separations

Review

Microextraction and Eco-Friendly Techniques Applied to Solid Matrices Followed by Chromatographic Analysis

Attilio Naccarato, Rosangela Elliani * and Antonio Tagarelli

Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via P. Bucci Cubo 12/C, I-87030 Arcavacata di Rende, Italy; attilio.naccarato@unical.it (A.N.); antonio.tagarelli@unical.it (A.T.)
* Correspondence: rosangela.elliani@unical.it

Abstract: In this review, a 5-year overview on environmentally friendly approaches for the extraction of the most relevant organic pollutants in soil, sediment, particulate matter, and sewage sludge coupled with chromatographic analysis is reported. Organic contaminants encompass various compounds derived from personal care products, industrial chemicals, microplastics, organic matter combustion, agricultural practices, and plasticizer material. The principles of green analytical chemistry (GAC) and green sample preparation (GSP) serve as a guideline for the development of more environmentally sustainable analytical protocols. This study focuses attention on microwave-assisted extraction (MAE), ultrasound-assisted extraction (UAE), matrix solid-phase dispersion (MSPD), and microextraction techniques, such as solid-phase microextraction (SPME), stir bar sorptive extraction (SBSE), hollow-fiber liquid-phase microextraction (HF-LPME), spray-assisted droplet formation-based liquid-phase microextraction (SADF-LPME), and dispersive liquid–liquid extraction (DLLME). These approaches represent the most relevant eco-friendly sample preparation for the advanced extraction of target analytes from environmental solid samples.

Keywords: eco-friendly approaches; microextraction techniques; solid matrices; green sample preparation; chromatographic analysis; organic environmental pollutants; greenness assessment; metric tools

check for updates

Academic Editor: Dimosthenis Giokas

Received: 18 April 2025
Revised: 8 May 2025
Accepted: 9 May 2025
Published: 14 May 2025

Citation: Naccarato, A.; Elliani, R.; Tagarelli, A. Microextraction and Eco-Friendly Techniques Applied to Solid Matrices Followed by Chromatographic Analysis. *Separations* **2025**, *12*, 124. https://doi.org/10.3390/separations12050124

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

The development of an analytical method entails four principal stages: sampling, sample preparation, instrumental analysis, and data analysis. Each step influences the reliability, accuracy, reproducibility, and sensitivity of the method and determines the time and cost of the analysis. Although significant advances have been made in chromatography and detection techniques, sample preparation remains a critical bottleneck in the implementation of an analytical method, as it involves the extraction and/or preconcentration of compounds of interest from a matrix to yield a sample at an appropriate concentration for instrumental analysis. Particularly for solid matrices, multi-step sample preparation procedures may exacerbate cumulative errors. The extraction of target compounds from soil, sediment, particulate matter, and sewage sludge is particularly laborious due to the complexity of the matrices, the presence of interfering compounds, and the low concentration of desired analytes [1,2]. Among the classical techniques for the extraction of analytes from solid matrices, Soxhlet extraction, introduced in 1879 by the German chemist Franz von Soxhlet, remains the oldest sample preparation technique in use. Soxhlet extraction has been endorsed as a standard method by the Environmental Protection Agency (EPA) and has recently been employed in monitoring studies of organochlorine pesticides and in the analysis of soil

samples for microplastics [3,4]. However, it is notoriously time-consuming and consumes large volumes of volatile and toxic organic solvents, which pose significant hazards to the health of analysts and the environment. Furthermore, a subsequent concentration and/or purification step is often required after extraction, potentially leading to analyte losses. Moreover, the extensive use of organic solvents results in increased operational costs due to their subsequent disposal [5]. The advent of green analytical chemistry (GAC) and green sample preparation (GSP) has driven the scientific community toward the development of more environmentally friendly analytical protocols [6,7]. In recent decades, there has been an increasing focus on designing analytical methods that reduce or eliminate organic solvent use and that incorporate innovative approaches such as miniaturization and the application of greener energy sources. Concurrently, advancements in on-line and automated sample preparation have facilitated high-throughput analyses, further enhancing overall method efficiency. The implementation of green and sustainable techniques minimizes risks to human health, reduces analysis times, and contributes to environmental protection as well as the sustainability of the analytical workflow [8]. Among the most relevant eco-friendly approaches for the advanced extraction of target analytes from environmental solid matrices are microwave-assisted extraction (MAE), ultrasound-assisted extraction (UAE), matrix solid-phase dispersion (MSPD), and microextraction techniques such as solid-phase microextraction (SPME), hollow-fiber liquid-phase microextraction (HF-LPME), spray-assisted droplet formation-based liquid-phase microextraction (SADF-LPME), dispersive liquid–liquid extraction (DLLME), and stir bar sorptive extraction (SBSE). Most of the techniques mentioned belong to the class of microextraction techniques (METs). These are characterized by reduced sample and extraction solvent volumes, minimized waste generation, high enrichment factors that improve sensitivity, shortened analysis times, and a high potential for automation [9]. Such features align well with the criteria established by various metric tools developed for the greenness assessment of sample preparation [10–14]. Solid environmental matrices—such as soil, sediment, particulate matter, and sewage sludge—are recognized as critical reservoirs for a multitude of pollutants, which they retain in the environment due to strong adsorption and persistence. A thorough investigation of these organic contaminants is crucial for assessing risks to both human health and environmental integrity. The major challenge in the determination of environmental pollutants lies in the wide spectrum of their physicochemical properties combined with the inherent complexity of the solid samples. Furthermore, these analytes are usually present at trace levels, thereby necessitating chromatographic analysis coupled with highly sensitive detectors, preceded by an efficient sample preparation step. This review aims to provide an update on environmentally friendly sample preparation techniques for the extraction of a wide range of organic contaminants from environmental solid samples. It focuses on the analytical methods reported in the last five years (2020–2024) that employ green extraction protocols and chromatographic analysis for various emerging contaminants in soils, sediments, particulate matter, and sewage sludge, and it also addresses the novel materials implemented in microextraction techniques.

2. Environmental Pollutants

Emerging contaminants (ECs) are a wide group of organic pollutants that are increasingly present in the environment. This group encompasses various compounds derived from personal care products, industrial chemicals, microplastics, organic matter combustion, agricultural practices, combustion by-products, and plasticizer material [15]. These organic compounds pose an increasing risk to human health, including hormonal, neurological, carcinogenic, and other long-term toxic effects. Persistent and bioaccumulative contaminants are typified by endocrine-disrupting compounds (ECDs)—including parabens (PBs),

bisphenols (BPs), phthalate acid esters (PAEs), pesticide residues, and polychlorinated biphenyls (PCBs)—as well as by organophosphate flame retardants (OPFRs), polybrominated diphenyl ethers, herbicides, UV filters, and polycyclic aromatic hydrocarbons (PAHs). These compounds tend to be highly stable and persistent, causing serious health and ecotoxicological concerns when released into the environment [16,17]. The occurrence of organic pollutants has been extensively investigated in environmental water samples and biological fluids to evaluate human exposure to these compounds. Analytical protocols for the assessment of a multiclass of organic UV filters [18–20], PBs [21], OPFRs [22], PAEs [23,24], benzotriazoles (BTRs), benzothiazoles (BTs), and benzenesulfonamides (BSAs) [25,26] in tap water, rivers, seawater, and wastewater matrices—primarily based on solid-phase microextraction (SPME) and microextraction by packed sorbent (MEPS)—have been implemented with satisfactory analytical performance. In saliva and urine, PAHs and ECDs such as PBs and BPs, as well as metabolites, including phthalate monoesters and monohydroxylated polycyclic aromatic hydrocarbons (OH-PAHs), were investigated using SPME [27–31], DLLME [32–35], MEPS [36,37], and liquid-phase microextraction (LPME) [38–40] coupled with various chromatographic analytical systems. During the last five years, numerous analytical methods for the determination of different classes of environmental pollutants in soil, sediment, particulate matter, and sewage sludge samples—based on extraction techniques such as MAE, UAE, MSPD, SPME, SBSE, DLLME, and LPME, as well as combinations thereof (e.g., MAE, UAE, and MSPD coupled with SPME)—have been developed. Figure 1 illustrates the distribution of published studies for each eco-friendly extraction technique applied to the preparation of soil, sediment, particulate matter, and sewage sludge samples.

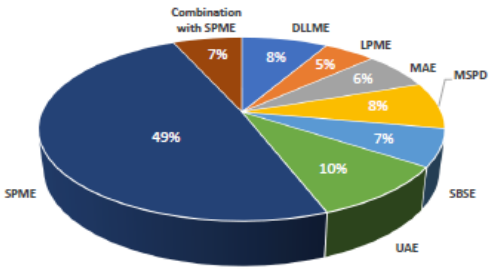


Figure 1. Distribution of the sample preparation techniques applied to the extraction of organic pollutants in solid environmental matrices.

3. Eco-Friendly Sample Preparation

Strategies for the analysis in solid matrices depend on the physicochemical properties of the analytes, particularly their volatility. In instances when target compounds exhibit insufficient volatility, extraction is typically carried out using a solid–liquid extraction technique. Subsequently, if the extracting medium is compatible with the instrumental system, the resulting solution may be directly analyzed. In this context, various analytical protocols based on green extraction methods, such as MAE, UAE, and MSPD, have been proposed in the last five years. A comprehensive list of solid sample extraction based on MAE, UAE, and MSPD is provided in Table 1. In cases where compatibility is not met, however, it will be necessary to subject the solution to a further extraction approach. In some cases, the combination of the aforementioned techniques with other green methodologies, particularly SPME, has resulted in environmentally friendly protocols. Moreover, SPME and other microextraction techniques have also been successfully employed for the analysis of volatile compounds by performing extraction directly in the headspace of the solid sample. These approaches are summarized in Tables 2 and 3.

3.1. Microwave-Assisted Extraction

The application of MAE for organic compounds was first introduced by Ganzler et al. in 1986 [41]. This technique utilizes microwave energy to enhance the extraction process by simultaneously heating both the solvent and the sample. The extraction mechanism relies primarily on two phenomena—ionic conduction and dipole rotation—that facilitate efficient heating. The ability of a solvent to absorb microwave energy and convert it into heat, thereby transferring this energy to other molecules, depends on some of its physical parameters, making the choice of solvent or mixture of solvents crucial. MAE is renowned for its high efficiency, significantly reduced extraction time, and solvent consumption when extracting a range of trace organic pollutants from solid environmental matrices. A graphic representation of MAE instrumentation is shown in Figure 2.

Moreover, MAE permits the simultaneous processing of a large number of samples while reducing energy consumption and costs compared to conventional methods [5,42,43]. A post-extraction purification step is usually required to clean the extract and mitigate matrix interferences that could affect analyte detection and quantification. Recently, MAE has been applied to the extraction of PAHs from soil, sediment, and sludge [44,45]. Ndwabu et al. developed and validated a method for extracting these analytes in sediment and sludge using MAE followed by GC-MS analysis [44]. They demonstrated that, after extraction, the use of filtration combined with solid-phase extraction (SPE) clean-up resulted in a better extraction efficiency of PAHs than the use of filtration alone. In another study, a method was implemented for the determination of phenanthrene, pyrene, chrysene, and benzo[a]pyrene in soil and sediment samples [45], comparing the extraction efficiency from spiked soil and sediment using supercritical fluid extraction (SFE) with ethanol as the modifier, MAE, and eucalyptus oil-assisted extraction (EuAE). The MAE parameters were optimized via a multivariate approach employing the Box–Behnken experimental design (BBD) [46]. Comparing MAE with other techniques showed that MAE is more efficient for the extraction of polar PAHs. However, SFE is the more robust method for extracting PAHs over the 0.5–10 mg/kg range from matrices of varying compositions, compared with MAE and EuAE. Furthermore, a group of pharmaceutical pollutants—cytostatic compounds characterized by mutagenic activity—was extracted by MAE from sediment and sludge at 60 °C for 5 min [47]. Although the developed analytical protocol did not include a purification step, direct LC-MS/MS analysis was performed after the extraction. Despite this, good sensitivity and LOD values ranging from 0.42 to 79.8 ng g^{-1} in sludge and 0.10 to 87.5 ng g^{-1}-were achieved. The method proposed is characterized by a simple procedure that is valid for both matrices (sludge and sediment) under the same extraction conditions and requires only a low amount of sample and only five minutes of extraction time. Finally, several biocides employed, among other things, in building materials were extracted by MAE from the particulate fraction of urban and surface waters and subsequently analyzed via LC-MS/MS [48]. The developed protocol allowed the particulate fraction of diverse water samples to be quantified at trace level, in the range of nanograms per gram of dry weight for most of the biocides and matrices.

3.2. Ultrasound-Assisted Extraction

UAE utilizes ultrasonic energy to induce a cavitation effect, during which bubble formation in the liquid phase and mechanical erosion of solid matrices occur. This process enhances the contact between the sample and the extraction solvent, leading to improved analyte recovery [5,49]. Several nitrated and oxygenated polycyclic aromatic hydrocarbons were extracted from $PM_{2.5}$ using UAE coupled with online SPE-LC-MS/MS, thereby increasing the automation of the analytical method and reducing analysis time [50]. This methodology represented the first instance of LC-MS/MS quantitative analysis for three carcinogenic dinitro-PAHs present in atmospheric $PM_{2.5}$. For the first time, organophos-

phate triesters, organophosphate diesters, and organophosphate hydroxylated degradation products were quantified in sediment via LC-MS/MS, with LOQ values ranging from 0.01 to 5.0 ng g^{-1} [51]. The optimized and validated method was applied to marine sediments, revealing high detection frequencies and elevated concentrations for many organophosphate triesters. Moreover, the co-occurrence of both organophosphate triesters and their degradation products, especially organophosphate hydroxylated degradation products, in sediment samples has been reported for the first time. The development of analytical methods for assessing several classes of emerging contaminants—including BTs, BTRs, BSAs, herbicides, PAHs, and polycyclic aromatic sulfur heterocycles (PASHs)—was carried out without performing a purification step after UAE [52–54]. When compared with the EPA's official MAE method for herbicide extraction from soil, UAE exhibited superior extraction efficiency for all investigated analytes while using a lower solvent volume at room temperature [53]. In this work, the application of the AGREEPrep tool resulted in a score of 0.7, indicating the environmental friendliness of the implemented method. Dvorakova et al. developed a method for the quantification of plastic additives (PAs), with different physicochemical properties, from soil [54]. They demonstrated that a binary extraction approach combining the quick, easy, cheap, effective, rugged, and safe (QuEChERS) method with UAE principles allowed the extraction of non-polar analytes that were not extracted by UAE alone. Moreover, it was proved that better analytical performance was achieved by eliminating the clean-up or pre-concentration phase in the sample preparation procedure. A novel approach for the extraction of PAHs and PASHs from sediments involved the use of a UAE microscale device (UAE-MSD) [55]. This configuration minimizes the required sample mass, solvent volume, and waste production, while enhancing automation by performing the extraction directly in the GC vial. Moreover, simultaneous extraction and clean-up eliminate the need for one of the concentration steps typically required by other procedures, thereby reducing the total time taken to process the sample.

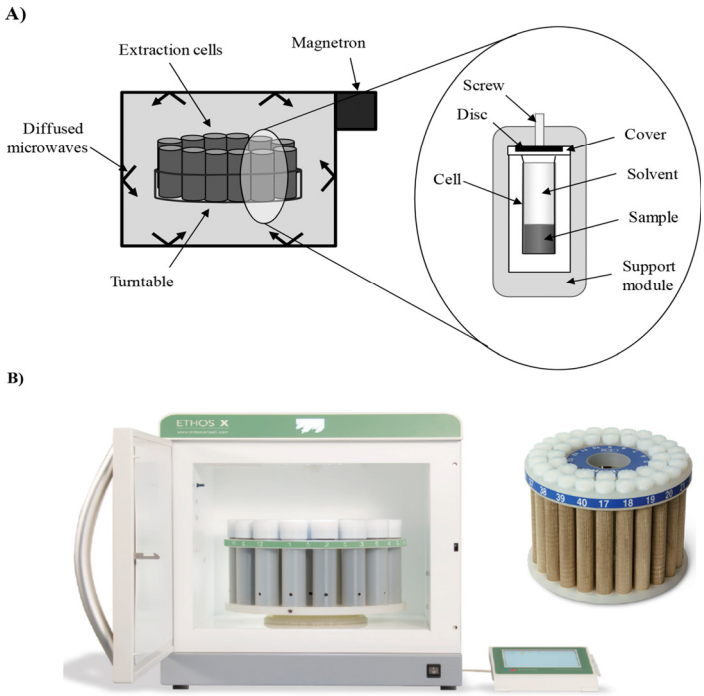


Figure 2. (**A**) Description of MAE components; (**B**) commercial MAE apparatus (reprinted from [43] with permission).

3.3. Matrix Solid-Phase Dispersion

MSPD was originally introduced by Barker et al. as a technique to extract drug residues from liver and muscle tissues [56]. This extraction technique is based on the disruption of the sample matrix followed by the dispersion of its components on an adsorbent, thereby creating an increased surface area for interaction. The resulting blend is then transferred into an empty cartridge and eluted with a small volume of solvent prior to instrumental analysis (Figure 3). As a microscale technique, MSPD requires only minimal sample amounts and low solvent volumes, integrating extraction and clean-up into a single step, thereby eliminating the need for additional steps prior to instrumental analysis [57].

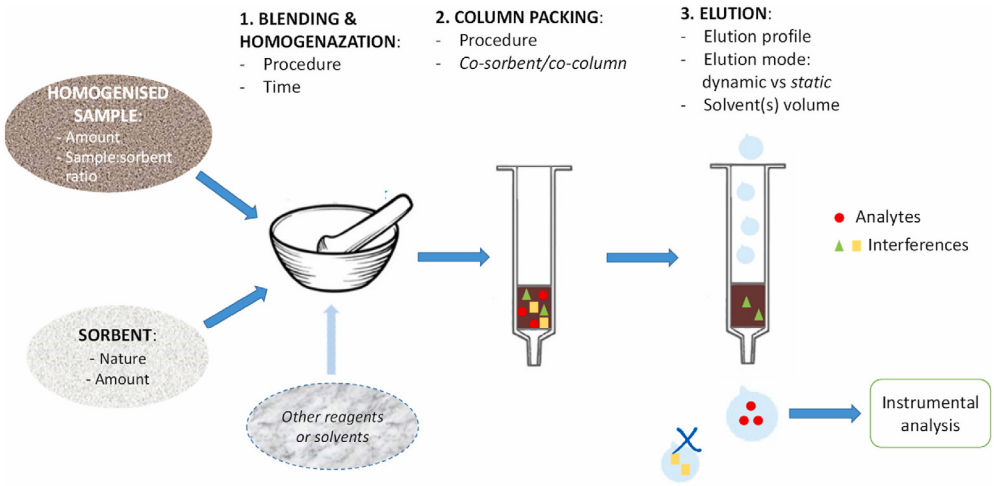


Figure 3. Representation of the three main steps involved in the MSPD process (reprinted from [57] with permission).

In recent years, novel materials and new combinations with classical sorbents have been implemented to improve selectivity and sorption capacity [58,59]. Rapid and sensitive analytical protocols for the quantification of several sulfonamides and OPFRs in soil and sludge followed by LC-MS/MS analysis were developed and validated [60,61]. Both methods provided for the use of classical sorbents and univariate optimization to determine the optimal sorbent type, sample-to-sorbent ratio, and elution solvent type and volume, while producing sample extracts ready for analysis in <20 min. Applying the latter method to real samples collected from wastewater treatment plants in Norway, where various sludge treatments were employed, revealed the presence of OPFRs in digested sludge samples. Overall, the data presented highlight the need to systematically assess the presence of OPFRs in order to thoroughly understand their mass balance in water from wastewater treatment plants and evaluate the potential risks associated with reintroducing them into the terrestrial environment when sludge is used as an agricultural fertilizer. Soares et al. implemented a fast and inexpensive vortex-assisted MSPD method for the simultaneous determination of pharmaceuticals and personal care products (PPCPs) and biocides in marine sediments [62]. The authors combined vortex-assisted extraction with MSPD to enhance analyte–solvent interaction, opting for the solid-support free approach because the composition of the analyzed matrix appeared, after the disruption, as a dried sediment with abrasive characteristics. This alternative sample preparation strategy reduced reagent use and waste generation while yielding good recoveries for all analytes. The addition of additives to the dispersing agent can further improve the dispersion of target analytes on the sorbent surface, promoting their migration from the matrix to the sorbent [63,64]. For example, a new ternary deep eutectic solvent was employed as a dispersing solvent to extract chlorophenols from river sediments [63]. This method not only reduced extraction

times but also increased extraction efficiency while maintaining excellent analytical performance. Sustainability assessment using the green analytical procedure index (GAPI) metric tool demonstrated the environmental friendliness of the proposed protocol. Moreover, a multiclass analysis for quantification of polyaromatic compounds such as PAHs and PCBs was achieved in sediment by combining 3-chloropropyl-functionalized silica particles with a conventional MSPD sorbent to improve desorption capacity [64]. The optimized MSPD method was then applied to extract analytes of interest from a certified matrix, and its performance was compared with that of a previously developed microwave-assisted extraction (MAE) method. Although both methods yielded high extraction efficiencies, MSPD required shorter extraction times and lower amounts of sample and solvent, ultimately providing a more purified extract. It is noteworthy that the robustness of the MSPD methodology was demonstrated through the extraction of aged sediments from a variety of sources, each exhibiting distinct mineralogical characteristics.

3.4. Solid-Phase Microextraction

Solid-phase microextraction (SPME) is a well-established technique for the extraction of semi-volatile and volatile compounds from various matrices [65–68]. SPME is regarded as a green extraction technique due to its ability for simultaneous extraction and preconcentration, while requiring minimal or even no use of organic solvents during the desorption step. As with other microextraction techniques, SPME addresses the need to reduce sample volume and solvent consumption and to make sample preparation faster and easier; it is also used for on-site applications. The SPME technique consists in exposing the fiber coating (extracting phase) to the sample for a given time. The transfer of analytes from the sample to the stationary phase can occur in both the headspace and direct immersion modes. To facilitate the transport of analytes from the solution to the fiber surface, some level of agitation is required. After equilibrium between the sample (or headspace) and coating is reached or after a specified time prior to reaching equilibrium, the fiber is inserted into the GC injector where the analytes are thermally desorbed for usually 1–2 min. A schematic figure of the SPME fundamentals is reported in Figure 4.

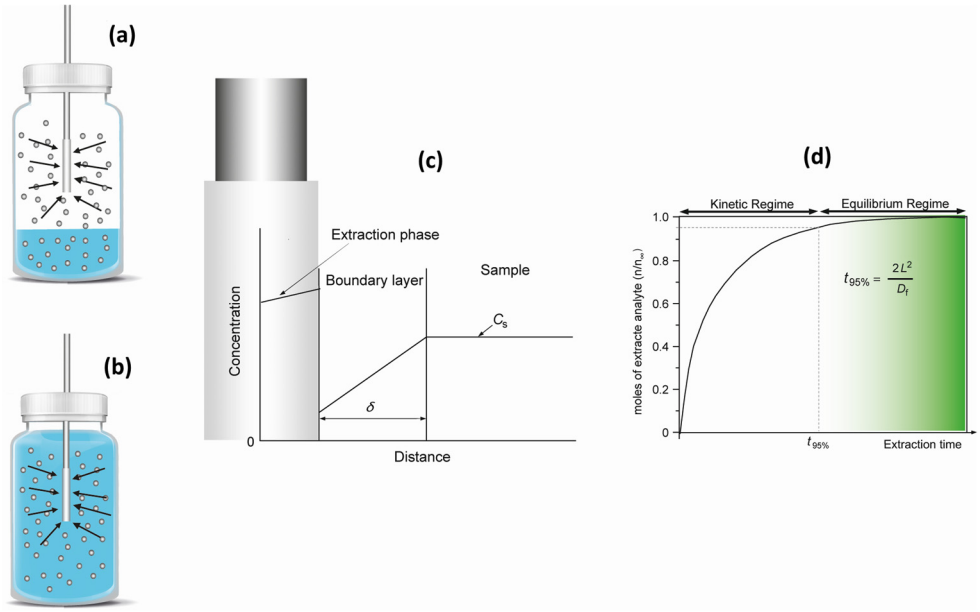


Figure 4. Graphic representation of the SPME principles: (**a**) headspace extraction mode; (**b**) immersion extraction mode; (**c**) boundary layer model configuration; (**d**) extraction time profile (reprinted from [65] with permission).

Table 1. Selected methods based on MAE, UAE, MSPD.

Analytes	Matrix	Extraction Approach	Volume and Type of Organic Solvent	Instrumentation	LOD	Linear Range	[Ref.]—Publishing Year
PAHs	Sediment and sludge	MAE + SPE as clean-up	50 mL n-hexane:acetone 1:1 (*v*/*v*)	GC-MS	0.025–1.211 µg/kg	0.01–0.8 mg/L	[44]—2023
PAHs	Soil and sediment	MAE	15 mL hexane:acetone 1:1 (*v*/*v*)	GC-MS	7.8–15.6 µg/kg (sediment) 15.6–31.3 µg/kg (soil)	0.5–10 mg/kg	[45]—2023
Cytostatic compounds	Sludge and sediment	MAE	14 mL MeOH	UHPLC-MS/MS	0.42–79.8 ng/g (sludge) 0.10–87.46 ng/g (sediment)	0.2–12 µg/g	[47]—2020
Biocides	Particulate fractions of urban and surface waters	MAE	20 mL of MeOH/DCM 60:40 (*v*/*v*)	HPLC-MS/MS	0.4–200 ng/g	0.05–250 µg/L	[48]—2020
NPAHs and OPAHs	$PM_{2.5}$	UAE + SPE clean-up	5 mL of MeOH	LC-MS/MS	0.001–0.042 µg/L	0.025–10 µg/L	[50]—2023
OPEs and organophosphate hydroxylated degradation products	Sediment	UAE + SPE clean-up	OP triesters and hydroxylated degradation products: 30 mL of ACN (UAE) and 9 mL of ACN (SPE); OP diesters: 30 mL MeOH (UAE) and 9 mL of MeOH (SPE)	LC-ESI-MS/MS	-	0.05–50 ng/g	[51]—2022
BTs, BTRs, and BSAs	$PM_{2.5}$ and PM_{coarse}	UAE	5 mL of ethyl acetate	GC-MS	0.001–0.08 ng/m^3 ($PM_{2.5}$) 0.002–0.14 ng/m^3 (PM_{coarse})	0.01–10 ng/µL	[52]—2020
Herbicides	Soils	UAE	10 mL of H_2O/MeOH 40:60 (*v*/*v*)	LC-MS/MS	0.010–0.097 ng/g	0.1–100 µg/L	[53]—2023
Plastic additives (PAs)	Soil	UAE + dSPE and UAE + QuEchERS	20 mL H_2O/MeOH 80:20 (*v*/*v*) and 20 mL n-hexane (UAE); 3 mL of ethyl acetate (dSPE); 10 mL of H_2O + 10 mL of ethyl acetate (UAE + QuEchERS)	UHPLC-MS/MS	-	0.1–100 ng/mL	[54]—2024
PAHs and PASHs	Marine sediment	UAE-MSD	500 µL of DCM:MeOH 65:35 (*v*/*v*)	GC-MS	8.8–30.2 ng/g	0.5–200 µg/L	[55]—2021
Sulfonamides	Soil	MSPD	3 g of C18 (dispersive sorbent); 12 mL of ACN (elution solvent)	HPLC-MS/MS	0.024–0.058 µg/kg	0.01–0.5 µg/mL	[60]—2024
OPFRs	Sewage sludge	MSPD	2 g of C18 (dispersive sorbent) 5 mL of acetone (elution solvent)	UPLC-ESI-MS/MS	-	0.02–150 ng/mL	[61]—2023
PPCPs and booster biocides	Sediment	VA-MSPD	5 mL of MeOH (elution solvent)	HPLC-(QqLIT)-MS-MS	0.13–11.06 ng/g	-	[62]—2021
Chlorophenols	River sediment	µMSPD	100 mg of Celite AZO + 150 µL of TDES (dispersive sorbent); 450 µL of ACN (elution solvent)	HPLC-PDA	1.04–2.48 µg/g	10–150 µg/g	[63]—2023
PAHs and PCBs	Sediment	MSPD	1 g of florisil + 0.5 g of 3-chloropropyl-bonded silica particles (dispersive sorbent); 5 mL acetone/hexane 50:50 (*v*/*v*) (elution solvent)	GC-MS	0.06–1.1 ng/g	0.05–3 mg/L	[64]—2021

Following its introduction in the early 1990s, the technique has undergone rapid development and expansion in terms of configurations, coating materials, and applications. In the last five years, several analytical approaches based on the SPME technique have been reported for solid matrices [69–101], proposing protocols for the quantitative analysis of pollutants [69–71,73–80,83,86,87,89–93,95–101] and, in some cases, natural components [81,84,85,88,94]. Numerous investigations were centered on the development of new coatings with the aim of improving extraction performance for specific classes of compounds, especially in terms of sensitivity and specificity [69–78]. Furthermore, the application of commercial devices and fiber coatings was investigated, with a particular focus on addressing environmental issues [79–93,99–101]. In addition, other works have been dedicated to the development of novel configurations with the purpose of enhancing the performance characteristics of conventional devices [94–97]. Various classes of compounds have been targeted in the proposed protocols, including well-established contaminants (PAHs [76,77,79,95–98], PCBs [75,95], PAEs [95], volatile amines [80], herbicides [73,74], pesticides [87,90,93], petroleum hydrocarbon volatile organic compounds [83], BTEX [95,100], phenols [78], PPCPs [95], BTs, BTRs, and BSAs [96]) as well as emerging polluting compounds, such as micro/nanoplastics [91], nitroaromatics [70], and nitro-polycyclic aromatic hydrocarbons [71,89].

3.4.1. Development of New Coatings

A novel SPME fiber based on an electrochemically prepared gold nanoparticles/poly 3,4-ethylenedioxythiophene composite on gold wire was proposed for the headspace cold fiber SPME analysis for 4-nitrotoluene, 1,3-dinitrobenzene, 2,4-dinitrotoluene, and 2,6-dinitrotoluene quantification from soil samples [70]. The combined use of a cooling apparatus to enhance extraction efficiency along with the newly developed coating ensured satisfactory analytical figures of merit and lower detection limits compared to previously reported methods. New coatings were also developed for the determination of herbicides in soil samples [73,74]. Specifically, a novel adsorbent based on a monolith/aminated carbon nanotube composite was prepared and employed as the extraction phase in multiple monolithic fiber solid-phase microextraction (MF-SPME) for the capture of phenoxycarboxylic acid herbicides [73]. A comparison of the features of the new protocol with those reported in the literature revealed that the sample consumption is lower and the volume of organic solvent utilized is reduced relative to other methods, with the exception of pipette tip solid-phase extraction. The introduction of a porous monolith-based magnetism-reinforced in-tube solid-phase microextraction is of crucial importance to the development of a novel protocol for the determination of sulfonylurea herbicides in soils [74]. A significant outcome of this investigation is that the utilization of a magnetic field during both the adsorption and desorption steps resulted in satisfying extraction efficiencies, which were higher than that achieved in the conventional in-tube SPME configuration. The use of covalent organic frameworks (COFs) as coatings for SPME fibers is the focus of two studies for the quantification of PAHs [77] and phenols [78] in soils. In the first work, a porphyrin-based COF was physically coated on stainless steel for the headspace solid-phase microextraction of PAHs prior to GC-FID determination. The method demonstrated excellent performance in terms of adsorption attributed to π–π, hydrophobic, and van der Waals interactions, offering several advantages over other published methods, such as simplicity, a solvent-free process, short extraction times, and minimal adsorbent usage. In the second study, an environmentally friendly in situ growth method was proposed for the preparation of an SPME coating based on COFs, providing a new idea for the preparation of SPME coatings. The application of the newly developed fiber in headspace mode for the determination of phenols in soils demonstrated higher extraction performance than that fabricated through

physical adhesion and commercial polyacrylate coating. Among the materials developed, metal–organic frameworks (MOFs) were also investigated for forensic [72] and environmental [71,76] applications. In the former, five different MOFs, namely IRMOF-8, MOF-5, UIO-66, ZIF-8, and MIL-101(Cr), were immobilized on a stainless steel wire using a physical adhesive method as a solid-phase microextraction (SPME) fiber coating and employed for the determination of triacetone triperoxide, a high-power explosive, transferred from a finger to a paper surface. For environmental applications, a novel SPME fiber coating based on MOFs was utilized for the quantification of nitroaromatics, specifically nitropolycyclic aromatic hydrocarbons (nitro-PAHs) [71]. In this study, a zeolite imidazolate framework-8/hexagonal boron nitride (ZIF-8/h-BN) fiber was prepared and utilized for the evaluation of the behavior of four nitro-PAHs, i.e., 2-nitrobiphenyl, 5-nitroacenaphthene, 2-nitrofluorene, and 1-nitropyrene, to study their bioavailability in sediments, exploiting the ability of SPME to assess freely dissolved hydrophobic organic compounds. In the other study [76], UiO-67/perfluorooctanoic acid coating material was synthesized on fiber using a solvent-assisted ligand incorporation (SALI) approach and applied to the determination of trace PAHs in seabed sediments by headspace SPME analysis. The incorporation of perfluorooctanoic acid resulted in an enhanced hydrophobicity and stability of the coating with respect to pure UiO-67.

3.4.2. Application of Commercial Devices and Fiber Coatings

Commercially available devices and fibers were primarily used for developing novel protocols to determine harmful contaminants [79,80,82,83,86,87,89–91], as well as for other applications such as ecological studies [85,88]. For example, the HS-SPME-GC-MS methods developed for the determination of some specific VOCs [85] and biogenic VOCs [88] in soil samples from vineyards demonstrated their potential applicability in broader agricultural research, facilitating the exploration of soil quality and microbial activity in different agricultural soils. Of particular interest are the recent developments of in situ SPME approaches aimed at evaluating the possible relationship between the volatilome and soil disturbance [81] and monitoring leaks in underground oil pipelines [83]. In the former case, a 50/30 µm DVB/CAR/PDMS fiber was used for the simultaneous in situ analysis of geosmin and 2-methylisoborneol from the air near a soil disturbance. The results showed that, in the type of soil studied, 2-methylisoborneol is a more reliable marker for the monitoring of soil disturbance. The method for locating underground pipeline leaks is based on the use of SPME for the sampling of petroleum hydrocarbon volatile organic compounds, including benzene, toluene, ethylbenzene, and xylene (BTEX), and a portable GC-MS for on-site analysis. The optimization procedure of SPME conditions revealed that extraction temperature and humidity significantly impact efficiency; specifically, maintaining a low temperature (around 4 °C) resulted in higher signals for all the analytes due to an increased distribution coefficient between the fiber coating and air, facilitating the movement of gaseous molecules into the extraction phase. Conversely, the effect of humidity on the signal is fiber-dependent, with PDMS-CAR being more affected by changing humidity. This phenomenon, which can be explained by the competition of water molecules with VOCs for absorption on the SPME fiber surface [102], has implications for the ability of SPME to withstand changes in humidity that can be critical in certain environmental monitoring and sample analysis applications. Of considerable interest is a study proposing a protocol based on cooling-assisted solid-phase microextraction (CA-SPME) coupled to GC–MS for determining poly(methyl methacrylate) micro/nanoplastics in soil samples [91]. CA-SPME was proposed for the simultaneous heating of samples and the cooling of the fiber coating, especially for applications in the headspace mode, to overcome the reduction in extraction efficiency associated with decreasing partition coefficients at elevated temperatures [103].

Exploiting the excellent performance of CA-SPME, the approach was extended to enable simultaneous thermal decomposition of poly(methyl methacrylate) micro/nanoplastics and the extraction of their decomposition products, which serve as indicator compounds prior to GC–MS analysis. This protocol resulted in a simple operating procedure with high sensitivity, while avoiding the need for organic solvents in the enrichment step.

3.4.3. SPME Coupled with Green Solid–Liquid Extraction Technique

Most SPME methods were designed to analyze volatile organic compounds (VOCs), thus employing headspace extraction of solid samples. However, other protocols were developed for the determination of semi-volatile compounds in the solid matrices from which the target analytes need to be extracted. The resulting solution was then subjected to a direct immersion SPME procedure, provided that the extraction medium was compatible with the fiber coating. The extraction of semi-volatile analytes from solids was commonly carried out by ultrasonic treatment [74–76,79,82,86], while other approaches include simple solid–liquid extraction [71,73,87], microwave-assisted extraction [98,99], accelerated solvent extraction [89], miniaturized solid–liquid extraction [90], and matrix solid-phase dispersion [101]. In one case, a new setup named ultrasound-assisted pressure-regulated solid-phase microextraction (UA-PR-SPME) was developed for the sampling of BTEX from contaminated soils using a handmade fiber based on graphene oxide composite coating [100,104]. Ten PPCPs were quantified in sewage sludge using an analytical method developed and optimized by Pérez-Lemus et al. [98]. The investigated analytes were extracted from sludge using MAE after matrix pre-treatment. SPME and an on-fiber derivatization step with N-terc-Butyldimethylsilyl-N-methyltrifluoroacetamide (MTBSTFA) were performed to identify target analytes by GC-MS analysis. In another work, BTs, BTRs, and BSAs were extracted from PM_{10} using a water/ethanol mixture during MAE [99]. The use of the hydroalcoholic solution allowed MAE to be coupled to SPME-GC-MS/MS analysis without a purification step. The whole analytical protocol resulted in a short analysis time, no use of organic solvent, a high degree of automation, and satisfactory LOD values (5.0–37 pg m^{-3}). A CA-SPME device was successfully coupled with MSPD extraction to improve the release of PAHs from soil by setting up a completely solvent-free approach [98]. In the work proposed by Brinco et al. [93], a novel application of DI-SPME LC-Tips was developed for the determination of ten pesticides in soils. The extraction using SPME LC-Tips—a new SPME configuration originally designed for biological sample analysis and characterized by coated fibers attached to a disposable, easy-to-handle micropipette tip—is performed under stir bar agitation in a soil slurry previously prepared with an aqueous solvent. The key advantages of this method include extensive automation capabilities, low capital cost per sample, and, most importantly, minimal generation of toxic waste.

3.4.4. Development of Novel Configurations

Of relevance are the studies aimed at modifying conventional SPME devices to perform extractions under tailored conditions and to improve the performance of traditional configurations [94–97]. Ahmed and Raynie [94] proposed a commercial dry-herb vaporizer as a sample heating device for direct desorption of volatile analytes into the device's headspace. In their approach, analytes were sorbed from the headspace of the vaping pen onto a 100 µm PDMS fiber, followed by desorption in the GC-MS injector. Samples of horseradish, cinnamon, and gasoline-spiked soil samples were analyzed by both the dry-herb vaporizer and conventional HS-SPME. The comparison of the two methods showed similar results, with the dry-herb vaporizer being more concentrated. In the study proposed by Zhu et al. [95], a new gas cycle-assisted HS-SPME system was developed to overcome the challenges associated with transferring low-volatility analytes from the sample matrix

to the headspace. This device, which is similar to vacuum-assisted HS-SPME, was designed to improve the evaporation rates of analytes by generating a large amount of air bubbles. The new approach resulted in a significant reduction in the equilibrium times for the PAHs, PCBs, and PAEs used as test compounds. Another innovative device, described by Maleki et al. [96] and termed in-syringe vacuum-assisted HS-SPME (ISV-HS-SPME), is also intended to be a valid alternative to the established vacuum-assisted HS-SPME apparatus. It utilizes a modified 40 mL veterinary syringe as both a vacuum provider and a sampling vessel, with the internal pressure adjusted by manually moving the plunger. The ISV system has been shown to enhance the extraction efficiency of PAHs and BTEX in solid samples by up to 175%. Derikvand et al. [97] further advanced vacuum-assisted HS-SPME by developing a novel, simple, and pocket-sized portable LP-HS-SPME device for sampling volatile and semi-volatile analytes from complex solid matrices. Instead of a conventional vacuum pump, the device uses a simple syringe to evacuate air, achieving vacuum levels comparable to those of a typical laboratory vacuum pump. The applicability and reliability of the proposed configuration were demonstrated through its successful application in the contaminated soil sample analysis for PAH quantification.

3.5. Stir Bar Sorptive Extraction

Stir bar sorptive extraction (SBSE) is a green analytical technology based on the equilibrium distribution of target compounds between an aqueous sample and an extraction phase, typically with PDMS coating on a magnetic stir bar. The principal advantage of SBSE lies in its ability to achieve high enrichment factors, owing to the large volume and extensive surface area of the extraction phase. Moreover, because SBSE involves minimal consumption of organic solvents throughout the entire process, it aligns closely with the principles of green analytical chemistry, rendering it an environmentally friendly technique. However, commercial availability of coated stir bars remains limited, prompting substantial research into novel stir bar coatings aimed at enhancing stability and increasing extraction efficiency for analytes of varying polarity [105]. Over the past five years, only a handful of methods have applied SBSE to solid matrices [85,106–108]. Three works used SBSE for the determination of short-chain chlorinated paraffins (SCCPs) and other halogenated persistent organic pollutants in sediments [106], benzotriazole ultraviolet absorbers in soils [107], and benzophenones in soils [108], after treatment of the solid matrix by ultrasonic solvent extraction. In the first study, the miniaturized sample preparation workflow based on combined ultrasonic extraction and SBSE was classified as "an excellent green analysis method" by the analytical EcoScale evaluation, confirming its low cost and environmental compatibility. By contrast, the latter two methods introduced new coatings: an azolinked porous organic polymer (PP)/PDMS composite [107] and a vinyl-functionalized covalent organic framework (COF-V) grown on polypropylene hollow fiber [108]. The Azo-PP/PDMS-coated stir bar exhibited rapid kinetics and high extraction efficiency for benzotriazoles, driven by π–π interactions and hydrogen bonding, making it an excellent choice for trace UV absorber analysis. Similarly, the COF-V-modified hollow-fiber stir bar demonstrated outstanding stability and sensitivity in extracting benzophenones.

Table 2. Selected methods based on SPME and SBSE techniques.

Analytes	Matrix	Extraction Approach	Coating Material	Volume and Type of Organic Solvent	Instrumentation	LOD	Linear Range	[Ref.]—Publishing Year
Benzene	Soil, vegetables	HS-SPME	nano-activated carbon/ionic liquid (NAC/IL)	-	GC-FID	-	0.1–3 mg/L	[69]—2021
Nitroaromatics	Soil	HS-CF-SPME	poly 3,4-ethylenedioxythiophene and gold nanoparticles composite coating on a gold wire (AuNPs/PEDOT@Au)	-	GC-FID	0.5–3 ng/g	0.5–250 ng/g	[70]—2023
Nitrated polycyclic aromatic hydrocarbons (NPAHs)	Sediments	Solid–liquid extraction + DI-SPME	zeolite imidazolate framework-8/hexagonal boron nitride (ZIF-8/h-BN)	-	GC-MS	0.42–0.61 ng/g	5–500 ng/g	[71]—2023
Triacetone triperoxide	Soil, paper	HS-SPME	metal–organic frameworks (MOFs), including IRMOF-8, MOF-5, UIO-66, ZIF-8, and MIL-101(Cr)	-	GC-MS	13 ng/mL	50–5000 ng/L	[72]—2023
Phenoxycarboxylic acids herbicides	Soil	Solid–liquid extraction + DI-MF-SPME	monolith/aminated carbon nanotubes composite (MACN)	1.99 mL of ACN + 498 µL MeOH	HPLC/DAD	0.20–0.61 µg/kg	2–500 µg/kg	[73]—2021
Sulfonylurea herbicides	Soil	UAE + IT-SPME	porous monolith-based magnetism-reinforced	1.96 mL of ACN	HPLC/DAD	0.30–1.5 µg/kg	1–300 µg/kg	[74]—2020
Polychlorinated biphenyls	Soil	UAE + DI-SPME	Nitrogen-rich carbon nitride	20.5 mL of acetone	GC-FID	3.1–11.1 pg/mL	0.01–1000 pg/mL	[75]—2021
Polycyclic aromatic hydrocarbons	Seabed sediment	UAE + HS-SPME	UiO-67/perfluorooctanoic acid (UiO-67/PFOA)	31 mL of acetone	GC-FID	0.003–0.008 ng/mL	0.01–20 ng/mL	[76]—2024
Polycyclic aromatic hydrocarbons	Soil	Solid–liquid extraction + HS-SPME	Porphyrin-based covalent organic framework	-	GC-FID	0.25–5 ng/mL	1–150 ng/mL	[77]—2021
Phenols	Soil	Solid–liquid extraction + HS-SPME	1,3,5-trimethylphloroglucinol-benzidine (TpBD) COF	-	GC-MS	0.39–0.72 ng/L	2–10,000 ng/L	[78]—2023
Polycyclic aromatic hydrocarbons, oxygenated polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons	Particulate ($PM_{2.5}$)	UAE + DI-CF-SPME	65 µm polydimethylsiloxane/divinylbenzene (PDMS/DVB)	150 µL of ACN	GC-MS	0.001–0.129 ng/m^3	0.32–94.68 ng/m^3	[79]—2020
Amines	Particulate ($PM_{2.5}$)	HS-SPME	85 µm polyacrylate (PA)	-	GC-MS/MS	0.01–49 pg/m^3	0.01–10 ng/µL	[80]—2020
Geosmin and 2-methylisoborneol	Soil	HS-SPME	50/30 µm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS)	-	GC-MS	0.16–0.72 ng/L	0.05–20 µg/L	[81]—2021
Semi-volatile organic compounds	Particulate ($PM_{2.5}$)	Solid–liquid extraction + DI-SPME	85 µm polyacrylate (PA)	150 µL of ACN	GC×GC/Q-TOFMS	-	-	[82]—2025
BTEX	Soil	HS-SPME	75 µm carboxen/polydimethylsiloxane (Car/PDMS) and 65 µm polydimethylsiloxane/divinylbenzene (PDMS/DVB)	-	Portable GC-MS	100–200 µg/m^3	-	[83]—2023
Biogenic Volatile Organic Compounds (BVOCs)	Plant	Dynamic BVOC Sampling System (DBSS)-HS-SPME	50/30 µm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS)	-	GC-MS	-	-	[84]—2021
VOCs	Soil	HS-SPME	95 µm Carbon Wide Range/Polydimethylsiloxane (CWR/PDMS)	-	GC-MS	0.039–1.20 µg/kg	-	[85]—2024
Ferrocene and five derivatives	Soil	UAE + DI-SPME	50/30 µm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS)	-	gas chromatography–microwave-induced plasma with atomic emission detection (GC-MIP-AED)	0.9–4 ng/g	0.01–20 ng/mL	[86]—2020

Table 2. *Cont.*

Analytes	Matrix	Extraction Approach	Coating Material	Volume and Type of Organic Solvent	Instrumentation	LOD	Linear Range	[Ref.]—Publishing Year
Herbicides	Soil	Solid–liquid extraction + IT-SPME	35% diphenyl-65% dimethyl polysiloxane	1 mL of MeOH	capillary liquid chromatography (capLC)-DAD	0.05–0.1 µg/g	0.5–4 µg/g	[87]—2024
BVOCs	Soil	HS-SPME	75 µm carboxen/polydimethylsiloxane (CAR/PDMS)	-	GC-MS	0.01–0.30 µg/kg	-	[88]—2023
Nitrated polycyclic aromatic hydrocarbons	Sediments	ASE + DI-SPME	65 µm polydimethylsiloxane/divinylbenzene (PDMS/DVB)	61.2 mL of dichloromethane	GC-MS/MS	0.020–0.472 ng/g	0.1–300 ng/g	[89]—2022
Pesticides	Soil	Miniaturized solid–liquid extraction (MISOLEX) + DI-SPME	65 µm polydimethylsiloxane/divinylbenzene (PDMS/DVB)	5 mL of acetone + 10 mL of petroleum ether	GC-MS	0.005–1.16 µg/kg	0.01–25 µg/L	[90]—2022
Poly(methyl Methacrylate) Micro/Nanoplastics	Soil	CA-SPME	50/30 µm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS)	-	GC-MS	0.28 µg	5–1000 µg	[91]—2024
Trichloroethylene (TCE)	Soil	HS-SPME	65 µm polydimethylsiloxane/divinylbenzene (PDMS/DVB)	-	Portable GC-MS	-	0–100 µg/L	[92]—2021
Pesticides	Soil	DI-SPME LC-Tips	C_{18}	700 µL of MeOH	GC-MS/MS	0.01–10 µg/kg	0.1–50 µg/kg	[93]—2024
VOCs	Gasoline-spiked soil, plant	HS-SPME	100 µm polydimethylsiloxane (PDMS)	-	GC-MS	-	-	[94]—2024
PAHs, PCBs, PAEs	Soil	UAE + gas-cycle-assisted (GCA) HS-SPME	100 µm polydimethylsiloxane (PDMS) and 65 µm polydimethylsiloxane/divinylbenzene (PDMS/DVB)	-	GC-FID	0.49–1.51 pg/mL	0.002–100 ng/mL	[95]—2021
PAHs, BTEX	Soil	In-syringe vacuum-assisted (ISV)-HS-SPME	hybrid of covalent triazine-based frameworks and metal–organic frameworks (COF/MOF)	-	GC-FID	0.07–5 ng/g	0.23–9000 ng/g	[96]—2023
PAHs	Soil	low-pressure (LP)-HS-SPME	Nano-octadecylsilica/polyvinyl alcohol (NODS/PVA)	-	GC-FID	3–50 ng/g	0.01–1300 ng/g	[97]—2021
PPCPs	Sewage sludge	MAE-DI-SPME-On-fiber derivatization with MTBSTFA	50/30 µm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS)	24 mL of water/MeOH mixture 95:5 (*v*/*v*) (MAE)	GC-MS	3.25–48.9 ng/g	146–2466 ng/g	[98]—2020
BTs, BTRs, BSAs	PM_{10}	MAE-DI-SPME	85 µm polyacrylate (PA)	15 mL of water/ethanol mixture 70/30 (*v*/*v*)	GC-MS/MS	0.021–0.21 ng/mL	17–100 ng/mL	[99]—2021
BTEX	Soil	Ultrasound-assisted pressure-regulated SPME (UA-PR-SPME)	Graphene oxide/gamma-aminopropyltriethoxysilane coated fiber (GO-APTES)	500 µL of MeOH (UAE)	GC-FID	0.1–0.4 ng/g	2.4–5000 ng/g	[100]—2020
PAHs	Soil	MSPD-CA-SPME	100 µm polydimethylsiloxane (PDMS)	-	GC-MS	4.2–8.5 ng/g	40–4000 ng/g	[101]—2020
VOCs	Soil	HS-SBSE	Polydimethylsiloxane (PDMS)	-	GC-MS	-	-	[85]—2024
Polychlorinated biphenyls, polybrominated diphenyl ethers, organochlorine compounds	Sediment	UAE + DI-SBSE	Polydimethylsiloxane (PDMS)	2.2 mL of MeOH	GC-MS/MS	0.029–6.5 ng/g	0.1–3000 ng/g	[106]—2021
Benzotriazole ultraviolet absorbers	Soil	UAE + DI-SBSE	Azo-linked porous organic polymers/polydimethylsiloxane (PP/PDMS)	18 mL of MeOH	HPLC-DAD	0.12–0.33 µg/L	0.5–100 µg/L	[107]—2020
Benzophenones	Soil and sunscreen	UAE + HF-SBSE	Covalent organic framework-V modified porous polypropylene	20 mL of MeOH + 150 µL of ACN	HPLC-UV	0.02–0.03 ng/mL	0.1–200 ng/mL	[108]—2022

3.6. Liquid-Phase Microextraction

The process of extracting components from one liquid into another immiscible or partially miscible liquid has been known since the early 19th century. However, interest in conventional liquid–liquid extraction (LLE) has declined over the past three decades due to its notable drawbacks, particularly the large volumes of organic solvents required. With the advent of green analytical chemistry in the mid-1990s, new miniaturized approaches—collectively termed liquid-phase microextraction (LPME)—were introduced to drastically reduce both sample and solvent consumption. Among these, single-drop microextraction (SDME), hollow-fiber LPME (HF-LPME), and dispersive liquid–liquid microextraction (DLLME) have become widely adopted techniques. The DLLME procedure involves the addition of extraction and disperser solvents into a sample, the formation of a cloudy solution/emulsion, the achievement of extraction equilibrium, and finally centrifugation to obtain the extraction phase enriched with analytes (Figure 5) [109].

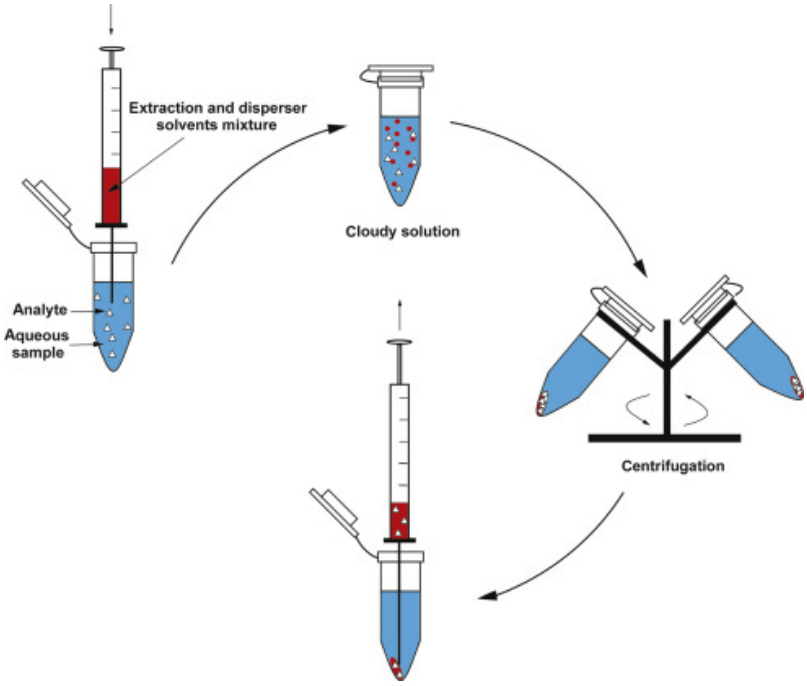


Figure 5. Graphic representation of DLLME steps (reprinted from [109] with permission).

Over the last five years, LPME methods applied to solid matrices have primarily focused on DLLME [110–116], HF-LPME [117,118], and spray-assisted droplet formation LPME (SADF-LPME) [119]. DLLME employs a ternary solvent system, i.e., aqueous sample (donor phase), extraction solvent (acceptor phase), and dispersant, to generate fine droplets of the extractant, achieving rapid equilibrium and high enrichment factors with only microliters of organic solvent [120]. Methods published in the last five years using DLLME addressed the determination of pesticides [110,116], endocrine-disrupting chemicals [111,114], and flame retardants [112], in various solid matrices, including food [110], soils [110,116], airborne fine particulate matter [111,112], sewage sludges [113], and sediments [114]. In particular, Yadav et al. [110] proposed a protocol based on the extraction by DLLME-solidified floating organic droplet (DLLME-SFO). This modified DLLME technique provides the addition of a few microdroplets of low-density extraction solvent to the aqueous phase to form a cloudy solution. After vortexing and centrifugation, the whole system is placed in an ice bath. As a consequence, a solidified floating organic droplet is formed that can be subjected to instrumental analysis [115]. The same approach was chosen in combination with the salting-out-assisted liquid–liquid extraction (SALLE) for the determination of four pyrethroids in various sam-

ples [116]. In the study presented by Naing et al. [111], another double-microextraction approach combining DLLME and vortex-assisted micro-solid-phase extraction (VA-μ-SPE) was developed for the determination of phthalate esters and bisphenol A adsorbed on $PM_{2.5}$. After an ultrasonic treatment of the sample, the aqueous solution obtained was first preconcentrated by DLLME and then subjected to VA-μ-SPE. The synergistic contribution of the two combined techniques led to important advantages such as high preconcentration of the analytes and good clean-up efficiency. Other combinations of extraction techniques were also proposed. For instance, quick, easy, cheap, efficient, rugged, and safe (QuEChERS) was combined with DLLME for the trace-level quantification of thirty-seven endocrine-disrupting compounds, including pesticides, bisphenols, musks, and UV filters, with the aim of studying the distribution of target analytes between water and sediments and their temporal and, in particular, seasonal variation [114]. In another work [113], magnetic ionic liquids (MILs) were used as extractant solvent in DLLME for the determination of polybrominated flame retardants in sewage sludge samples. Due to their good dispersing ability in aqueous solutions, one advantage of using MILs is the elimination of the centrifugation step commonly used in DLLME technique. The issues associated with the direct injection of MIL into the GC-MS system were overcome by the use of a pyrolyzer, which ensures optimum analytical and instrumental performance while reducing contamination. The use of hollow-fiber LPME (HF-LPME) is the key step in two protocols developed for the determination of pesticides in soil samples [117,118]. HF-LPME utilizes a hollow-fiber membrane to extract and concentrate analytes from different sample matrices [121]. The role of the membrane is to act as a selective barrier, allowing the extraction of the target analytes by a diffusion process from the sample into the organic solvent inside the membrane and, at the same time, preventing the passage of large molecules and particulate matter, resulting in an effective clean-up of the sample. The greenness of HF-LPME was demonstrated by Oliveira Martins et al. [117] in the application of this methodology to the determination of multiclass pesticides in soil samples. The environmental impact of the developed method was evaluated using the AGREEprep software version 0.91 (https://mostwiedzy.pl/en/wojciech-wojnowski,174235-1/agreeprep, accessed on 8 May 2025), which showed a higher degree of environmental friendliness of the HF-LPME protocol compared to some traditional pesticide extraction approaches for soil samples, such as QuEChERS, Soxhlet solvent extraction, and ultrasonic solvent extraction. In another work [119], SADF-LPME was applied as an extraction technique for the analysis in moss and rock–soil samples from Antarctica for the quantification of twenty-nine trace endocrine-disrupting compounds and pesticides. The developed approach is characterized by the use of a simple and inexpensive apparatus for the dispersion process, making the final protocol dispersive solvent-free and more environmentally friendly.

Table 3. Selected methods based on LPME techniques.

Analytes	Matrix	Extraction Approach	Volume and Type of Organic Solvent	Instrumentation	LOD	Linear Range	[Ref.]—Publishing Year
Pesticides	Soil, sugarcane, and jaggery	Solid–liquid extraction + DLLME-SFO	1 mL of ACN (Solid–liquid extraction) 50 µL of 1-Dodecanol (extractant solvent for DLLME-SFO) 3 mL of acetone (UAE)	GC-µECD	0.868–2.522 ng/g	6.25–100 ng/g	[110]—2022
Phthalate esters and bisphenol A	Particulate ($PM_{2.5}$)	UAE + DLLME + vortex-assisted micro-solid-phase extraction (VA-µ-SPE)	400 µL of acetone (dispersive solvent for DLLME), 70 µL of chloroform (extractant solvent for DLLME) 100 µL of acetone (extractant solvent for VA-µ-SPE)	GC-MS/MS	0.07–0.15 ng/mL	0.3–100 ng/mL	[111]—2021
Flame retardants	Sewage sludge	DLLME	3 µL of ACN (dispersive solvent), 10 mg of ($[P^{+}_{6,6,6,14}]_2[MnCl_4^{2-}]$) MIL (extractant solvent), 20 µL of methanol (desorption solvent)	Py-GC–MS	16.9–375 µg/L	200–6000 µg/L	[113]—2024
Pesticides, bisphenols, musks and UV filters	Sediment	QuEChERS + DLLME	10 mL of ACN (QuEChERS) 85 µL of carbon tetrachloride (extractant solvent for DLLME))	GC-MS	0.005–2.5 ng/mL	0.01–40 ng/mL	[114]—2022
Pyrethroid insecticides	Soil	UAE + SALLE + DLLME-SFO	17 mL of ACN (UAE) 300 µL of 1-undecanol (extractant solvent for DLLME-SFO)	GC-MS	1.5–6.1 ng/mL	5–5000 ng/mL	[116]—2020
Pesticides	Soil	Solid–liquid extraction + HF-LPME	20.0 µL of octanol (acceptor solvent)	LC-MS	66.1–198.1 µg/L	500–1000 µg/L	[117]—2023
Herbicides and metabolites	Soil	Solid–liquid extraction + HF-LPME	1 mL of di-hexyl ether (acceptor solvent) 25 g of ACN (UAE)	HPLC-UV	0.1–0.3 µg/kg	2–60 µg/kg	[118]—2023
Endocrine-disrupting compounds and pesticides	Moss, rock–soil	UAE + SADF-LPME	0.1326 g of a mixture dichlormethane: 1,2-dichloroethane (1:1 *v*/*v*) (SADF-LPME)	GC-MS	1.0–6.6 ng/g	3.8–205 ng/g	[119]—2024

4. Conclusions and Future Directions

This review underscores recent progress in the extraction of organic pollutants from environmental solid matrices using eco-friendly and microextraction approaches hyphenated with chromatographic analysis. The advent of green analytical methods has demonstrably minimized risks to human health and advanced environmental protection, while enhancing the sustainability of the analytical workflow. Sample preparation of solid matrices represents a hard challenge due to trace-level analyte concentrations and matrix complexity. In the past five years, intensified research into MAE-, UAE-, and MSPD-based techniques has enabled drastic reductions in solvent volume, sample size, and processing time. Moreover, both UAE and MSPD have been downscaled into microscale devices. Beyond these approaches, microextraction techniques, including SPME, SBSE, DLLME, HF-LPME, and SADF-LPME have been shown to promote sustainability and automation by enabling extraction and pre-concentration in a single step, often eliminating organic solvents entirely. SBSE and DLLME were applied to solid samples previously pretreated by other techniques, mainly UAE. New coatings were synthesized for SBSE to improve stability, sensitivity, and extraction efficiency. MILs were proposed as an extractant solvent in DLLME for the determination of target analytes, eliminating the centrifugation phase and allowing the direct injection into the instrumental system. SPME in the HS mode is the only technique that was applied directly to solid matrices for the determination of VOCs. Over the past five years, the main focus in SPME was on the development of new fiber coatings for enhancing extraction sensitivity and specificity and novel configurations to improve the performance of commercial devices. Semi-volatile analytes were analyzed in environmental matrices by SPME in combination with MSPD or MAE. The aqueous extract obtained from the solid samples by means of MAE was directly subjected to SPME analysis, increasing the throughput of the analytical protocol, minimizing organic solvent volumes, and avoiding the environmentally harmful solvents. In the forthcoming years, endeavors must concentrate on the miniaturization and integration of solid-sample extraction techniques, such as MAE, UAE, and MSPD, into microdevice platforms that fully embody GSP and the twelve principles of green analytical chemistry. This approach aims to reduce solvent and sample consumption, energy use, and waste while enhancing throughput and reproducibility. The systematic development and environmental evaluation of biodegradable DESs for dispersive MSPD is of equal importance. Comprehensive studies of their long-term biodegradability, ecotoxicity, and extraction performance are vital to ensure that they do not introduce persistent or harmful by-products. Headspace SPME remains unparalleled for direct VOC sampling from solids, and further innovation in fiber coatings—leveraging MOFs, COFs, and polymeric ionic liquids—can drive sensitivity and selectivity to new heights. Concurrently, machine learning-driven design of experiments (DoE) approaches hold the promise of automating and accelerating parameter optimization across microextraction workflows.

Author Contributions: Conceptualization, R.E.; supervision, R.E., A.N., and A.T.; visualization, R.E.; writing—original draft, R.E., A.T., and A.N.; writing—review and editing, R.E., A.T., and A.N. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Wieczorek, M.N.; Zhou, W.; Pawliszyn, J. Perspective on sample preparation fundamentals. *Adv. Sample Prep.* **2024**, *10*, 100114. [CrossRef]
2. Câmara, J.S.; Perestrelo, R.; Berenguer, C.V.; Andrade, C.F.P.; Gomes, T.M.; Olayanju, B.; Kabir, A.; Rocha, C.M.R.; Teixeira, J.A.; Pereira, J.A.M. Green Extraction Techniques as Advanced Sample Preparation Approaches in Biological, Food, and Environmental Matrices: A Review. *Molecules* **2022**, *27*, 2953. [CrossRef] [PubMed]
3. Khuman, S.N.; Lee, H.-Y.; Cho, I.-G.; Chung, D.; Lee, S.Y.; Lee, J.; Oh, J.-K.; Choi, S.-D. Monitoring of organochlorine pesticides using pine needle, pine bark, and soil samples across South Korea: Source apportionment and implications for atmospheric transport. *Chemosphere* **2025**, *370*, 144043. [CrossRef] [PubMed]
4. Peneva, S.; Le, Q.N.P.; Munhoz, D.R.; Wrigley, O.; Wille, F.; Doose, H.; Halsall, C.; Harkes, P.; Sander, M.; Braun, M.; et al. Microplastic analysis in soils: A comparative assessment. *Ecotoxicol. Environ. Saf.* **2025**, *289*, 117428. [CrossRef]
5. Mitra, S. *Sample Preparation Techniques in Analytical Chemistry*; John Wiley & Sons: Hoboken, NJ, USA, 2003.
6. Gałuszka, A.; Migaszewski, Z.; Namieśnik, J. The 12 principles of green analytical chemistry and the SIGNIFICANCE mnemonic of green analytical practices. *TrAC-Trends Anal. Chem.* **2013**, *50*, 78–84. [CrossRef]
7. López-Lorente, A.I.; Pena-Pereira, F.; Pedersen-Bjergaard, S.; Zuin, V.G.; Ozkan, S.A.; Psillakis, E. The ten principles of green sample preparation. *TrAC-Trends Anal. Chem.* **2022**, *148*, 116530. [CrossRef]
8. Kokosa, J.M.; Przyjazny, A. Green microextraction methodologies for sample preparations. *Green Anal. Chem.* **2022**, *3*, 100023. [CrossRef]
9. Schettino, L.; Peris-Pastor, G.; Benedé, J.L.; Chisvert, A. A comprehensive review on the use of microextraction techniques in the analysis of cosmetic products. *Adv. Sample Prep.* **2022**, *3*, 100024. [CrossRef]
10. Wojnowski, W.; Tobiszewski, M.; Pena-Pereira, F.; Psillakis, E. AGREEprep e Analytical greenness metric for sample preparation. *TrAC-Trends Anal. Chem.* **2022**, *149*, 116553. [CrossRef]
11. Ballester-Caudet, A.; Campíns-Falcó, P.; Pérez, B.; Sancho, R.; Lorente, M.; Sastre, G.; González, C. A new tool for evaluating and/or selecting analytical methods: Summarizing the information in a hexagon. *TrAC-Trends Anal. Chem.* **2019**, *118*, 538–547. [CrossRef]
12. Nowak, P.M.; Kościelniak, P. What Color Is Your Method? Adaptation of the RGB Additive Color Model to Analytical Method Evaluation. *Anal. Chem.* **2019**, *91*, 10343–10352. [CrossRef] [PubMed]
13. Nowak, P.M.; Wietecha-Posłuszny, R.; Pawliszyn, J. White Analytical Chemistry: An approach to reconcile the principles of Green Analytical Chemistry and functionality. *TrAC-Trends Anal. Chem.* **2021**, *138*, 116223. [CrossRef]
14. González-Martín, R.; Gutiérrez-Serpa, A.; Pino, V.; Sajid, M. A tool to assess analytical sample preparation procedures: Sample preparation metric of sustainability. *J. Chromatogr. A* **2023**, *1707*, 464291. [CrossRef] [PubMed]
15. Khan, S.; Naushad, M.; Govarthanan, M.; Iqbal, J.; Alfadul, S.M. Emerging contaminants of high concern for the environment: Current trends and future research. *Environ. Res.* **2022**, *207*, 112609. [CrossRef]
16. Richardson, S.D. Water Analysis: Emerging Contaminants and Current Issues. *Anal. Chem.* **2009**, *81*, 4645–4677. [CrossRef]
17. Pintado-Herrera, M.G.; González-Mazo, E.; Lara-Martín, P.A. In-cell clean-up pressurized liquid extraction and gaschromatography–tandem mass spectrometry determination ofhydrophobic persistent and emerging organic pollutants in coastal sediments. *J. Chromatogr. A* **2016**, *1429*, 107–118. [CrossRef]
18. Vila, M.; Celeiro, M.; Lamas, J.P.; Garcia-Jares, C.; Dagnac, T.; Llompart, M. Simultaneous in-vial acetylation solid-phase microextraction followed by gas chromatography tandem mass spectrometry for the analysis of multiclass organic UV filters in water. *J. Hazard. Mater.* **2017**, *323*, 45–55. [CrossRef]
19. Trujillo-Rodríguez, M.J.; Nan, H.; Anderson, J.L. Expanding the use of polymeric ionic liquids in headspace solid-phase microextraction: Determination of ultraviolet filters in water samples. *J. Chromatogr. A* **2018**, *1540*, 11–20. [CrossRef]
20. Mei, M.; Huang, X. Online analysis of five organic ultraviolet filters in environmental water samples using magnetism-enhanced monolith-based in-tube solid phase microextraction coupled with high-performance liquid chromatography. *J. Chromatogr. A* **2017**, *1525*, 1–9. [CrossRef]
21. Fumes, B.H.; Lanças, F.M. Use of graphene supported on aminopropyl silica for microextraction of parabens from water samples. *J. Chromatogr. A* **2017**, *1487*, 64–71. [CrossRef]
22. Naccarato, A.; Elliani, R.; Sindona, G.; Tagarelli, A. Multivariate optimization of a microextraction by packed sorbent-programmed temperature vaporization-gas chromatography–tandem mass spectrometry method for organophosphate flame retardant analysis in environmental aqueous matrices. *Anal. Bioanal. Chem.* **2017**, *409*, 7105–7120. [CrossRef] [PubMed]
23. Amiri, A.; Chahkandi, M.; Targhoo, A. Synthesis of nano-hydroxyapatite sorbent for microextraction in packed syringe of phthalate esters in water samples. *Anal. Chim. Acta* **2017**, *950*, 64–70. [CrossRef] [PubMed]
24. Amiri, A.; Ghaemi, F. Microextraction in packed syringe by using a three-dimensional carbon nanotube/carbon nanofiber–graphene nanostructure coupled to dispersive liquid-liquid microextraction for the determination of phthalate esters in water samples. *Microchim. Acta* **2017**, *184*, 3851–3858. [CrossRef]
25. Elliani, R.; Tagarelli, A.; Naccarato, A. Assessment of benzothiazoles, benzotriazoles and benzenesulfonamides in environmental waters using an optimized combination of microextraction by packed sorbent with programmed temperature vaporization-gas chromatography tandem-mass spectrometry. *Talanta* **2023**, *258*, 124410. [CrossRef]

26. Naccarato, A.; Gionfriddo, E.; Sindona, G.; Tagarelli, A. Simultaneous determination of benzothiazoles, benzotriazoles and benzosulfonamides by solid phase microextraction-gaschromatography-triple quadrupole mass spectrometry in environmental aqueous matrices and human urine. *J. Chromatogr. A* **2014**, *1338*, 164–173. [CrossRef]
27. Martín Santos, P.; Campo, L.; Olgiati, L.; Polledri, E.; del Nogal Sánchez, M.; Fustinoni, S. Development of a method to profile 2- to 4-ring polycyclic aromatic hydrocarbons in saliva samples from smokers and non-smokers by headspace-solid-phase microextraction-gas chromatography-triple quadrupole tandem mass spectrometry. *J. Chromatogr. B* **2020**, *1152*, 122273. [CrossRef]
28. Elliani, R.; Naccarato, A.; Malacaria, L.; Tagarelli, A. A rapid method for the quantification of urinary phthalate monoesters: A new strategy for the assessment of the exposure to phthalate ester by solid-phase microextraction with gas chromatography and tandem mass spectrometry. *J. Sep. Sci.* **2020**, *43*, 3061–3073. [CrossRef]
29. Naccarato, A.; Elliani, R.; Tagarelli, A. A protocol based on solid phase microextraction -gas chromatography-tandem mass spectrometry for the monitoring of parabens and bisphenols in human saliva. *J. Chromatogr. A* **2023**, *1707*, 464303. [CrossRef]
30. Naccarato, A.; Elliani, R.; Tagarelli, A. A direct immersion-solid-phase microextraction method for the automated determination of 3- to 6-ring polycyclic aromatic hydrocarbons in saliva by gas-chromatography-tandem mass spectrometry. *J. Chromatogr. A* **2024**, *1736*, 465404. [CrossRef]
31. Naccarato, A.; Gionfriddo, E.; Elliani, R.; Pawliszyn, J.; Sindona, G.; Tagarelli, A. Investigating the robustness and extraction performance of a matrix-compatible solid-phase microextraction coating in human urine and its application to assess 2–6-ring polycyclic aromatic hydrocarbons using GC–MS/MS. *J. Sep. Sci.* **2018**, *41*, 929–939. [CrossRef]
32. González-Martín, R.; Trujillo-Rodríguez, M.J.; Freire, M.G.; Ayala, J.H.; Pino, V. Effervescence tablets based on magnetic ionic liquids as simple microdevices for the in situ dispersive liquid-liquid microextraction of urinary biomarkers. *Anal. Chim. Acta* **2024**, *1328*, 343187. [CrossRef] [PubMed]
33. Lepri de Oliveira, M.; Alves Rocha, B.; de Oliveira Souza, V.C.; Barbosa, F., Jr. Determination of 17 potential endocrine-disrupting chemicals in human saliva by dispersive liquid-liquid microextraction and liquid chromatography-tandem mass spectrometry. *Talanta* **2019**, *196*, 271–276. [CrossRef] [PubMed]
34. Gupta, M.K.; Jain, R.; Singh, P.; Ch, R.; Mudiam, M.K.R. Determination of Urinary PAH Metabolites Using DLLME Hyphenated to Injector Port Silylation and GC–MS-MS. *J. Anal. Toxicol.* **2015**, *39*, 365–373. [CrossRef] [PubMed]
35. Alves Rocha, B.; Ruiz Brandão da Costa, B.; Perez de Albuquerque, N.C.; Moraes de Oliveira, A.R.; Oliveira Souza, J.M.; Al-Tameemi, M.; Dobal Campiglia, A.; Barbosa, F., Jr. A fast method for bisphenol A and six analogues (S, F, Z, P, AF, AP) determination in urine samples based on dispersive liquid-liquid Microextraction and liquid chromatography-tandem mass spectrometry. *Talanta* **2016**, *154*, 511–519. [CrossRef]
36. Martín Santos, P.; Jiménez Carracedo, C.; del Nogal Sánchez, M.; Pérez Pavón, J.L.; Cordero, B.M. A sensitive and automatic method based on microextraction by packed sorbents for the determination of polycyclic aromatic hydrocarbons in saliva samples. *Microchem. J.* **2020**, *152*, 104274. [CrossRef]
37. Silveira, R.S.; Rocha, B.A.; Rodrigues, J.L.; Barbosa, F., Jr. Rapid, sensitive and simultaneous determination of 16 endocrine disrupting chemicals (parabens, benzophenones, bisphenols, and triclocarban) in human urine based on microextraction by packed sorbent combined with liquid chromatography tandem mass spectrometry (MEPS-LC-MS/MS). *Chemosphere* **2020**, *240*, 124951. [CrossRef]
38. Moreira Fernandez, M.A.; Coelho André, L.; de Lourdes Cardeal, Z. Hollow fiber liquid-phase microextraction-gas chromatography-masss pectrometry method to analyze bisphenol A and other plasticizer metabolites. *J. Chromatogr. A* **2017**, *1481*, 31–36. [CrossRef]
39. Wang, X.; Sun, Z.; Luo, X.; Wang, K.; Zhang, S.; Ji, Z.; Gao, Y.; You, J. A novel switchable solvent liquid-phase microextraction technique based on the solidification of floating organic droplets: HPLC-FLD analysis of polycyclic aromatic hydrocarbon monohydroxy metabolites in urine samples. *New J. Chem.* **2020**, *44*, 3038. [CrossRef]
40. Gomes, J.M.; Araujo Almeida, T.F.; Aparecida da Silva, T.; de Lourdes Cardeal, Z.; Costa Menezes, H. Saliva biomonitoring using LPME-GC/MS method to assess dentistry exposure to plasticizers. *Anal. Bioanal. Chem.* **2020**, *412*, 7799–7810. [CrossRef]
41. Ganzler, K.; Salgó, A.; Valkó, K. Microwave extraction: A novel sample preparation method for chromatography. *J. Chromatogr. A* **1986**, *371*, 299–306. [CrossRef]
42. Naccarato, A.; Tassone, A.; Moretti, S.; Elliani, R.; Sprovieri, F.; Pirrone, N.; Tagarelli, A. A green approach for organophosphate ester determination in airborne particulate matter: Microwave-assisted extraction using hydroalcoholic mixture coupled with solid-phase microextraction gas chromatography tandem mass spectrometry. *Talanta* **2018**, *189*, 657–665. [CrossRef] [PubMed]
43. Llompart, M.; Celeiro, M.; Dagnac, T. Microwave-assisted extraction of pharmaceuticals, personal care products and industrial contaminants in the environment. *TrAC-Trends Anal. Chem.* **2019**, *116*, 136–150. [CrossRef]
44. Ndwab, S.; Malungana, M.; Mahlambi, P. Comparison of Ultra-Sonication and Microwave Extraction Followed by Filtration or Filtration and Solid-Phase Extraction Clean-Up for PAH Determination from Sediment and Sludge: Human Health and Ecological Risk Assessment. *Appl. Sci.* **2023**, *13*, 5619. [CrossRef]

45. Kariyawasam, T.; Doran, G.S.; Howitt, J.A.; Prenzler, P.D. Optimization and Comparison of Microwave-Assisted Extraction, Supercritical Fluid Extraction, and Eucalyptus Oil–Assisted Extraction of Polycyclic Aromatic Hydrocarbons from Soil and Sediment. *Environ. Toxicol. Chem.* **2023**, *42*, 982–994. [CrossRef] [PubMed]
46. Ferreira, S.L.C.; Brums, R.E.; Ferreira, H.S.; Matos, G.D.; David, J.M.; Brandão, G.C.; Da Silva, E.G.P.; Portugal, L.A.; Dos Reis, P.S.; Souza, A.S.; et al. Box-Behnken design: An alternative for the optimization of analytical methods. *Anal. Chim. Acta* **2007**, *597*, 179–186. [CrossRef]
47. Santana-Viera, S.; Tuček, J.; Torres-Padrón, M.E.; Sosa-Ferrera, Z.; Santana-Rodríguez, J.J.; Halko, R. Cytostatic compounds in sludge and sediment: Extraction and determination by a combination of microwave-assisted extraction and UHPLC–MS/MS. *Anal. Bioanal. Chem.* **2020**, *412*, 3639–3651. [CrossRef]
48. Paijens, C.; Frère, B.; Caupos, E.; Moilleron, R.; Bressy, A. Determination of 18 Biocides in Both the Dissolved and Particulate Fractions of Urban and Surface Waters by HPLC-MS/MS. *Water Air Soil Pollut.* **2020**, *231*, 210. [CrossRef]
49. Boinis, N.; Konomi, A.; Gkotsis, G.; Nika, M.-C.; Thomaidis, N.S. Trends in extraction techniques for the determination of organic micropollutants in liver tissues of vertebrates. *Anal. Bioanal. Chem.* **2025**, *417*, 535–553. [CrossRef]
50. Wang, C.; Zhu, W.; Shi, Z.; Li, J. A Sensitive Online SPE-LC–APCI–MS/MS Method for Simultaneous Determination of 17 Nitrated and Oxygenated Polycyclic Aromatic Hydrocarbons in Atmospheric Particulate Matter. *Chromatographia* **2023**, *86*, 677–688. [CrossRef]
51. Zhang, L.; Meng, L.; Wang, H.; Lu, D.; Luo, X. Development and validation of a liquid chromatography-tandem mass spectrometry method for comprehensive detection of organophosphate esters and their degradation products in sediment. *J. Chromatogr. A* **2022**, *1665*, 462826. [CrossRef]
52. Nuñez, A.; Vallecillos, L.; Marcé, R.M.; Borrull, F. Occurrence and risk assessment of benzothiazole, benzotriazole and benzenesulfonamide derivatives in airborne particulate matter from an industrial area in Spain. *Sci. Total Environ.* **2020**, *708*, 135065. [CrossRef]
53. Castiñeira-Landeira, A.; Vazquez, L.; Gonzalez-Leirado, H.; Llompart, M.; Dagnac, T. Ultrasound-assisted extraction followed by liquid chromatography coupled to tandem mass spectrometry for the simultaneous determination of multiclass herbicides in soil. *Anal. Bioanal. Chem.* **2023**, *415*, 7197–7209. [CrossRef]
54. Dvorakova, D.; Tsagkaris, A.S.; Pulkrabova, J. Novel strategies for the determination of plastic additives derived from agricultural plastics in soil using ultrahigh-performance liquid chromatography tandem mass spectrometry (UHPLC-MS/MS). *Sci. Total Environ.* **2024**, *946*, 174492. [CrossRef] [PubMed]
55. Bahia, P.V.B.; Nascimento, M.M.; Hatje, V.; de Andrade, J.B.; Machado, M.E. Microscale extraction combined with gas chromatography/mass spectrometry for the simultaneous determination of polycyclic aromatic hydrocarbons and polycyclic aromatic sulfur heterocycles in marine sediments. *J. Chromatogr. A* **2021**, *1653*, 462414. [CrossRef] [PubMed]
56. Barker, S.A.; Long, A.R.; Short, C.R. Isolation of drug residues from tissues by solid phase dispersion. *J. Chromatogr. A* **1989**, *475*, 353–361. [CrossRef] [PubMed]
57. Ramos, L. Current trends in the determination of organic compounds in foodstuffs using matrix solid phase dispersion. *TrAC-Trends Anal. Chem.* **2024**, *172*, 117601. [CrossRef]
58. Wianowska, D.; Gil, M. New insights into the application of MSPD in various fields of analytical chemistry. *TrAC-Trends Anal. Chem.* **2019**, *112*, 29–51. [CrossRef]
59. Ramos, L. Use of new tailored and engineered materials for matrix solid-phase dispersion. *TrAC-Trends Anal. Chem.* **2019**, *118*, 751–758. [CrossRef]
60. Yuan, J.P.; Liu, C.; Jiang, H.; Zhou, Z.; Xie, M.; Sun, Y. Rapid and Simultaneous Determination of 13 Sulfonamides in Soil by Matrix Solid-Phase Dispersion With High-Performance Liquid Chromatography-Tandem Mass Spectrometry. *J. Sep. Sci* **2024**, *47*, e70015. [CrossRef]
61. Castro, G.; Sørmo, E.; Yu, G.; Sait, S.T.L.; González, S.V.; Arp, H.P.H.; Asimakopoulos, A.G. Analysis, occurrence and removal efficiencies of organophosphate flame retardants (OPFRs) in sludge undergoing anaerobic digestion followed by diverse thermal treatments. *Sci. Total Environ.* **2023**, *870*, 161856. [CrossRef]
62. Soares, K.L.; Sunyer-Caldú, A.; Barbosa, S.C.; Primel, E.G.; Fillmann, G.; Diaz Cruz, M.S. Rapid and cost-effective multiresidue analysis of pharmaceuticals, personal care products, and antifouling booster biocides in marine sediments using matrix solid phase dispersion. *Chemosphere* **2021**, *267*, 129085. [CrossRef] [PubMed]
63. El-Deen, A.K.; Shimizu, K. Miniaturized ternary deep eutectic solvent-based matrix solid-phase dispersion: A green sample preparation method for the determination of chlorophenols in river sediment. *J. Sep. Sci.* **2023**, *46*, 2200717. [CrossRef]
64. Portet-Koltalo, F.; Tian, Y.; Berger-Brito, I.; Benamar, A.; Boulangé-Lecomte, C.; Machour, N. Determination of multi-class polyaromatic compounds in sediments by a simple modified matrix solid phase dispersive extraction. *Talanta* **2021**, *221*, 121601. [CrossRef]
65. Shahvar, A.; Naccarato, A.; Saraji, M.; Lucena, R.; Cárdenas, S. Solid-phase microextraction. In *Analytical Sample Preparation with Nano- and Other High-Performance Materials*; Elsevier: Amsterdam, The Netherlands, 2021; pp. 33–77. [CrossRef]
66. Bonacci, T.; Mazzei, A.; Naccarato, A.; Elliani, R.; Tagarelli, A.; Brandmayr, P. Beetles "in red": Are the endangered flat bark beetles Cucujus cinnaberinus and C. haematodes chemically protected? (Coleoptera: Cucujidae). *Eur. Zool. J.* **2018**, *85*, 129–137. [CrossRef]

67. Naccarato, A.; Elliani, R.; Cavaliere, B.; Sindona, G.; Tagarelli, A. Development of a fast and simple gas chromatographic protocol based on the combined use of alkyl chloroformate and solid phase microextraction for the assay of polyamines in human urine. *J. Chromatogr. A* **2018**, *1549*, 1–13. [CrossRef]
68. Giglio, A.; Brandmayr, P.; Dalpozzo, R.; Sindona, G.; Tagarelli, A.; Talarico, F.; Zetto, T.; Ferrero, E.A. The Defensive Secretion of Carabus lefebvrei Dejean 1826 Pupa (Coleoptera, Carabidae): Gland Ultrastructure and Chemical Identification. *Microsc. Res. Tech.* **2009**, *72*, 351–361. [CrossRef]
69. Afzali, A.; Vahidi, H.; Fakhraie, S. Benzene extraction in environmental samples based on the mixture of nanoactivated carbon and ionic liquid coated on fused silica fiber before determination by headspace solid-phase microextraction-gas chromatography. *Anal. Method Environ. Chem. J.* **2021**, *4*, 68–78. [CrossRef]
70. Akbarian, M.; Gholamalizadeh, A.; Ahmar, H.; Banitaba, M.H. Application of poly 3,4-ethylenedioxythiophene and gold nanoparticles composite on a gold wire as a coating for determination of nitroaromatics in soil using cold fiber solid phase microextraction combined with gas chromatography. *Environ. Nanotechnol. Monit. Manag.* **2023**, *20*, 100804. [CrossRef]
71. Kong, J.; Cao, X.; Huang, W.; Li, C.; Xian, Q.; Yang, S.; Li, S.; Sun, C.; He, H. Predicting the bioavailability of nitro polycyclic aromatic hydrocarbons in sediments: ZIF-8/h-BN solid-phase microextraction versus Tenax extraction. *Environ. Poll.* **2023**, *318*, 120896. [CrossRef]
72. Xie, W.; Zhu, X.; Mei, H.; Guo, H.; Li, H.; Wang, P.; Li, Y.; Deng, X.; Zhu, J.; Hu, C. Metal-organic frameworks as solid-phase microextraction adsorbents for the determination of triacetone triperoxide by gas chromatography-mass spectrometry. *Forensic Sci. Int.* **2023**, *352*, 111852. [CrossRef]
73. Chen, H.; Luo, S.; Huang, X. Development of monolith/aminated carbon nanotubes composite-based solid-phasemicroextraction of phenoxycarboxylic acids herbicides in water and soil samples. *J. Sep. Sci.* **2021**, *44*, 4284–4294. [CrossRef]
74. Pang, J.; Song, X.; Huang, X.; Yuan, D. Porous monolith-based magnetism-reinforce d in-tub e solid phase microextraction of sulfonylurea herbicides in water and soil samples. *J. Chromatogr. A* **2020**, *1613*, 460672. [CrossRef] [PubMed]
75. Zhang, X.; Han, L.; Li, M.; Qin, P.; Li, D.; Zhou, Q.; Lu, M.; Cai, Z. Nitrogen-rich carbon nitride as solid-phase microextraction fiber coating for high-efficient pretreatment of polychlorinated biphenyls from environmental samples. *J. Chromatogr. A* **2021**, *1659*. [CrossRef]
76. Li, D.; Qin, M.; Lou, X.; Zhu, J.; Ma, W.; Zhang, N.; Lu, M. Constructing perfluorinated UiO-67 for enrichment of polycyclic aromatic hydrocarbons in seawater and seabed sediments. *J. Chromatogr. A* **2024**, *1737*, 465463. [CrossRef]
77. Yu, C.; Wu, F.; Luo, X.; Zhang, J. Porphyrin-based covalent organic framework coated stainless steel fiber for solid-phase microextraction of polycyclic aromatic hydrocarbons in water and soil samples. *Microchem. J.* **2021**, *168*, 106364. [CrossRef]
78. Guo, W.; Tao, H.; Shuai, Q.; Huang, L. Architectural engineering inspired in situ growth of covalent organic frameworks as outstanding fiber coating for solid-phase microextraction of phenols. *Microchem. J.* **2023**, *189*, 108564. [CrossRef]
79. dos Santos, R.R.; de Lourdes Cardeal, Z.; Menezes, H.C. Phase distribution of polycyclic aromatic hydrocarbons and their oxygenated and nitrated derivatives in the ambient air of a Brazilian urban area. *Chemosphere* **2020**, *250*, 126223. [CrossRef] [PubMed]
80. Choi, N.R.; Lee, J.Y.; Ahn, Y.G.; Kim, Y.P. Determination of atmospheric amines at Seoul, South Korea via gas chromatography/tandem mass spectrometry. *Chemosphere* **2020**, *258*, 127367. [CrossRef]
81. Conrady, M.W.; Bauer, M.; Jo, K.D.; Cropek, D.M.; Busby, R.R. Solid-phase microextraction (SPME) for determination of geosmin and 2-methylisoborneol in volatile emissions from soil disturbance. *Chemosphere* **2021**, *284*, 131333. [CrossRef]
82. Batista, J.M.; Valenzuela, E.F.; Costa Menezes, H.; Cardeal, Z.L. An exploratory study of volatile and semi-volatile organic compounds in $PM_{2.5}$ atmospheric particles from an outdoor environment in Brazil. *Environ. Sci. Pollut. Res. Int.* **2025**, *32*, 657–676. [CrossRef]
83. Wang, L.; Cheng, Y.; Wu, C.; Luo, F.; Lin, Z.; Naidu, R. Rapid on-site detection of underground petroleum pipeline leaks and risk assessment using portable gas chromatography-mass spectrometry and solid phase microextraction. *J. Chromatogr. A* **2023**, *1696*, 463980. [CrossRef] [PubMed]
84. Pasquini, D.; Gori, A.; Ferrini, F.; Brunetti, C. An Improvement of SPME-Based Sampling Technique to Collect Volatile Organic Compounds from Quercus ilex at the Environmental Level. *Metabolites* **2021**, *11*, 388. [CrossRef]
85. Kaikiti, K.; Omirou, M.; Ioannides, I.M.; Agapiou, A. Mapping soil VOCs using three green sample extraction techniques and GC-MS. *Microchem. J.* **2024**, *207*, 111851. [CrossRef]
86. Peñalver, R.; Campillo, N.; López-García, I.; Hernández-Córdoba, M. Solid-phase microextraction for the determination of iron organic compounds in seawaters and soils by gas chromatography coupled to microwave-induced plasma with atomic emission detection spectrometry. *Microchem. J.* **2020**, *154*, 104630. [CrossRef]
87. Rodríguez-Palma, C.E.; Campíns-Falcó, P.; Herráez-Hernández, R. Assessing the Dissipation of Pesticides of Different Polarities in Soil Samples. *Soil Syst.* **2024**, *8*, 71. [CrossRef]
88. Kaikiti, K.; Omirou, M.; Savvides, S.; Ioannides, I.M.; Agapiou, A. HS-SPME-GC-MS analysis of Cyprus vineyard soil for VOCs determination. *Sustain. Chem. Environ.* **2023**, *2*, 100021. [CrossRef]

89. Kong, J.; Gao, Z.; Hu, G.; Huang, W.; Zhou, S.; He, H.; Xian, Q.; Sun, C. Solid-phase microextraction combined with gas chromatography/triple quadrupole tandem mass spectrometry for determination of nitrated polycyclic aromatic hydrocarbons in sediments. *J. Sep. Sci.* **2022**, *45*, 1094–1105. [CrossRef] [PubMed]
90. Simon, M.P.; Knuth, D.; Böhm, L.; Wiltschka, K.; Schatz, M.; Düring, R.-A. A miniaturized method for fast, simple, and sensitive pesticide analysis in soils. *J. Soils Sediments* **2022**, *22*, 496–508. [CrossRef]
91. Xu, S.; Li, H.; Xiao, L.; Wang, M.; Feng, S.; Fan, J.; Pawliszyn, J. Quantitative Determination of Poly(methyl Methacrylate) Micro/Nanoplastics by Cooling-Assisted Solid-Phase Microextraction Coupled to Gas Chromatography-Mass Spectrometry: Theoretical and Experimental Insights. *Anal. Chem.* **2024**, *96*, 2227–2235. [CrossRef]
92. Wang, L.; Cheng, Y.; Naidu, R.; Chadalavada, S.; Bekele, D.; Gell, P.; Donaghey, M.; Bowman, M. Application of portable gas chromatography–mass spectrometer for rapid field based determination of TCE in soil vapour and groundwater. *Environ. Technol. Innov.* **2021**, *21*, 101274. [CrossRef]
93. Brinco, J.; Carvalho, R.; Gomes da Silva, M.; Guedes, P.; Ribeiro, A.B.; Mateus, E.P. Extraction of pesticides from soil using direct-immersion SPME LC-Tips followed by GC-MS/MS: Evaluation and proof-of-concept. *J. Chromatogr. A* **2024**, *1735*, 465295. [CrossRef] [PubMed]
94. Ahmed, A.K.M.A.; Raynie, D.E. Development of Dry-herb vaporizer-assisted solid-phase Microextraction for the analysis of volatile Organic compounds. *Adv. Sample Prep.* **2024**, *10*, 100112. [CrossRef]
95. Zhu, W.; Qin, P.; Han, L.; Zhang, X.; Li, D.; Li, M.; Wang, Y.; Zhang, X.; Lu, M.; Cai, Z. Gas-cycle-assisted headspace solid-phase microextraction coupled with gas chromatography for rapid analysis of organic pollutants. *Chem. Commun.* **2021**, *57*, 8810. [CrossRef] [PubMed]
96. Maleki, S.; Hashemi, P.; Adeli, M. A simple and portable vacuum assisted headspace solid phase microextraction device coupled to gas chromatography based on covalent organic framework/metal organic framework hybrid for simultaneous analysis of volatile and semi-volatile compounds in soil. *J. Chromatogr. A* **2023**, *1705*, 464195. [CrossRef]
97. Derikvand, A.; Ghiasvand, A.; Dalvand, K.; Haddad, P.R. Fabrication and evaluation of a portable low-pressure headspace solid-phase microextraction device for on-site analysis. *Microchem. J.* **2021**, *168*, 106362. [CrossRef]
98. Pérez-Lemus, N.; López-Serna, R.; Pérez-Elvira, S.I.; Barrado, E. Sample pre-treatment and analytical methodology for the simultaneous determination of pharmaceuticals and personal care products in sewage sludge. *Chemosphere* **2020**, *258*, 127273. [CrossRef]
99. Naccarato, A.; Tassone, A.; Martino, M.; Elliani, R.; Sprovieri, F.; Pirrone, N.; Tagarelli, A. An innovative green protocol for the quantification of benzothiazoles, benzotriazoles and benzosulfonamides in PM10 using microwave-assisted extraction coupled with solid-phase microextraction gas chromatography tandem-mass spectrometry. *Environ. Pollut.* **2021**, *285*, 117487. [CrossRef] [PubMed]
100. Beiranvand, M.; Ghiasvand, A. An ultrasound-assisted pressure-regulated solid-phase microextraction setup for fast and sensitive analysis of volatile pollutants in contaminated soil. *Environ. Sci. Pollut. Res.* **2020**, *27*, 36306–36315. [CrossRef]
101. Xu, S.; Li, H.; Wu, H.; Xiao, L.; Dong, P.; Feng, S.; Fan, J. A facile cooling-assisted solid-phase microextraction device for solvent-free sampling of polycyclic aromatic hydrocarbons from soil based on matrix solid-phase dispersion technique. *Anal. Chim. Acta* **2020**, *1115*, 7–15. [CrossRef]
102. Jalili, V.; Barkhordari, A.; Ghiasvand, A. A comprehensive look at solid-phase microextraction technique: A review of reviews. *Microchem. J.* **2020**, *152*. [CrossRef]
103. Zhang, Z.; Pawliszyn, J. Quantitative extraction using an internally cooled solid phase microextraction device. *Anal. Chem.* **1995**, *67*, 34–43. [CrossRef]
104. Jalili, V.; Barkhordari, A.; Ghiasvand, A. New extraction media in microextraction techniques. A review of reviews. *Microchem. J.* **2020**, *153*, 104386. [CrossRef]
105. He, M.; Wang, Y.; Zhang, Q.; Zang, L.; Chen, B.; Hu, B. Stir bar sorptive extraction and its application. *J. Chromatogr A* **2021**, *1637*, 461810. [CrossRef] [PubMed]
106. Tölgyessy, P.; Nagyová, S.; Roško, V.; Hucko, P. Simultaneous determination of short-chain chlorinated paraffins and other classes of persistent organic pollutants in sediment by gas chromatography–tandem mass spectrometry after ultrasonic solvent extraction combined with stir bar sorptive extraction. *Chem. Pap.* **2021**, *75*, 5645–5661. [CrossRef]
107. Wang, Z.; He, M.; Chen, B.; Hu, B. Azo-linked porous organic polymers/polydimethylsiloxane coated stir bar for extraction of benzotriazole ultraviolet absorbers from environmental water and soil samples followed by high performance liquid chromatography-diode array detection. *J. Chromatogr. A* **2020**, *1616*, 460793. [CrossRef]
108. Liu, Z.; Zhou, W.; Hong, Y.; Hu, W.; Li, W.; Chen, Z. Covalent organic framework-V modified porous polypropylene hollow fiber with detachable dumbbell-shaped structure for stir bar sorptive extraction of benzophenones. *J. Chromatogr. A* **2022**, *1664*, 462798. [CrossRef]
109. Wianowska, D.; Gil, M.; Olszowy, M. Miniaturized methods of sample preparation. In *Handbook on Miniaturization in Analytical Chemistry*; Elsevier: Amsterdam, The Netherlands, 2020; pp. 99–125.
110. Yadav, P.; Singh, R.; Gupta, N.; Kumar, S.; Singh Thakur, R.; Khan, A.H.; Ghazi Ansari, N.; Kumar Patel, D. Modified DLLME-SFO approach for evaluation of multiclass agrochemicals and its associated risk assessment: Soil, Saccharum officinarum and Jaggery. *Food Chem. Adv.* **2022**, *1*, 100032. [CrossRef]
111. Naing, N.N.; Xue Yi Goh, E.; Kee Lee, H. Enhanced microextraction of endocrine disrupting chemicals adsorb e d on airborne fine particulate matter with gas chromatography–tandem mass spectrometric analysis. *J. Chromatogr. A* **2021**, *1637*, 461828. [CrossRef]

112. Naccarato, A.; Tassone, A.; Martino, M.; Moretti, S.; Macagnano, A.; Zampetti, E.; Papa, P.; Avossa, J.; Pirrone, N.; Nerentorp, M.; et al. A Field Intercomparison of Three Passive Air Samplers for Gaseous Mercury in Ambient Air. *Atmos. Meas. Tech.* **2021**, *14*, 3657–3672. [CrossRef]
113. Rodrigues, T.; Chibana Ferreira, K.; Isquibola, G.; Faza Franco, D.; Anderson, J.L.; de Oliveira Merib, J.; Clairmont Feitosa de Lima Gomes, P. Investigating a new approach for magnetic ionic liquids: Dispersive liquid-liquid microextraction coupled to pyrolysis gas-chromatography-mass spectrometry to determine flame retardants in sewage sludge samples. *J. Chromatogr. A* **2024**, *1730*, 465038. [CrossRef]
114. Cunha, S.C.; Ferreira, R.; Marmelo, I.; Vieira, L.R.; Anacleto, P.; Maulvault, A.; Marques, A.; Guilhermino, L.; Fernandes, J.O. Occurrence and seasonal variation of several endocrine disruptor compounds (pesticides, bisphenols, musks and UV-filters) in water and sediments from the estuaries of Tagus and Douro Rivers (NE Atlantic Ocean coast). *Sci. Total Environ.* **2022**, *838*, 155814. [CrossRef] [PubMed]
115. Pour, P.H.; Daryanavard, S.M.; Memar, M.; Naccarato, A. Development of Ultrasound-Assisted Dispersive Liquid–Liquid Microextraction Based on Solidification of Floating Organic Droplets and Deep Eutectic Solvents for Multi-Class Pesticide Analysis in Agricultural Waters. *Microchem. J.* **2025**, *212*, 113404. [CrossRef]
116. Zhu, M.; Niu, Z.; Zhang, W.; Zhang, J.; Wen, Y. The combination of two microextraction methods coupled with gas chromatography for the determination of pyrethroid insecticides in multimedia environmental samples: Air, water, soil, urine and blood. *Water Environ. J.* **2020**, *34*, 503–515. [CrossRef]
117. Oliveira Martins, R.; Guimarães Souza, G.; Santos Machado, L.; Lopes de Araújo, G.; Costa Simas, R.; Gonçalves da Silva, B.J.; Damin, V.; Rodrigues Chaves, A. Hollow fiber liquid-phase microextraction of multiclass pesticides in soil samples: A green analytical approach for challenging environmental monitoring analysis. *Microchem. J.* **2023**, *193*, 109028. [CrossRef]
118. Moret, S.; Hidalgo, M.; Sanchez, J.M. Hollow-Fiber Liquid-Phase Microextraction (HF-LPME) Coupled On-Line to Liquid Chromatography for the Determination of the Herbicides 2,4-Dichlorophenoxyacetic Acid and 2-Methyl-4-chlorophenoxyacetic Acid and Their Main Metabolites in Soil Samples. *Separations* **2023**, *10*, 273. [CrossRef]
119. Tuğba Zaman, B.; Dalgıç Bozyiğit, G.; Şaylan, M.; Seda Koçoğlu, E.; Kartoğlu, B.; Aydın, E.S.; Girgin, A.; Borahan, T.; Oflu, S.; Kılınç, Y.; et al. Implementation of simple and effective fine droplet formation-based spray-assisted liquid phase microextraction for the simultaneous determination of twenty-nine endocrine disruptor compounds and pesticides in rock, soil, water, moss, and feces samples from antarctica using gas chromatography-mass spectrometry. *Environ. Sci. Pollut. Res.* **2024**, *31*, 10920–10933. [CrossRef]
120. Rezaee, M.; Assadi, Y.; Milani Hosseini, M.-R.; Aghaee, E.; Ahmadi, F.; Berijani, S. Determination of Organic Compounds in Water Using Dispersive Liquid-Liquid Microextraction. *J. Chromatogr. A* **2006**, *1116*, 1–9. [CrossRef]
121. Pedersen-Bjergaard, S.; Rasmussen, K.E. Liquid-Liquid-Liquid Microextraction for sample preparation of biological fluids prior to capillary electrophoresis. *Anal. Chem.* **1999**, *71*, 2650–2656. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.