-SPE	HybridSPE-Phospholipid and C_{18}, (50/50, *w/w*)	n.s.	Stir rate: 20 000 rpm; Stir time: 10 min; centrifuged for 5 min at 7000 rpm. Washing: 1 mL of 70% methanol in water, mixed for 10 min and centrifuged for 5 min. Elution: 1 mL methanol: ammonium (95:5, *v/v*)	LC-Q-TOF-MS	n.s.	[102]
Cholecalciferol	Milk	1.0 mL	D-μ-SPE	3DG-Fe_3O_4@Sp	10.23 μg/L	Stir time: 15 min; Desorption solvent: 400 μL acetonitrile; Desorption time: 4 min	HPLC-UV	71–113	[103]
Flavonoids	Dark tea, chocolate, vegetable and fruit juice	10.0 mL	D-μ-SPE	MANPs	0.66–3.63 μg/L	pH sample: 4.9; Stir time: 2.1 min; Desorption solvent: 100 μL tetramethylammonium chloride and lactic acid; Desorption time: 5 min	HPLC-UV	>91	[104]
Flavonoids	Apple, grape juice, green tea	0.5–1.0 g	Magnetic D-μ-SPE	SiO_2@Fe_3O_4	2.98 μg/L	Extraction time: 10 min; Desorption solvent: 250 μL of ethanol; Desorption time: 2 min	HPLC-UV	97	[105]

Legend: μ-SPE: Micro-solid-phase extraction; Cu- and S- @SnO_2-NPs-AC: Copper and sulfide into the tetragonal structure of SnO_2-nanoparticles; D-μ-SPE: Dispersive micro-solid-phase extraction; FD: Fluorescence detector; HPLC: High-performance liquid chromatography; LC-MS/MS: liquid chromatography–tandem mass spectrometry; LC-Q-TOF-MS: Liquid chromatography/quadrupole time-of-flight mass spectrometry; MANPs: Magnetic agarose nanoparticles; MAX: Mixed-mode anion- exchange a reversed-phase sorbent; MCX: Mixed-mode cation-exchange a reversed-phase; n.s.: Not specified; RRLC-MS/MS: Rapid resolution liquid chromatography coupled to tandem mass spectrometry; MIP: molecularly imprinted polymer; UV: Ultraviolet detector; UV-Vis: ultraviolet-visible detector; WAX: Mixed-mode weak anion-exchange a reversed-phase sorbent; WCX: Mixed-mode weak cation-exchange a reversed-phase sorbent; Ref.: Reference.

2.6. Molecularly Imprinted Polymers

Molecularly imprinted polymers (MIPs) are tailor-made materials with recognition sites able to rebind a target molecule specifically in preference to other closely-related compounds [106]. These sorptive materials are the latest development in MSPE coatings and can be used for very selective extractions of analytes [60,107,108]. The first MISPE procedure was reported by Sellergren in 1994 [60,109], and since that time, this technique has been developed and is widely used in many research areas [60].

MIP particles have been packed in cartridges and columns for performing SPE, allowing the development of a great variety of MISPE-based analytical methods for the selective extraction and determination of organic compounds in bio-, food, and environmental samples [110]. They have also been widely used as artificial receptors in catalysis, sensors, and drug development and screening [60,111]. MIPs used for SPE can be synthesized by non-covalent imprinting, covalent imprinting, and hybridization of covalent and non-covalent imprinting, also called semi-covalent imprinting [60,109]. These materials are obtained by polymerizing functional and cross-linking monomers around a template molecule, leading to a highly cross-linked polymer. Once polymerization has taken place, the template molecule is removed, and binding sites with shape, size and functionalities complementary to the target analyte are established [110].

The template molecule is removed after polymerization, and subsequently, binding sites with similar shape, size, and functionality to the target analyte are generated [110]. Since these synthetic polymers present predetermined selectivity towards a given analyte or a group of structurally related species [60,112], this results in an imprinted polymer that is stable, robust, and resistant to a wide range of pH, solvents, and temperatures. Therefore, their behaviour emulates the interactions established by natural receptors to retain a target molecule in a particular way but without the associated stability limitations. It also has the benefit of being a low-cost synthesis approach [60,110,113,114]. Combining MIPs with microextraction techniques provides powerful analytical tools with the characteristics of both technologies: simplicity, flexibility, and selectivity [110]. MIP has drawbacks, including difficulties with optimization, the length of time required for any analysis, and the potential impossibility of long-term use due to analyte build-up [113,114].

Recently, there have been reports of applications of MIP in traditional SPE to determinate flavonoids (myricetin, quercetin, and naringin, among others) in extracts of plants, essentially using HPLC [115–120]. For example, molecularly imprinted polymers prepared by a surface imprinting were used to direct extraction of flavonoids from Gingko leaves, obtaining recoveries of 97% [117]. However, also MIPs have been applied in different separation methods, such as SBSE and MSPD.

The published research on the determination and quantification of the analytes being studied in natural products is summarised in Table 7.

Table 7. Application of MISPE techniques for extraction of several compounds in natural products.

Compounds	Sample	Amount	Mode	Type of Sorbent	Limit of Detection	Condition of Extraction	Instrument	Recovery (%)	Ref.
Rosmarinic acid	Aerial parts of *Rosmarinus officinalis* L.	113.0 g	SPE	MIP	2.01 μg/mL	Loading solvent: 2 mL acetonitrile/water (97.5:2.5, *v/v*); Washing solvent: 2 mL of water; Elution solvent: 2 mL of methanol: acetic acid (9:1, *v/v*).	HPLC/DAD/MS	81	[121]
Salidroside	*Rhodiola crenulata* root powder	1.0 g	SPE	MIP (200 mg)	0.21 μg/L	Loading solvent: methanol Washing solvent: 1 mL methanol: water (5:95, *v/v*); Elution solvent: 2 mL methanol: acetic acid (1:9, *v/v*)	HPLC-UV	88–97	[122]
Paclitaxel	Pacific yew tree powder	10.0 g	n.s.	MIP	n.s.	Extraction solvent: 400 mL of methanol; extraction time: 30 min	HPLC	n.s.	[123]
Coumarins, 7-hydroxycoumarin, 7-methoxycoumarin	food and plant extracts	1.0 g	SPE	MMIPs	1.04–5.92 μg/g	Conditioning: 3 mL of methanol: acetic acid (9:1, *v/v*) and 5 mL of analyte solvent (methanol/water 1/1, *v/v*); Stir time 30 min at 22 °C. Washing: 2 mL water; Elution: 1.25 mL methanol: acetic acid (9:1, *v/v*) and stirred for 30 min.	HPLC-DAD	71.4–90.3	[124]
Oblongifolin C	*Garcinia yunnanensis* Hu	45.0 g	SPE	MIP	n.s	Loading solvent: methanol-water (80:20, *v/v*); Eluting solution: methanol-water (50:50, *v/v*) and 70:30 (*v/v*)	HPLC	48–77	[125]
Matrine, oxymatrine, and sophocarpine	*Sophora moorcroftiana* (roots, stems, leaves, and seeds)	1.0 mL	SPE	double-templated molecularly imprinted polymers	9.23–15.42 ng/g	Wash with water, acetic acid/MeOH (20:80, *v/v*), and acetonitrile; Loading solvents: MeOH, acetonitrile, and water; Washing solvents: (2 mL) of n-hexane, carbon tetrachloride (CCl4), methylene chloride (CH2Cl2), acetonitrile, MeOH, and water; Elution solvent: acetic acid-MeOH.	HPLC–MS/MS	73–98	[126]

Table 7. *Cont.*

Compounds	Sample	Amount	Mode	Type of Sorbent	Limit of Detection	Condition of Extraction	Instrument	Recovery (%)	Ref.
Myricetin	*Carthamus tinctorius* L. and *Abelmoschus manihot*	15.0 g	SPE	MIP	0–25 μg/mL	Column rinsed with 5 mL water and 5 mL methanol (×3). Extract solution was loaded on the column at a flow rate of 0.2 mL/ min. Wash with 10 mL pure water (×3) and 10 mL 10% methanol–water (*v/v*) (×3). Elution with 10 mL of methanol–acetic acid (8:2, *v/v*).	HPLC-DAD	79–84	[116]
Flavonoids	*Astragali Radix* extract	10.0 mL	SPE	calycosin-MIPs	n.s.	Conditioning: 10 mL of methanol; Sample load flow rate: 1 mL/min; Washing: 9 mL of methanol and 12 mL of methanol: acetic acid (9:1 *v/v*); Elution: methanol: acetic acid	HPLC-UV	n.s.	[115]
Flavonoids	*Ginkgo* leaves	4.0 g	SPE	MIP	n.s.	Conditioning: methanol; Sample loading flow rate: 1 mL/min; Washing: 12 mL of acetone; Elution: 9 mL methanol: acetic acid (9:1, *v/v*)	HPLC-UV	n.s.	[117]
Naringin	*Citri grandis* extract	n.s.	SPE	SMIMs	n.s.	Conditioning: 5 mL methanol; Washing: 4 mL of methanol; Elution: 4 mL of ethanol: water: acetic acid (50:50:2)	HPLC-UV	84	[118]
Naringin; genistein	*Sophora japonica* or shaddock peels	10.0 g or 5.0 g	SPE	MIP	n.s.	Washing: ethanol; Elution: ethanol: acetic acid (4:1, *v/v*)	HPLC-UV	n.s.	[119]
Flavonoids	*Ginkgo biloba* tea	5.0 g	SPE	h-BN-MIP	n.s.	Washing: 1 mL deionized water; Elution: 1 mL ethanol	HPLC-UV	98–100	[120]

Legend: DAD: Diode array detector; h-BN: Hexagonal boron nitride; HPLC: High-performance liquid chromatography; LC: Liquid chromatography; MIP: Molecularly imprinted polymer; MMIPS: Magnetic molecularly imprinted polymer; MS/MS: Tandem mass spectrometry; MS: Mass spectrometry; n.s.: Not specified; SMIMs: Surface molecularly imprinted polymer microspheres; SPE: Solid-phase extraction; UV: Ultraviolet detector; Ref.: Reference.

3. Conclusions

Pawliszyn et al. published the first works on SPME in the 1990s, and several microextraction procedures have appeared since. Concerning the analysis of natural compounds, there is no doubt that HS-SPME is the most used approach. Its advantages, such as the fact that no organic solvents are used, the safety for the operator, sustainability, renewability, and reusability of materials, make this technique the ideal prototype of the so-called "green" procedures in sample preparation, according to the AGREEprep analytical greenness metric tool. Despite this, other approaches such as MEPS or SBSE are being increasingly used, perhaps due to the speed and simplicity of the extractions, or, in the case of MEPS, due to the advent of fully automated devices (eVol® or MEPS syringes). There has been a great deal of attention concerning developing modified sorbents, such as multi-walled carbon nanotubes (MWCNTs) and MIPs, probably due to their high selectivity.

However, one of the main challenges of using those approaches is obtaining pure and well-characterized materials, as well as the fact that they are not commercially available, which poses a problem to laboratories and industry. Therefore, a great range of opportunities have appeared for developing greener sample preparation methods while ensuring high analytical performance concerning the chemical characterization of natural compounds. One should bear in mind that applying environmentally benign sample preparation methods is a social responsibility of analysts, as it contributes to pollution reduction and sustained development.

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