separations

MDPI

Review

Recent Applications and Newly Developed Strategies of Solid-Phase Microextraction in Contaminant Analysis: Through the Environment to Humans

Attilio Naccarato [1,*] **and Antonio Tagarelli** [2,*]

[1] CNR-Institute of Atmospheric Pollution Research, Division of Rende, UNICAL-Polifunzionale, I-87036 Arcavacata di Rende, CS, Italy
[2] Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via P. Bucci Cubo 12/C, I-87036 Arcavacata di Rende, CS, Italy
* Correspondence: attilio.naccarato@iia.cnr.it (A.N.); a.tagarelli@unical.it (A.T.)

Received: 10 October 2019; Accepted: 1 November 2019; Published: 6 November 2019

Abstract: The present review aims to describe the recent and most impactful applications in pollutant analysis using solid-phase microextraction (SPME) technology in environmental, food, and bio-clinical analysis. The covered papers were published in the last 5 years (2014–2019) thus providing the reader with information about the current state-of-the-art and the future potential directions of the research in pollutant monitoring using SPME. To this end, we revised the studies focused on the investigation of persistent organic pollutants (POPs), pesticides, and emerging pollutants (EPs) including personal care products (PPCPs), in different environmental, food, and bio-clinical matrices. We especially emphasized the role that SPME is having in contaminant surveys following the path that goes from the environment to humans passing through the food web. Besides, this review covers the last technological developments encompassing the use of novel extraction coatings (e.g., metal-organic frameworks, covalent organic frameworks, PDMS-overcoated fiber), geometries (e.g., Arrow-SPME, multiple monolithic fiber-SPME), approaches (e.g., vacuum and cold fiber SPME), and on-site devices. The applications of SPME hyphenated with ambient mass spectrometry have also been described.

Keywords: solid phase microextraction (SPME); air analysis; environmental waters analysis; soil analysis; food monitoring; on-site sampling; human biomonitoring (HBM); chromatography; ambient mass spectrometry; ultra-trace analysis

---

1. Introduction

The evolution of modern lifestyles due to the development of industrial civilization has influenced the relationship between humankind and his environment. If, on the one hand, the quality of life has generally changed considerably during the past decades, we may be facing a turnaround. Indeed, for many years, the impact that the current living habits have had on the environment has been underestimated and the receptiveness to topics such as sustainable development has only been recently established. The impact on the environment occurs in many ways, and with a different extent. Generally, less evident but equally important is the impact due to the inordinate use of chemical products. Although their daily use contributes to improving our quality of life, their uncontrollable dispersion in the environment associated with low biodegradability is undoubtedly the main mode of introduction of pollutants into the biological cycles, including those involving humans through nutrition and direct exposure. In this context, the identification and quantification of contaminants in environmental, food, and bio-clinical matrices find more and more space in both routine and research laboratories often driven by growing regulatory attention at the national and international level.

Solid-phase microextraction (SPME) is a well-established green technique for simultaneous extraction and pre-concentration of the compounds from a variety of matrices. Since its introduction in the early 1990s, this technique has been experiencing rapid development and growth in terms of coating materials, geometries and applications. Although SPME is only part of the broad panorama of microextraction analytical techniques, it plays an important role. Given the simplicity, versatility, and availability in different formats, SPME addresses several challenges associated with the traditional sample preparation procedures and we expect a noteworthy impact on the methods of analysis in the next coming years. The purpose of this review is to highlight the role that SPME is having in contaminant monitoring through the path that goes from the environment to humans. To this end, we revised the studies focused on the analysis of persistent organic pollutants (POPs), pesticides, and emerging pollutants (EPs) including personal care products (PPCPs). We wanted to cover solely the most impactful advancements published in the last 5 years (2014–2019) giving to the reader a picture of the aspects towards the research is directed and at the same time highlighting as the broadly available panorama of SPME strategies can effectively solve even highly complex analytical problems.

2. The Beginning Step: Environmental Matrices

The journey undertaken by contaminants starts from their release into the environment in at least one of its components, i.e., air, water, soil. As constitutive elements of the biosphere, they are factors in a continuous dynamic equilibrium characterized by exchanges between them and make up a complex system with the life forms they host. In the environmental field, the SPME is a technique that includes a high number of studies: in particular in the analysis of environmental waters, whereas to a less extent are the applications to air and soil associated matrices (Figure 1 and Table 1).

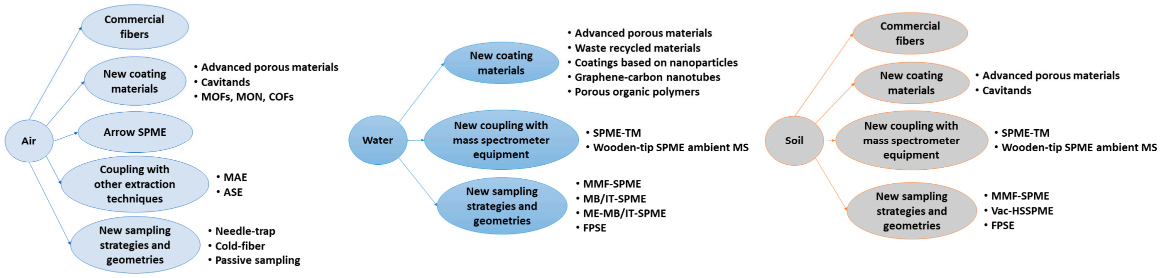

Figure 1. Main solid-phase microextraction—geometries and strategies used in the analysis of environmental matrices during the covered period (2014–2019).

2.1. *Air*

Although ambient air may seem a simple matrix for less experienced analysts, it presents important analytical challenges because of the difficulty in sampling and calibration procedures. The air comprises many components of both organic and inorganic nature present in the gaseous and particulate phase which are in continuous mixing. In air can occur complex reactions the may convert the pollutants into other chemical species. Unlike the other environmental components, in the air, the analytes can be quickly transported covering even long distances around the world. In addition, phenomena such as release, volatilization, deposition, and resuspension driven by weather conditions lead to cycles of reduction and increase of pollutants and contribute to introducing of new contaminants from soil or water. To further complicate the matrix, due to the presence of suspended particulate matter, the analytes can be present as gaseous compounds as well as bound to the particles, depending on their chemical–physical properties.

In air sampling, the SPME has been exploited in different geometries and strategies (Figure 1, Table 1). The areas in which the research has mainly been addressed during the last five years have regarded the use of commercially available coatings, as well as the development of new coatings and their application. Many studies have been conducted in indoor environments in order to monitor exposure to volatile organic compounds (VOCs) and semivolatile organic compounds (SVOCs) that are released into the air by many activities [1–3], but also by used furnishing [4,5]. Commercially available (divinylbenzene/carboxen/polydimethylsiloxane) DVB/CAR/PDMS fiber has been successfully employed in a method for the simultaneous analysis of trihalomethanes (THMs) such as trichloromethane, bromodichloromethane, dibromochloromethane, and tribromomethane, in ambient air [1]. This method was validated for swimming pool air, bearing improvements over previous methods such as a decrease in instrumental runtime, minimization of sample contamination, and elimination of the need for harsh chemicals. Similarly, other commercially available SPME fibers, such as a carboxen/polydimethylsiloxane (CAR/PDMS) and polydimethylsiloxane-divinylbenzene (PDMS/DVB) fiber, were used in the investigation of some VOCs present in a laboratory environment [2] and in the implementation of a method for the analysis of trace carbonyls based on on-fiber derivatization with (pentafluorobenzyl)hydroxylamine (PFBHA) and gas chromatographic (GC) analysis, which was then applied to the monitoring in dated office rooms [5].

As regards the application in an outdoor environment, among the most interesting applications there is the use of the SPME fibers in the arrow version (Figure 2). SPME Arrow consists of a steel rod coated with a larger amount of sorbent material than the traditional SPME fiber, while still being compatible with desorption in a standard GC liner due to its dimensions and sharp, closed tip. The sorbent-coated rod can be withdrawn in a steel tube when the device is not in use. Because of the steel rod, the device is less fragile than a conventional SPME fiber [6].

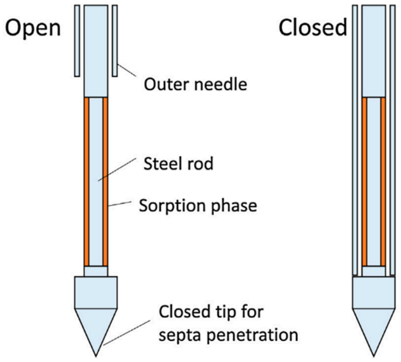

Figure 2. The Arrow SPME system with sorbent exposed (left) and with sorbent covered by a steel tube (right) [6].

The SPME Arrow device coated with commercial and self-made functionalized mesoporous silica materials was used on board an aerial drone, which was used for the simultaneous collection of air samples in two difficult access places such as boreal forest and wetland [7]. The sampled VOCs were detected by gas chromatography with a polar column and mass spectrometry. Established pollutants such as polycyclic aromatic hydrocarbons (PAHs), and other hazardous substances including phthalates, adipates, vulcanizing agents and antioxidants were successfully analyzed in the air generated above synthetic turf football fields following heating of the rubber material using a PDMS/DVB as fiber coating in headspace mode [8]. Benzene, toluene, ethylbenzene, and xylenes (BTEX) in ambient air have been the target of one research with the aim of developing a simpler, low-budget, and accurate method for their quantification based on SPME and gas chromatography coupled with mass spectrometry (GC–MS) [9]. This article shows how in urban areas with highly contaminated air, 20 mL vials can be used for the collection of air samples, and a 100 µm polydimethylsiloxane (PDMS) fiber can be used to sufficiently preconcentrate the analytes before the analysis with GC–MS. Exposure to ambient HCN concentration in a residential area close to a gold mine was assessed by SPME using 75 µm CAR/PDMS fiber [10]. Given the low detection limit, this method provides promising results for monitoring ambient HCN concentrations, and at the same time, minimizes the work for sample preparation, reducing the time and cost of the monitoring.

SPME is not only exploited for direct sampling in the air but it is also used as a convenient strategy for the introduction of the analytes into a gas chromatographic system after the sample preparation step. This strategy was recently used to quantify a class of largely studied pollutants such as organophosphate esters (OPEs) [11,12] bound to airborne particulate matter by a green protocol based on the combination of microwave-assisted extraction (MAE) and SPME followed by gas chromatography coupled with tandem mass spectrometry (GC-MS/MS) analysis [13]. Similarly, aliphatic and aromatic amines (AA) in indoor air were investigated by SPME-GC-MS after the ultrasonic extraction of XAD-2 adsorbent without derivatization [3]. In this paper, the author reached detection limits lower from about a factor of five in comparison to direct injection. This result, consequence of the solvent-less nature of SPME injection, is consistent with the improvement in chromatographic performance reported in the literature, also in the analysis of polar compounds with SPME [14]. The use of commercial SPME fibers has also recently found space in the quantification of some pesticides in atmospheric samples. Thirty-one pesticides belonging to different chemical classes (urea, phenoxy acids, pyrethrenoïds, etc.) and commonly used in non-agricultural areas such as public or private gardens were investigated. After the sampling on glass fiber filters and on XAD-2 resin traps followed by the extraction using the accelerated solvent extraction (ASE) technique, an 85 μm polyacrylate (PA) fiber was immersed in the ASE extract to preconcentrate the analytes before GC-MS analysis with on-injector derivatization using N-methyl-N-(tert.-butyldimethylsilyl) trifluoroacetamide (MtBSTFA) [15].

Porous materials are attracting the attention of the scientific community in numerous scientific fields due to their properties and different possible uses. In this connection, also in the development of SPME coatings these so-called advanced porous materials and cavitands find space, and their use for the analysis of pollutants in the air constitutes a robust line of research still growing [16]. In particular, interesting articles have recently been published on the development of new coatings based on materials such as metal-organic frameworks (MOFs) and covalent organic frameworks (COFs), and their application in air analysis. These were followed by other papers focused on the use of microporous organic network (MON), or other hybrids materials with MON, which made it possible to improve the extraction efficiency by countering the tendency of some competitors such as water molecules to occupy the pores of MOF [17,18]. Most of the recent applications of these materials have focused on the analysis of established pollutants in particulate matter after a previous extraction of the analytes from the solid matrix [17–19], whereas a COFs coated fiber-based with gas chromatography-mass spectrometric detection was used in the investigation of some volatile and harmful benzene homologs by exploiting the favorable π-π and hydrophobic interactions between the π-conjugated aromatic groups of the coating and the aromatic rings of the analytes [20]. This material was followed by the use of functionalized cavitand that, given its molecular structure, allowed to obtain high enrichment factors, very low detection limits and increased selectivity toward the benzene. For this reason, this coating was proposed as a selective SPME coating for the determination of BTEX at trace levels even for the assessment of short-term exposure in workers [21].

Analytical approaches that are not yet fully explored are the needle-trap and cold-fiber SPME, partly because of the difficulty in commercially obtaining the necessary equipment for the analytic set-up [22,23]. Recently, some studies have been published on SPME fibers used as a passive sampling device to get the Time-Weighted Average (TWA) concentration of VOCs. These papers aim to improve the technique in terms of accuracy, particularly with longer sampling times [24,25]. Advances in this field could contribute in the coming years to the effective use of the SPME in the environmental monitoring programs targeted to the chronic exposure or background concentrations.

2.2. Water

The presence of organic and inorganic pollutants in the environmental waters is a serious problem for human health and the well-being of ecosystems. Protecting this important environmental sector involves national and international monitoring interventions along with regulatory legislative actions, which are necessarily based on the results of analytical studies in the environmental field. Using microextraction techniques, such as the SPME, have offered a significant contribution to the identification and quantification of established and emerging pollutants in environmental waters by offering reliable analysis tools with growing selectivity and sensitivity [26]. In the last 5 years, the number of published articles in which the SPME is employed to address analytical issues in environmental waters is remarkable (Table 1). Most of these investigations (over one hundred in the covered period) were directed on the development of new coating materials and their use in real case scenarios (Figure 1). These studies, in terms of numbers, are followed by works in which new strategies in using SPME are presented, e.g., new coupling with mass spectrometer equipment [27–29] or the development of a new mechanically robust SPME sampler for the on-site sampling [30]. The involved classes of molecules are various and include both pollutants traditionally investigated such as PAHs [19,31–41] and polychlorinated biphenyls (PCBs) [33,42–45], and new polluting molecules such as dyes [46], additives for materials [14], new pesticides [47–53], antibiotics [54–57], pollutants coming from a number of polluting processes including those in industries [58–60], and last but not least, ultraviolet filters, whose determination in natural water is one of the issues that is attracting greater interest [37,61–73].

The investigation of PAHs is still current, and despite the numerous studies already present in the literature, PAHs are the target in many studies because of their high relevance as pollutants, and for this reason, they are also used as reference compounds to test new SPME uses and coating materials [74,75]. Some noteworthy applications report the successful analysis in environmental waters using coating based on polymer materials [31], MOF [19,32–34], mesoporous carbon materials [35], polyhedral oligomeric silsesquioxanes (POSSs) [36], titanium dioxide-nanosheets [37], coatings based on nanoparticles [38,75], nanotubes (MONTs) [39,40], and material derived from low-cost waste such as biochar [41]. The latter analytical strategy seems particularly interesting as it opens new scenarios involving the recovery of waste materials and their exploitation in an analytical context. Similarly, BTEX were also taken as a reference for verifying the analytical performance of a new SPME coating in environmental waters. These studies were mainly carried out by prof. Ouyang's group, which has achieved satisfactory results for analysis of river, lake, pond and seawater by developing SPME coatings that exploit different materials such as tri-metal centered MOFs (tM-MOFs) [76], graphene–carbon nanotubes (G-CNTs) [77], Prussian blue nanoparticles-doped graphene oxide [75], knitting aromatic polymers (KAPs) [78] and porous organic polymers (POPs) [79] including Scholl-coupling microporous polymers [80].

Among the most impactful trends, there is the application of the newly developed geometries to real environmental case studies. Multiple monolithic fiber solid-phase microextraction (MMF-SPME) was developed as a new extraction approach for aqueous samples; considering its peculiarities, it is proposed as an improved alternative to the traditional SPME in terms of extraction capacity, mass-transfer speed and flexibility [48,81–84]. MMF-SPME consists of four independent thin fibers bound together to form a fiber bunch (Figure 3).

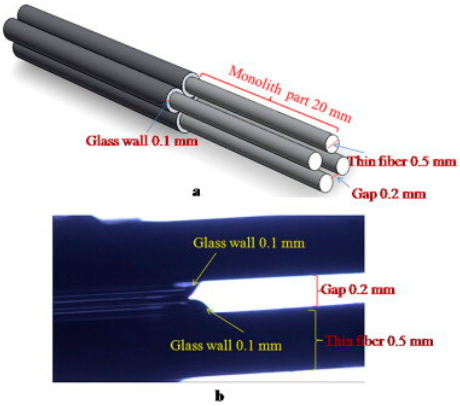

Figure 3. Schematic diagram of MMF-SPME (**a**) and the microscope image of the gap between thin fibers (**b**) [81].

Similarly, monolithic fiber has also found application in the in-tube SPME (IT-SPME) through the development of novel materials such as the MOF-monolithic adsorbent with enhanced surface area, which was successfully used to detect fluoroquinolones at ultra-trace level in river water [54], but also the development of new strategies such as magnetism-enhanced monolith-based in-tube solid-phase microextraction (ME-MB/IT-SPME). This technique used modified absorbent material with Fe_3O_4 nanoparticles and the exertion of a variable magnetic field to overcome the main drawbacks of the traditional monolith-based in-tube solid-phase microextraction (MB/IT-SPME), that is the low extraction efficiency; this method was used for the extraction of triazines from river and lake water [85].

Recently, Kabir and Furton proposed the fabric phase sorptive extraction (FPSE) [86] which is a new promising member of the sorbent-based sorptive microextraction group. This technique overcomes some of the major shortcomings of traditional SPME related to the sorbent coating technique and the geometry of the microextraction device such as the small primary contact surface area and the low amount (typically ~0.5 µL) of sorbent loading that often results in poor extraction sensitivity. Despite its recent development, FPSE has not only been used for the analysis of pollutants such as non-steroidal anti-inflammatory drugs [87], and cytostatic compounds in environmental water [88], but it has already been the topic of some studies focused on its own evolution that suggest interesting scenarios in the next years [89,90].

2.3. Soil

The monitoring of pollutants in the soil is very important to ensure environmental and food safety. The main pollutants that are being investigated are pesticides, petroleum hydrocarbons, PAHs, PCBs, pharmaceuticals, and industrial residuals. Although soil is one of the environmental compartments together with water and air, unlike them, the presence of pollutants in the soil presents different analytical challenges determined by the complexity of the matrix. Compared with the pollution of air and water, soil pollution is very nonhomogeneous and often local because of a slower diffusion of chemicals. Moreover, soil samples have different physicochemical properties and affinity to analytes [91]. In fact, the main issue in soil analysis using SPME is certainly related to the matrix effect, which can affect the reliability of the analysis and lead to the fouling of the fiber coating caused by irreversible adsorption of macromolecules on the extraction phase. This occurrence can result in the changes in fiber properties and the extraction performance of the fiber upon subsequent use. Currently, despite the recent technical developments, the use of SPME in soil analysis is still a challenge and requires, at least during method development, robust expertise in the field.

During the last five years, SPME has found a place in the analysis of soil pollutants in several respects. Similar to what we highlighted for the study in environmental waters, a significant part of the research is aimed at the development and use of new, better-performing coatings, above all in terms of sensitivity and specificity (Figure 1, Table 1). A cavitand-based SPME coating was synthesized and used for the selective determination of nitroaromatic explosives and explosive taggants at ultratrace levels [92]. Among the most used materials, the MOFs have a leading role. Their application as SPME coating for soil analysis has been extensively investigated in recent years, both as regards the use of new structural variants and their synthesis. After their preparation, these SPME fibers were successfully used in the analysis of trace levels of fungicides [93], PAHs [19,94–96], PCBs [97,98], polybrominated diphenyl ethers (PBDEs) [99].

As for commercial fibers, their use in soil analysis still has many potentials and they have been used not only in method development for new harmful contaminants [100–102] but rather as an analytical tool to carry out other studies, principally with ecological–environmental purposes. Indeed, given its analytical features, SPME allows for the determination of analyte free concentration and for this reason it has been used in bioavailability [103], bio-accessibility [104], and soil sorption studies involving the binding potential of dissolved organic matter (DOM) and the effects of bioremediation on contaminated industrial and agricultural soils [105,106].

Of particular interest is also the deployment of untraditional SPME approaches including the fabric-phase sorptive extraction used for alkyl phenols determination [107], MMF-SPME exploited for the sulfonylurea herbicides assay [47], ionic liquid-coated PTFE tube used for mercury extraction before cold vapor atomic absorption spectrometry (CV-AAS) determination [108], and vacuum-assisted headspace solid-phase microextraction (Vac-HSSPME). The latter was recently reviewed by Psillakis [109] and appears to be a promising route for the analysis of pollutants in solid matrices such as soil because increasing the volatility of the analytes, it allows the analysis in HS-SPME with the consequent reduction of the matrix effect and improvement of the fiber lifetime.

Table 1. Selected SPME applications in environmental matrices.

Analytes	Matrix	SPME Approach and Coating Material	Instrumentation	Calibration Range	[Ref] Publishing Year
THMs	Ambient air	Fiber—DVB/CAR/PDMS	GC-MS	2–5000 μg/m^3	[1]—2019
VOCs	Indoor air	fiber—CAR/PDMS	GC-MS, GC-FID	-	[2]—2018
aliphatic and aromatic amines	Indoor air	Fiber—DVB/CAR/PDMS	GC-MS	10–50,000 ng/m^3	[3]—2018
OPEs	Indoor air	fiber—PDMS	GC-MS	0.05–500 mg/m^3	[4]—2017
Formaldehyde, acetaldehyde, acetone, hexanal	Indoor air	fiber—PDMS/DVB	GC-MS, GC-FID	-	[5]—2014
VOCs	Ambient air	SPME Arrow—Carbon WR, Carbon WR/PDMS, PDMS/DVB, lab-made functionalized mesoporous silica material	GC-MS	-	[7]—2019
PAHs, phthalates, adipates, vulcanisation additives and antioxidants	Ambient air	fiber—PDMS/DVB	GC-MS	0.01–2 μg/L	[8]—2018
BTEX	Ambient air	fiber—PDMS	GC-MS	2–200 mg/m^3	[9]—2016
HCN	Ambient air	fiber—CAR/PDMS	GC-MS	5–500 μg/L	[10]—2017
OPEs	PM10	fiber—DVB/CAR/PDMS	GC-MS/MS	0.1–10 ng/mL	[13]—2018
pesticides of different chemical classes	Ambient air and PM	fiber—PA	GC-MS	2–2000 ng of each pesticide	[15]—2014
Short-chain chlorinated paraffin	water, sediment, organisms, and PM	fiber—hollow microporous organic network (H-MON)	GC-MS	0.05–10 ng/mL	[17]—2018
PAHs	environmental water, PM2.5, and smoked meat	fiber—MOF@microporous organic network (MON) hybrid materials	GC-MS/MS	0.1–500 ng/L	[18]—2016
nitrated polycyclic aromatic hydrocarbons	environmental water, PM2.5, and soil	fiber—porphyrinic zirconium MOF	GC-MS	0.4–400 ng/L	[19]—2017
benzene homologues	indoor air	fiber—Covalent organic frameworks (COF)	GC-MS	0.10–20 ng/L	[20]—2017
BTEX	ambient air	fiber—functionalized tetraquinoxaline cavitand	GC-MS	3.5–470 ng/m^3	[21]—2016

Table 1. *Cont.*

Analytes	Matrix	SPME Approach and Coating Material	Instrumentation	Calibration Range	[Ref] Publishing Year
acrolein	ambient air	cold fiber—PDMS	GC-MS	-	[23]—2017
Acetic acid	indoor air	fiber—Car/PDMS	GC-MS	-	[25]—2019
pesticides	river water	SPME-TM	DART-MS/MS DART-orbitrap	0.10–100 ng/mL	[27]—2017
triazine herbicides obtained	lake water	IT-SPME	DART-MS/MS	0.02–0.46 ng/mL	[28]—2014
perfluorinated compounds (PFCs)	lake and river water	wooden-tip SPME ambient MS	LC-MS/MS orbitrap	0.5−100 ng/L	[29]—2014
PAHs	rain and river water	IT-SPME—PEEK tube was packed with polyester fibers	LC- diode array detector	0.03–80 µg/L	[31]—2016
PAHs	lake and river water	fiber—boron nitride nanotube	GC-MS/MS	1–1000 ng/L	[40]—2014
PAHs	river water	fiber—peanut shell-derived biochar materials	GC-MS	10–2000 ng/L	[41]—2019
PAHs	lake water	fiber—MOF	GC-MS	0.01–10 µg/L	[32]—2019
PCBs	lake and river water	fiber—MOF	GC-MS	1–50 ng/L	[33]—2015
PAHs	lake and river water	fiber—zeolite imidazolate MOF	GC-MS	10–20,000 ng/L	[34]—2019
PAHs	lake and river water	fiber—hollow mesoporous carbon spheres	GC-MS	5–2000 ng/L	[35]—2017
PAHs	river water	fiber—titanium dioxide-nanosheets	HPLC-UV	0.05–300 mg/L	[37]—2015
PAHs	volcanic area water	fiber—silver nanoparticles	GC-FID	5–300 µg/L	[38]—2018
nitro-polycyclic aromatic hydrocarbons (NPAHs)	lake and snow water	fiber—metal–organic nanotubes	GC-MS/MS	10–1000 ng/L	[39]—2018
PCBs	river water	fiber—bamboo charcoal	GC-MS/MS	0.2–1000 ng/L	[42]—2014
PCBs	seawater	fiber—metal–organic nanotubes	GC-MS/MS	10–5000 pg/L	[43]—2016
PCBs	pond and lake water	fiber—multimodal porous carbons (MPCs)	GC-ECD	10–1000 ng/L	[44]—2019
PCBs	pond, river, underground and lake water	fiber—metal–organic nanotubes	GC-MS/MS	0.1–500 ng/L	[45]—2014

Table 1. *Cont.*

Analytes	Matrix	SPME Approach and Coating Material	Instrumentation	Calibration Range	[Ref] Publishing Year
Sudan dyes	lake water	PEEK tube—zeolitic imidazolate frameworks	HPLC-UV	0.02–20 ng/mL	[46]—2019
sulfonylurea herbicides (SUHs)	lake, river and well water	MMF-SPME—mixed functional monomers	HPLC-DAD	0.1–200 µg/L	[47]—2018
triazine herbicides	lake and river water	MMF-SPME—polydopamine-based monolith	HPLC-DAD	0.1–200 µg/L	[48]—2016
chlorinated herbicides	river water	Fiber—polyethersulfone	GC-MS	0.05–5 ng/mL	[49]—2014
organophosphorous pesticides	well water	fiber—metal-organic framework/polyethersulfone nanocomposite (TMU-4/PES)	GC-NPD	0.015–50 µg/L	[50]—2018
organochlorine pesticides	well and pond water	fiber—gold nanoparticles	GC-ECD	0.56–10 µg/L	[51]—2016
organochlorine pesticides	river and pond water	fiber—nitrogen-doped ordered mesoporous polymer (NOMP)	GC–MS	9−1500 ng/L	[52]—2016
carbamate pesticides	river water	MMF-SPME—boron-rich coating	HPLC-DAD	0.057–0.96 µg/L	[53]—2019
fluoroquinolones	river water	IT-SPME—MOF-monolith composite	HPLC-FLD	0.001–5.0 µg/L	[54]—2019
cefaclor and cefalexin	lake water	stir bar—molecular imprinted polymers and magnetic carbon nanotubes	HPLC-UV	15–320 ng/mL	[55]—2017
sulfadiazine	well water	stir bar—graphene oxide-silica composite reinforced	UV-vis	5–150 µg/L	[57]—2017
nitrophenols	lake and river water	MMF-SPME—AMED coating	HPLC-DAD	0.5–200 µg/L	[58]—2015
chlorophenol and nitrophenols	river and spring water	fiber—cobalt (II)-based metal-organic nanotubes (Co-MONTs)	GC-MS	0.5–1000 ng/L	[59]—2017
ultraviolet filters	river and rain water	fiber—phenyl functionalization of titania nanoparticles	HPLC-UV	0.005–25 µg/L	[61]—2015
ultraviolet filters	river and rain water	fiber—gold nanoparticles	HPLC-UV	0.10–400 µg/L	[70]—2014
ultraviolet filters	river and rain water	fiber—silica nanoparticle	HPLC-UV	0.05–300 µg/L	[71]—2017

Table 1. *Cont.*

Analytes	Matrix	SPME Approach and Coating Material	Instrumentation	Calibration Range	[Ref] Publishing Year
ultraviolet filters	river water	IT-SPME—polyaniline coating	HPLC-DAD	0.06–100 µg/L	[62]—2017
ultraviolet filters	river water	fiber—oriented ZnO nanosheets	HPLC-UV	0.05–500 ng/mL	[63]—2019
ultraviolet filters	river water	fiber—nitrogen-enriched carbonaceous material	HPLC-UV	0.2–200 µg/L	[65]—2017
ultraviolet filters	river water	fiber—in situ fabricated rod-like TiO_2 coating	HPLC-UV	0.05–200 µg/L	[68]—2014
BTEX, organochlorine pesticides	sea, pond and river water	fiber—Prussian blue nanoparticles-doped graphene oxide	GC-MS	1–1000 ng/L, 2–2000 ng/L	[75]—2019
BTEX	pond and river water	fiber—tri-metal centered metal-organic frameworks (tM-MOFs)	GC-MS	5–2000 ng/L	[76]—2017
BTEX	lake and river water	fiber—graphene-carbon nanotubes composite	GC-MS	5–5000 ng/L	[77]—2018
BTEX	river water	fiber—porous organic polymers	GC-MS	2–500 ng/L	[79]—2017
BTEX and PAHs	pond and river water	fiber—microporous polymer	GC-MS	1–20,000 ng/L	[80]—2018
benzoylurea insecticides	river water	MMF-SPME—poly(methacrylic acid-co-ethylene dimethacrylate)	HPLC-DAD	0.10–200 µg/L	[82]—2015
endocrine disrupting	lake and river water	MMF-SPME—polymeric ionic liquid-based adsorbent	HPLC-UV	0.10–200 µg/L	[83]—2017
perfluoroalkane sulfonamides	lake and river water	MMF-SPME—polymeric material with boron	HPLC-MS/MS	0.0025–30.0 µg/L	[84]—2019
estrogens	lake and river water	magnetism-enhanced monolith-based in-tube IT-SPME—polymeric monolith with modified Fe_3O_4 nanoparticles	HPLC-DAD	0.5–200 µg/L	[85]—2016
non-steroidal anti-inflammatory drugs	river water	fabric phase sorptive extraction—poly(dime-thyldiphenylsiloxane); poly(tetrahydrofuran);	GC-MS	3–20,000 ng/L	[87]—2015
triazine herbicides	river water	Stir fabric phase sorptive extraction	UPLC-DAD	0. 26–1.50 µg/L	[89]—2015

Table 1. *Cont.*

Analytes	Matrix	SPME Approach and Coating Material	Instrumentation	Calibration Range	[Ref] Publishing Year
nitroaromatic Explosives	soil	fiber—quinoxaline-bridged cavitand	GC-MS	120–1200 ng/Kg	[92]—2014
PAHs	soil	fiber—nanoporous carbon derived from an aluminum- based MOF	GC-MS	0.1–12 µg/L	[95]—2015
PCBs	soil	fiber—different MOF networks	GC-MS	0.01–600 ng/L	[97]—2018
PCBs	soil	fiber—MOF MIL-88B	GC-MS	5–200 ng/L	[98]—2014
polybrominated diphenyl ethers	soil	fiber—Ag(I)-organic frameworks	GC-µECD	0.1–500 ng/g	[99]—2015
dimethylhydrazine	soil	fiber—Car/PDMS	GC-MS	0.5–2.5 mg/Kg	[100]—2018
1-methyl-1H-1,2,4-triazole	soil	fiber—PDMS/DVB	GC-MS	-	[102]—2015
DDE	soil	fiber—PDMS	GC-MS	-	[103]—2017
PCBs	soil	fiber—PDMS	GC-MS	-	[104]—2019
PAHs	soil	fiber—PDMS	HPLC-UV	-	[106]—2016
mercury	soil	ionic liquid coated PTFE tube	CV AAS	0.5–60 ng/mL	[108]—2014

3. The Spread Step: Food Matrices and Drinking Water

Chemical pollution of food is perceived as a global safety issue. Most times, the source of contaminants is the environment where the food has been produced. This is the situation of several organic substances coming from industrial processes or, in general, from human activities that persist in the environment and become globally dispersed in air and water sources, and therefore concentrate on fruits, vegetables, and animals through the food chain. Because of the type of contamination, some food products may be more contaminated than others owing to factors such as the specific exposure to pollutants or the differences in plant uptake systems from the ecosystem.

Food samples are complex matrices which often consist of compounds such as proteins, fats, acids, bases, and salts that can largely interfere with the analysis. Moreover, for solid foods, SPME is usually forerun by other previous extraction procedures to get an analyzable liquid extract.

3.1. Drinking Water

Intensive industrialization of the world has resulted in an increased input of organic pollutants, which may significantly affect the quality of surface waters that are often sources of drinking water for a large part of the world's population. Since most water contaminants are toxic and dangerous, not only to humans but also to animals and plants, these pollutants should be monitored in tap and surface waters. As with environmental water samples, microextraction techniques and in particular SPME have been giving a significant contribution to the determination of several contaminants in drinking water. Given the presence of drawbacks in the use of a traditional commercial coating, such as limited variety of the fibers available, insufficient thermal or solvent instability and limited selectivity, the greatest efforts have been made in the development of new coating materials to offer reliable analysis tools with better selectivity and sensitivity (Figure 4, Table 2).

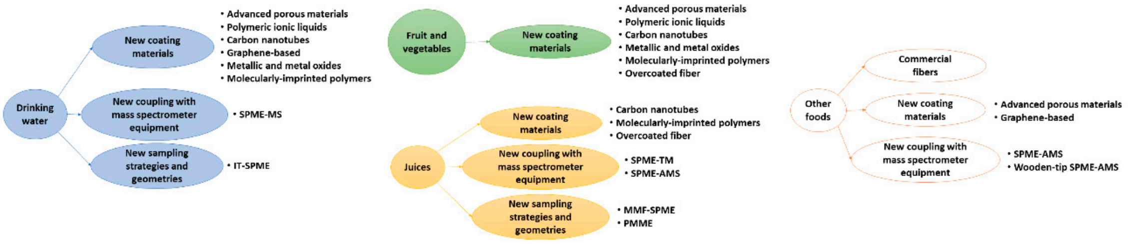

Figure 4. Main solid-phase microextraction geometries and strategies used in the analysis of food matrices during the covered period (2014–2019).

The use of carbon nanotubes (CNTs) has been exploited for the extraction of benzene derivatives [110,111], and phthalates [112] from drinking water samples. Owing to the carbon backbone provided by a two-dimensional structure with unique structural and chemical properties, CNTs are highly hydrophobic and mostly applied to extract hydrophobic analytes, through π-π stacking interactions. However, the surface of CNTs can be modified by chemical and physical functionalization to introduce different functional groups, resulting in enhanced dispersibility and accessible surface. In above-cited papers, CNTs have been combined with a polypyrrole/titanium oxide composite [111], multiwalled carbon nanotubes (MWCNT) functionalized with polyimidazolium ionic liquid was coated on an electrodeposited polyaniline film supported by a stainless-steel fiber [110], and MWCNTs on polystyrene (PS) microspheres have been designed and prepared by layer-by-layer assembly via electrostatic interaction [112]. In general, these coatings offered excellent thermal stability, high EFs and low LODs compared with other analytical methods. The MWCNTs composite microspheres could be of substantial scientific and technological interest with potential applications for the extraction of pollutants in environmental samples. Conductive polymers (CPs) have been also exploited as SPME coating for the extraction of contaminants from drinking water. In particular, thermal and mechanical stability of the polypyrrole-based SPME fibers have been evaluated for the analysis of haloanisoles in tap water [113] whereas polyaniline/silver (PANI/Ag) composites were prepared, and fabricated into SPME coatings for the extraction of bifenthrin from tap water and the following matrix-free laser desorption/ionization (LDI) of the target analyte [114].

Graphene, functional graphene materials or graphene composites have been successfully used as SPME coatings to detect various organic contaminants. In particular, several functionalized graphene coatings have been developed in order to enhance its extraction capacity and, above all, its selectivity for specific analytes. For example, hydroxy-terminated poly(ethylene glycol) (PEG) grafted onto graphene sheets was prepared via a covalent interaction and then PEG-g-graphene was coated on the etched stainless steel wire by a sol-gel process [115]. This coating was tested for the determination of volatile aromatic compounds (VACs) in tap and mineral waters. In another work, polyethylene glycol–graphene oxide (PEG–GO) sol-gel coating was successfully applied for the analysis of aromatic amines in aqueous samples as target compounds [116]. Due to the adsorptive and inherent advantages of GO nano-sheets as well as the performance of the sol-gel coating technology, this fiber exhibited a porous surface structure, good precision and accuracy, high selectivity and sensitivity, longer life span (over 200 uses) and high thermal stability. Similarly, graphene coatings have also found application in the IT-SPME for the determination of triazines [117,118]. In one case, a method was developed based on the use of a packed column containing graphene oxide supported on aminopropyl silica and following analysis by high performance liquid chromatography and tandem mass spectrometry (HPLC-MS/MS) [117], whereas in the other one a coated column was prepared by the covalent modification of monolayer graphene oxide sheets onto the inner wall of a fused-silica capillary [118]. Other porous carbons have been selected and developed as novel SPME coatings focusing on the two key factors for the choice of suitable porous carbons: surface area and pore structure. Li et al. proposed a C18 composite fiber, prepared with a new method and applied to the analysis of organochlorine pesticides (OCPs) in drinking water samples [119]. The prepared fiber showed excellent thermal stability, solvent resistance and extraction performance more than seven times higher than those of commercial fibers. Ordered mesoporous carbon film [120] and different activated carbon-polymer monoliths [120] were also used as a coating for the quantification of BTEX and phthalates in drinking waters, respectively.

MOFs are porous hybrid materials composed of metal ions at their center, and organic linkers. In the last years, they have become very popular as SPME coatings, due to the easy modification of their pore surfaces, which can lead to enhanced selectivity toward specific analytes. A wide variety of MOFs was proposed in the literature depending upon fiber format, the method used for assembling MOFs onto the fiber surface, the metal ion and ligand in the synthesis of MOFs. Metal-organic aerogel (MOA)/MIL-53(Fe) was fabricated by gluing them on a nichrome wire using silicone glue [121] and the resulting fiber was applied to the analysis of chlorobenzenes in tap water. In another application for the determination of chlorobenzene in HS mode, three types of MOFs with Zn and Cd as metal centers were synthesized with 4,4-biphenyldicarboxylate, terephthalic acid, and 2,6-naphthalene dicarboxylate as ligands [122]. MOF coatings were also prepared by using 2-aminoterephthalic acid and Al salts and termed MIL-53 (Al). These MOFs were employed for the extraction of organochlorine pesticides [123] and PAHs [95]. Experimental results showed that the NH_2-MIL-53(Al) SPME coating was solvent resistant and thermostable, and its efficiency for organochlorine pesticides was higher than that of commercially available SPME fiber coatings such as polydimethylsiloxane, polydimethylsiloxane-divinylbenzene, and polyacrylate. A sol-gel coating technique was applied for the preparation of a solid-phase microextraction fiber by coating the metal-organic framework UiO-67 onto a stainless-steel wire. The prepared fiber was explored for the HS-SPME of nitrobenzene compounds from tap water [124]. Again, the sol-gel technique was used for the preparation of fiber by coating MIL-101 onto stainless steel wires. The prepared fiber was explored for the HS-SPME of seven VACs [125]. Metal-organic nanotubes (MONTs) are a novel class of hybrid materials that bridge inorganic and organic nanotubes and possess the advantages of CNTs and MOFs. The study conducted by Li et al. investigates the feasibility of using $[Cu_3(\mu_3\text{-}O)(\mu\text{-}OH)(\text{triazolate})_2]^+$

MONTs (Cu-MONTs) as an SPME coating material to extract PCBs from water samples for GC-MS/MS detection [45]. The novel fibers achieved good thermal stability (~340 °C), high enhancement factors (396–1343), excellent repeatability (2.12–7.22%), wide linear ranges (0.1–500 ng/L) and low LODs (3.9–21.7 pg/L) for PCBs. A particular subfamily of MOFs, i.e., zeolitic imidazolate frameworks (ZIFs), was prepared in chemically resistant plastic microtubes for SPME on a polydopamine layer [126]. The extraction efficiency of ZIFs modified microtube was systematically investigated and more than 500-fold enrichment was obtained for analysis of PAHs in tap water.

Ionic liquids (ILs) seem to be an excellent alternative for the currently used SPME fiber sorptive materials, due to the change of their physical and chemical properties by the selection of appropriate ions. Several ILs-based SPME coatings have been prepared to achieve enhanced robustness and therefore a longer lifetime of fiber. A new stationary phase microextraction with physically fixed ionic ILs as sorptive coatings was proposed by Kang et al. for the determination of phosphorus flame retardants (PFR) in tap water [127]. Among the four ILs tested, the coating based on 1-octyl-3-methyloimidazole hexafluorophosphate demonstrated the best performances. Moreover, the prepared fiber has higher extraction capacity, better mechanical stability, lower cost, and comparable reproducibility compared with the commercially available SPME fibers. Several crosslinked polymeric ionic liquid (PIL)-based sorbent coatings of different natures were prepared for the determination of polar organic pollutants [128]. The PIL coatings contained either vinyl alkyl or vinyl benzyl imidazolium-based ($ViCnIm^-$ or$ViBCnIm^-$) IL monomers with different anions, as well as different dicationic IL crosslinkers. In the work proposed by Pena-Pereira et al., three bis(trifluoromethanesulfonyl)imide anion-based ILs were used to prepare ionogel fibers for the quantification of chlorinated organic pollutants [129]. Ionogels were a family of hybrid materials in which ionic liquids are confined in a sol-gel network. The ionogel based on 1-butyl-1methylpyrrolidinium bis(trifluoromethanesulfonyl)imide [C_4C_1Pyrr][TFSI] exhibited the best performances in terms of extractability of target analytes. Cross-linked PIL bucky gels were proposed by free-radical polymerization of polymerizable ionic liquids gelled with MWCNT [130]. The PIL bucky gel sorbent coatings demonstrated higher efficiency for the extraction of PAHs from tap water respect to the neat PIL-based sorbent coating, due to a significant enhancement of the π–π interaction between the sorbent coatings and the aromatic analytes. Neat crosslinked PIL sorbent compatible with high-performance liquid chromatography was proposed by Yu et al. [131]. Six structurally different PILs were crosslinked to nitinol supports and applied for the determination of phenols, and multiclass insecticides. Superior extraction performance compared to the other studied PILs was achieved by the PIL-based sorbent coating polymerized from the IL monomer 1-vinyl-3-(10-hydroxydecyl) imidazolium chloride [VC_{10}OHIM][Cl] and IL crosslinker 1,12-di(3-vinylbenzylimidazolium) dodecane dichloride [$(VBIM)_2C_{12}$] 2[Cl]. ILs were used as coatings also for the particular design of the capillary for IT- SPME system, called fiber-in-tube SPME. In particular, to improve the durability and extraction efficiency of an ionic liquid coating, 1-dodecyl-3-vinylimidazolium bromide was polymerized and grafted onto basalt fibers [132]. The tube was connected to an HPLC instrument and the system was applied to the extraction of phthalates from bottled water.

Another extensively exploited strategy in the development of new coating materials is the usage of metallic and metal oxides nanomaterials. For the analysis of drinking water, a palladium coating was fabricated on the SPME fiber by a simple in situ oxidation–reduction process to quantify PAHs and phthalates [133]. Moreover, new materials based on Co-Al bimetallic hydroxide nanocomposites [134] and gold nanoparticles [135] were proposed for fiber IT-SPME configuration in order to assay PAHs in tap water. Silica is another kind of inorganic material that has been widely used due to its features, such as the controllable morphology, excellent stability, and easy modification. VOCs were analyzed by ionogel fibers prepared by sol-gel processing using methyltrimethoxysilane as the silicon alkoxide precursor with the IL 1-methyl-3-butylimidazolium bis(trifluoromethylsulfonyl)imide ([C4MIM][TFSI]) confined within the hybrid network [136]. Enrichment factors in the range 275–7400 were obtained under optimum conditions. Remarkably, IL-rich SPME fibers yielded extractability up to 20-fold higher than that of the SPME fiber obtained after removal of the IL by solvent extraction. The very promising results obtained with ionogel fibers make us consider them as an excellent option for the preparation of advanced SPME coatings. Another silica-based material was used for the determination of chlorophenols [137]. In this work, the prepared continuous ordered mesoporous silica film supported on the anodized titanium wire demonstrated higher extraction efficiency toward the selected chlorophenols compared to the commercial PA fiber. Electrospinning is the most commonly used technique for the fabrication of SPME nanofibers from a wide range of materials. A polyetherimide (PEI) nanofibrous coating was prepared for the assay of PAHs, demonstrating a high filtration capacity and an increased extraction capacity for the analytes [138]. The applicability of inorganic oxide nanoparticles on the extraction efficiency of polyethylene terephthalate-based nanocomposites was evaluated by HS-SPME of BTEX [139]. Four types of nanoparticles including Fe_3O_4, SiO_2, CoO, and NiO were examined as the doping agents and, among them, the presence of SiO_2 in the prepared nanocomposite was prominent. BTEX were also analyzed by using sol-gel hybrid organic-inorganic materials prepared in the presence of polyethyleneoxide (PEO) non-ionic surfactants (Triton X-100) [140]. After the analytical procedure was optimized, the dynamic linear range obtained using PDMS-TX100 and PDMS-no TX100 fibers was 4–200,000 and 100–200,000 pg/mL and the limits of detection were 1–3 and 30–300 pg/mL, respectively. Molecularly imprinted polymers (MIPs) are typically synthesized from the copolymerization of a complex (the template and functional monomer), which can form recognition sites being able to rebind a target molecule. In recent years, MIPs have been prepared as monoliths by in situ polymerization directly within micro-columns or capillaries. Recently, several kinds of MIPs have been prepared and used as SPME coatings. For drinking water, a nanostructured molecularly imprinted fiber based on methyltriethoxysilane as the sol-gel precursor was prepared for the extraction of simazine [141]. Actually, SPME can also be coupled with MS directly without chromatographic separation, producing workflows that are not only more robust, sensitive, and selective, but also faster, cheaper, and cleaner. In 2016, Mirabelli et al. proposed a new strategy for the direct coupling of SPME with mass spectrometry, based on thermal desorption of analytes extracted on the fibers, followed by ionization with a dielectric barrier discharge ionization (DBDI) source [142]. The coupling of SPME with mass spectrometry reported in this study has several novel aspects. The work is the only one employing a thermal desorption of SPME fibers for a direct coupling with ambient ionization. This system has allowed to achieve LODs in the low-ng/L range for pesticides belong to various classes in tap water samples using the commercial PDMS/DVB fiber. The advantage over chromatographic approaches, in addition to the much shorter analytical procedure, is the absence of suppression effects from chromatography solvents. Finally, the small overall size of the setup could also allow one to perform in situ analyses with portable MS instruments.

3.2. Fruits and Vegetables

Fruits and vegetables, as a group of crops from the horticulture class, have very wide importance both as a source of food and health care. Fruits and vegetables are among the most studied food kind in terms of both nutritional principles and contaminants. Also for this food category, SPME has been contributing to the determination of several pollutants in various matrices. As for the water matrix, in the last five years, most of the studies have been focused on preparing new coating materials to be used instead of commercial fibers (Table 2).

A crosslinked PIL on a functionalized stainless steel wire through the oxidized MWCNT was fabricated by Feng et al. for the analysis of naphthol in pomelo and orange samples [143]. The following SPME extraction was carried out in multiple HS mode involving several consecutive extraction cycles of the same sample. The CNTs-based coating was also proposed for the determination of carbamate pesticides in apple and lettuce matrices [144]. In this work, a poly(3,4-ethylenedioxythiophene)-ionic liquid polymer functionalized multiwalled carbon nanotubes (PEDOT-PIL/MWCNTs) composite coating was fabricated which was successively dipped in Nafion solution. The outer layer Nafion enhances the durability and stability of the coating, being robust enough for replicated extraction for at least 150 times. Authors reported the direct GC analysis of carbamates without derivatization, in analogy to other studies [145,146]. Nanohybrids of CNTs/metal oxides have been applied to the determination of pollutants in vegetables. In particular, the synthesis of CNTs@SiO_2 nanohybrids with high surface area as an SPME coating was carried out and the obtained fiber was used for the assay of four organophosphorus pesticides in pear, grape, and eggplant [147]. The extracted compounds were detected using gas chromatography–corona discharge ion mobility spectrometry (GC-CD-IMS), demonstrating that the developed CNTs@SiO_2 fiber presented better extraction efficiency than the commercial SPME fibers (PA, PDMS, and PDMS/DVB). The same instrumental approach was employed for the analysis of organophosphorus pesticides in cucumber, lettuce, and apple by extracting the analytes with a polypyrrole/montmorillonite nanocomposites coating directly deposited on a Ni-Cr wire [148]. Polypyrrole/montmorillonite nanocomposites film provided a high specific surface due to non-smooth porous structure, resulting in the higher loading capacity and thermal stability. A comparison of the prepared fiber with commercial fibers revealed that the fabricated fiber has higher extraction efficiency for the extraction of OPPs relative to commercial PDMS and PDMS/DVB fibers and pure Ppy. Polypyrrole was also considered for the fabrication of polypyrrole nanowire (PPy NW) which was utilized for the quantification in headspace mode of bisphenol A in canned beans, corn, and peas [149]. The developed protocol involves the detection of the analyte by ion mobility spectrometry (IMS) without chromatographic separation. In a work based on MIP coating, an SPME fiber was developed on silica fiber via sol-gel using calixarene as a functional monomer for extraction of organophosphorus pesticides from apple and pineapple samples [150]. A comparison of MIP-SPME was made with liquid-liquid extraction coupled with gas chromatography demonstrating that much lower limits of detection and better recoveries were achieved by the SPME approach. The porous carbon can be directly obtained by the carbonization of different materials to achieve higher surface area and more abundant pores. In the work carried out by Liang et al., the carbon precursor was a barley husk biomaterial [151]. The obtained carbon was coated onto a stainless-steel wire through the sol-gel technique to prepare a solid-phase microextraction fiber for the extraction of trace levels of twelve multiclass pesticides from vegetable samples. COFs are analogs of metal-organic frameworks without metal in their structure. Wu et al. have designed a novel hydrazone COF and developed a polydopamine (PDA) based method to immobilize COF on a stainless steel fiber for carrying out the HS-SPME quantitative analysis of pyrethroids in apple and cucumber samples [152]. The authors ascribe the very satisfactory performances of this new coating firstly to hydrophobic nature of COFs and, secondly, to the fact of the hydrazone COF possesses abundant phenyl rings and –C=N groups, which provide strong π-π stacking interaction with pyrehroids. In another study reported by the same group, cross-linked hydrazone COFs were prepared via the thiol-ene “click” reaction and applied for the extraction of pesticides in cucumber [153]. The comparison of the cross-linked hydrazone COFs-based fiber with PDMS (7, 85, 100 μm), Car/PDMS, and PA fibers demonstrated that the extraction efficiency of the new coating is superior respect to commercial ones.

MOFs represent a suitable material as SPME coatings also in combination with graphene oxide. In particular, a hybrid material of the zinc-based metal-organic framework-5 and graphene oxide was prepared as a novel fiber coating material and the prepared fiber was used for the extraction of five triazole fungicides from grape, apple, cucumber, celery cabbage, pear, cabbage, and tomato samples [154]. This new fiber was stable enough for 120 extraction cycles without a significant loss of extraction efficiency. The same authors prepared a new coating material, a zeolitic imidazole framework-67 (ZIF-67) templated nanoporous carbon, Co-NPC, by one-step direct carbonization of ZIF-67 without using any other carbon precursors [155]. Successively, the SPME fiber prepared by coating the Co-NPC onto a functionalized stainless-steel wire was used for the determination of five organochlorine pesticides.

ILs, as stable coating compounds in SPME, were also employed together with other materials. For the analysis of vegetable samples, a new ionic liquid 1-vinyl-3-butylimidazolium ditrifluoro methyl sulfimide -calixarene coated fiber has been synthesized on the surface of quartz fiber by the sol-gel method [156]. The fiber was then applied to the assay of triazines in garlic sprout, cherry tomato, strawberry, cole, cabbage, cucumber, and tomato. Although potato is a common food in many countries and, as a consequence, is extensively studied [157], only one study is reported about the determination of contaminants in this matrix [158]. In this application, graphene oxide was firstly chemical-bonded on the support and then the novel 1-aminoethyl-3-methylimidazolium bromide ($C_2NH_2MIm^+Br^-$) or polymeric 1-vinyl-3-hexylimidazolium bromide (poly($VHIm^+Br^-$)) was assembled to the surface of GO by surface radical chain-transfer reaction, respectively. Afterward, $C_2NH_2MIm^+NTf_2{}^-$-GO-coated and poly($VHIm^+NTf_2{}^-$)-GO-coated fibers were obtained through on-fiber anion exchange. Extraction performance of ILs and PILs coatings with different anions were investigated with PAHs and PAEs as the model analytes. Finally, the proposed poly($VHIm^+NTf_2{}^-$)-GO-SPME fiber was used to determine several PAHs and phthalates in potatoes and food-wrap samples, respectively.

The metal oxides can be hybrid with organic/inorganic materials, leading to higher extraction efficiency and great convenience for the coating preparation. A biocompatible environmentally friendly SPME fiber coating (halloysite nanotubes-titanium dioxide (HNTs-TiO_2)) was prepared by Saraji et al. [159]. HNTs-TiO_2 was chemically coated on the surface of a fused-silica fiber using a sol-gel process and the fiber was evaluated in the determination of parathion in apple, strawberry, and celery. The HNTs-TiO_2 fiber was compared in terms of extraction efficiency with bare-silica (sol-gel based coating without HNTs-TiO_2), HNTs, carbon nanotubes and commercial SPME fibers (PA, PDMS, and PDMS-DVB). The HNTs-TiO_2 fiber showed the highest extraction efficiency among the studied fibers. In another application, zinc oxide hybridized with graphite-like C_3N_4 (ZnO/g-C_3N_4) nanoflowers based SPME coating was fabricated [160]. This fiber was successfully used for the simultaneous determination of nine pesticides in cucumber, pear, and green tea. The high extraction performance of ZnO/g-C_3N_4 nanoflowers fiber towards the pesticide residues may be due to its high dispersion in solution and to the pesticide hydrogen bonding interaction force and the π-π stacking interaction force between the analytes and the organic linker of the ZnO/g-C_3N_4.

Recently, a new matrix-compatible fiber was developed by Pawliszyn and coworkers by modification of the solid coating of a commercial SPME fiber with a thin layer of polydimethylsiloxane [161]. In particular, the outer PDMS layer was employed to protect the polydimethylsiloxane/divinylbenzene (PDMS/DVB), thereby merging the proven suitability of PDMS for sampling in complex matrixes and the extraction capability associated with the original solid porous coating. In the last five years, this fiber was tested for the determination of pesticides and contaminants in various fruits and vegetables in direct immersion mode [162–164]. In an application of DI-SPME for the extraction of multiclass pesticides and other contaminants in the avocado pulp, the polydimethylsiloxane-divinylbenzene-polydimethylsiloxane (PDMS/DVB/PDMS) compared to the DVB/PDMS coating, showed excellent robustness and matrix compatibility for oily matrices [162]. The optimized extraction conditions involving dilution of avocado puree with water and cleaning steps pre- and post-desorption extended the coating lifetime, with enhanced reproducibility for more than 100 consecutive extraction cycles. The robustness and endurance of this new coating were evaluated for analyses of vegetables (i.e., spinach, tomato, and carrot) that present different analytical challenges such as pigmentation, water content, interfering matrix compounds, and vegetable texture [163]. Multiclass pesticides and other contaminants were selected as target analytes to test PDMS/DVB/PDMS fiber in new challenging analytical scenarios. The PDMS/DVB/PDMS fiber was shown to be suitable for use for more than one hundred extractions in raw blended vegetable samples. Moreover, the overcoated fiber was revealed to provide advancements not only in terms of robustness and durability, but also in cleanability and sensitivity in respect to the commercial coating (Figure 5).

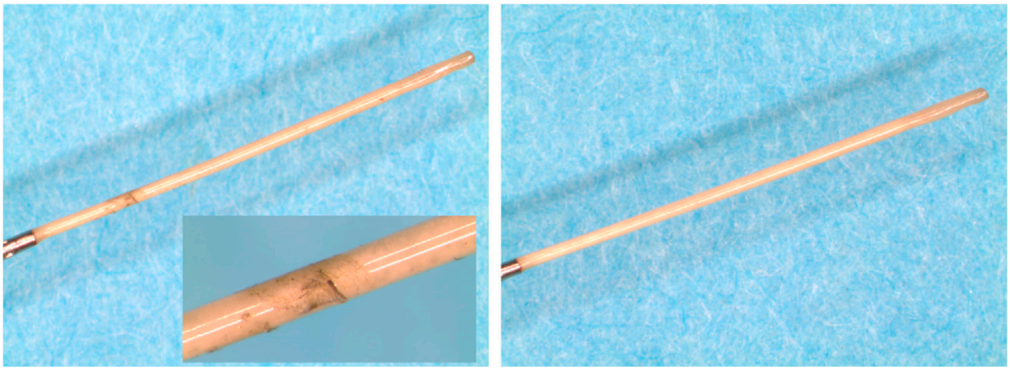

Figure 5. PDMS/DVB/PDMS fiber lifetime evaluation in spinach: stereomicroscope images of the fiber before (**left**) and after (**right**) manual cleaning of the coating [163].

In another application, a method for the determination of 40 pesticides, belonging to 21 different classes, was optimized for extractions from the grape pulp by means of Design of Experimental (DoE), using the matrix compatible PDMS/DVB/PDMS coating in direct immersion mode [164]. In the broad area of chemometrics, which plays an important role in many scientific disciplines [165–167] experimental design is a multivariate approach to achieve the optimization of a procedure by evaluating the factors simultaneously. The following instrumental analysis was carried out by GC-ToFMS. Commercial PDMS fiber was used by Abdulra'uf et al. for the assay of pesticides belong to various classes in apple, tomato, cucumber, and cabbage [168]. In this study, the authors proposed the sonication of samples for 5 min prior to HS-SPME extraction in order to improve the partition of the targeted analytes into the sample headspace.

3.3. Juices

Juices are also among the most analyzed food commodities by SPME for safety assessment. A CNTs-based coating was prepared for in-tube and glass capillary SPME configurations [28,169]. In the first work, IT-SPME directly coupled with DART-MS has been reported [28] and applied to the determination of triazine herbicides in orange juice samples. The extraction device consisted of a syringe barrel coupled to one end of the syringe pinhead. A capillary column replaced the other end of the pinhead. This method greatly improved the detection sensitivity, compared with the offline mode, because the majority of the desorption solvent was introduced into DART-MS for detection. The limits of detection (LODs) of the proposed method for the six triazine herbicides were only 0.02–0.14 ng/mL, and the negative matrix effect was minimized due to the IT-SPME procedures. In the study reported by Wang et al. a polymer monolith microextraction (PMME) procedure coupled to plasma-assisted laser desorption ionization mass spectrometry (PALDI-MS) was developed [169]. The extraction device used a "Dip-it" sampler coated with an MWNT incorporated monolith, and laser effectively desorbed the triazines adsorbed on monoliths. In another two works, the direct interface of microextraction technologies to mass spectrometry (SPME-transmission mode, SPME-TM) was proposed and applied to the analysis of multiclass pesticides in various matrices such as grape juice, orange juice, cow milk, and surface water [27,170]. These studies demonstrated the great potential of SPME-TM as a tool for fast concomitant screening and quantitation of agrochemicals in complex matrices. Limits of quantitation in the sub-nanogram-per-milliliter range were attained and the total analysis time did not exceed 2 min per sample [27]. Moreover, it was demonstrated the suitability of SPME-TM for on-site semi-quantitative analyses of target analytes in complex matrices via DART coupled to portable mass spectrometry [170].

In another application, a poly(methacrylic acid-co-ethylene dimethacrylate) monolith was prepared and used as the sorbent of multiple monolithic fiber solid-phase microextraction (MMF-SPME) [82]. The combination of MMF-SPME with high-performance liquid chromatography-diode array detection (MMF-SPME-HPLC-DAD) showed good analytical performance for the quantification of five benzoylurea insecticides in grape and orange juice samples. HPLC-UV was also used for the analysis of parabens in orange, lemon, and peach juices, milk, and waters after the extraction by an in-tube fiber with a nanostructured polyaniline-polypyrrole composite as a coating [171]. Under the optimized conditions, part-per-trillion (ppt) level detection limits were achieved for the analytes. Besides, shorter sample analysis time, more accurate quantification, and satisfactory reproducibility were achieved by in-tube SPME-HPLC, which are favorable for routine analysis of the parabens in various matrices.

Molecularly imprinted fibers were prepared by de Souza Freitas et al. to extract triazole fungicides from grape juice samples followed by gas chromatography-mass spectrometry analysis [172]. This coating, synthesized from methacrylic acid, ethylene glycol dimethacrylate, and triadimenol as a template, is able to renew its selective binding sites because of the gradual thermal decomposition of the polymeric network.

A novel hybrid material incorporating porous aromatic frameworks and an ionic liquid, 1-triethoxy silyl)-propyl-3-aminopropyl imidazole hexafluorophosphate, was developed and applied to the analysis of organochlorine pesticides in apple juice, peach juice, and milk [173]. These materials, prepared in general by combining gel and ionic liquids, are made up of highly conjugated repeating aromatic monomers that involve a strong enrichment ability for benzene homologs. The work reported by Pelit et al. describes the novel usage of polythiophene–ionic liquid modified clay surfaces for fiber production and the following application to the analysis of multiclass pesticides in grape juice samples [174]. Among the fibers developed, the polythiophene fiber co-deposited with C12mimBr modified clay has given the best results in terms of recoveries and sensitivities.

The metal-oxide coating was used also for fruit juice analysis. In the study published by Vinas et al. was described the use of magnetic nanoparticles of cobalt ferrite, with oleic acid as the surfactant ($CoFe_2O_4$/oleic acid) for the determination of alkylphenols in orange, pineapple, apple, peach, and grapefruit juices [175]. This demonstrated that appropriate modification of the magnetic core with oleic acid as a surfactant is useful for overcoming some limitations such as the chemical stability and oxidation of magnetic nanoparticles.

Forty pesticides pertaining to various classes were determined by a fast and sensitive direct immersion–solid-phase microextraction gas chromatography time-of-flight mass spectrometry (DI-SPME-GC-ToFMS) method in grapes employing a PDMS/DVB/PDMS fiber (i.e., PDMS-overcoated fiber) [164]. The validated method yielded good accuracy, precision, and sensitivity. With regard to the limitations of the proposed approach, the DI-SPME method did not provide a satisfactory performance toward more polar pesticides and highly hydrophobic pesticides, such as pyrethroids. The PDMS/DVB/PDMS coating was successfully used for the quantitative determination of multiclass pesticides in grape juice by direct coupling to mass spectrometry through dielectric barrier discharge ionization (DBDI) [176]. The use of a matrix compatible SPME coating is critical especially when a direct-MS analysis is carried out for complex food matrices since the occurrence of matrix effects is drastically minimized or avoided. Moreover, the throughput of the analytical procedure is extremely high, since no matrix pre-treatment is necessary due to the anti-fouling properties of the SPME coating used.

3.4. Other Foods

Various contaminants were determined by SPME technique in other food commodities (Table 2), such as milk [29,177–182], fish [183–187], honey [188–190], tea [191–193], coffee [194,195], oil [196,197], butter [198], rice [199], chili [166,200,201], and seaweeds [202]. In particular, in milk SPME has been exploited in different coatings. The MOF-based coating was prepared for the analysis of bisphenol A [177], commercial fibers were used to assay organochlorine pesticides [178] and PAHs [179], whereas graphene-based fiber was fabricated for the determination of PCBs [180]. A very interesting approach for the analysis of contaminants in complex matrices was developed by Deng et al. [29]. In this work, a surface coated wooden tip was proposed and realized for the first time to form a novel SPME probe that was used for a new SPME and ambient mass spectrometry hyphenated strategy. The proposed SPME-AMS method was applied to the direct ultra-trace analysis of perfluorinated compounds which has been recognized as one of the hot research topics in recent years [203,204].

Analysis of several pollutants (i.e., PAHs, anesthetics, trihalomethanes, furan, organophosphorus pesticides, personal care products, PCBs) in fish was carried out by the conventional ex vivo SPME extraction by using various coatings [185–187] and by the in vivo SPME approach. In vivo SPME is introduced as a low-invasive technique that utilizes biocompatible probes and has been used in a number of animal studies, and the results have shown that it is capable of extracting trace endogenous components from a living system [205,206]. In the last five years, in vivo SPME was applied to the analysis in living fish of benzo[a]pyrene in order to examine cellular responses to BaP exposure [183] and of anesthetics by using a biocompatible custom PDMS fiber [184].

One of the strategies of coupling SPME with ambient mass spectrometry is the surface desorption/ionization of analytes from SPME for AMS. One of the reported ambient ionization techniques coupled with SPME via this strategy is the desorption corona beam ionization (DCBI) [207]. SPME coupled with DCBI is performed by placing an SPME in the stream position of reactive species, and the analytes enriched on SPME was directly desorbed/ionized after the reactive species impacted on the surface of SPME. The reported SPME coupled with DCBI-MS methods were based on thin-film microextraction (TFME). This configuration was proposed by Chen et al. for the determination of Sudan dyes (I-IV) and Rhodamine B in chili oil and chili powder [200]. A small piece of commercial carbon nanotube film was used for the extraction of 1 mL of the sample solution. After extraction, the carbon nanotube film was attached to the front end of a glass capillary, and then transferred to the visible plasma beam of the DCBI source for surface desorption/ionization of the enriched analytes for MS analysis. In another application, the coupling of SPME with ambient mass spectrometry was again proposed for the analysis of Sudan dyes in chili powder [201]. In this case, a bifunctional monolith dip-it, prepared by in situ polymerization of poly(BMA–EDMA–MAA) monolith in the glass capillary of dip-it, was used as an SPME device for direct analysis in real-time mass spectrometry (DART-MS). This sample loading device showed a strong affinity to four Sudan dyes through hydrophilic interaction and hydrogen bond interaction and could be directly analyzed by DART-MS without organic solvent elution or laser desorption.

Table 2. Selected SPME applications in food matrices.

Analytes	Matrix	SPME Approach and Coating Material	Instrumentation	Calibration Range	[Ref] Publishing Year
benzene derivatives	tap water	fiber—PANI-PIL/MWCNTs	GC-FID	0.05–250 µg/L	[110]—2015
BTEX	tap water, mineral water	fiber—polypyrrole/CNT/TiO_2	GC-FID	0.03–500 µg/L	[111]—2015
aromatic amines	tap water	fiber—poly(ethylene glycol)–graphene oxide	GC-FID	1–2000 ng/L	[116]—2015
triazines	mineral water	IT-SPME—graphene oxide	HPLC-MS/MS	0.2–4 µg/L	[117]—2018
triazines	tap water	IT-SPME—GO	LC-MS/MS	5–500 ng/L	[118]—2015
PAHs	tap water	IT-SPME—zeolitic imidazolate framework (ZIF)—ZIF-8	HPLC-FLD	0.01–5 µg/L	[126]—2015
phenols, multiclass insecticides	tap water	fiber—PIL-1-vinyl-3-(10-hydroxydecyl) imidazolium chloride [VC_{10}OHIM][Cl]	HPLC-UV	1–500 µg/L	[131]—2016
phthalates	bottle water	IT-SPME—1-dodecyl-3-vinylimidazolium bromide	HPLC-DAD	0.03–12 µg/L	[132]—2018
PAHs	tap water	IT-SPME—Co-Al bimetallic hydroxide nanocomposites	HPLC-DAD	0.003–15 µg/L	[134]—2018
PAHs	tap water	IT-SPME—gold nanoparticles	HPLC-DAD	0.01–20 µg/L	[135]—2018
VOCs	tap water, mineral water	fiber—hybrid silica-based material with IL 1-methyl-3-butylimidazolium bis(trifluoromethylsulfonyl)imide ([C4MIM][TFSI])	GC—barrier ionization discharge (GC-BID)	0.025–75 µg/L	[136]—2014
chlorophenols	tap water	fiber—Ordered mesoporous silica (OMS)	GC-FID	0.2–200 µg/L	[137]—2017
PAHs	tap water	fiber—polyetherimide	GC-MS	0.005–1.2 µg/L	[138]—2014
BTEX	tap water	fiber—polyethylene terephthalate nanocomposites	GC-MS	0.01–1 µg/L	[139]—2015
BTEX	tap water, mineral water	fiber—PDMS-TX100	GC-FID	0.004–200 µg/L	[140]—2014
multiclass pesticides	tap water	fiber—PDMS/DVB	MS—dielectric barrier discharge ionization (DBDI)	0.01–30 µg/L	[142]—2016

Table 2. *Cont.*

Analytes	Matrix	SPME Approach and Coating Material	Instrumentation	Calibration Range	[Ref] Publishing Year
parabens	tap water, milk, juice	in-tube—polyaniline–polypyrrole composite	HPLC-UV	0.07–50 µg/L	[171]—2015
furan	tap water, canned tuna	fiber—MIP with pyrrole as template	GC-MS	0.5–100 µg/L	[186]—2016
benzoylurea insecticides	orange juice, grape juice	fiber—poly(methacrylic acid-co-ethylene dimethacrylate)	HPLC-DAD	0.5–200 µg/L	[82]—2015
multiclass pesticides	fruit juices	fiber—polythiophene-ionic liquid-Montmorillonite (PTh-IL-Mmt)	GC-ECD	0.5–10 µg/L	[174]—2015
multiclass pesticides	grape juice	fiber—PDMS/DVB/PDMS	DBDI-MS	0.5–100 µg/L	[176]—2018
alkylphenols	fruit juices	magnetic dispersive—$CoFe_2O_4$/oleic acid	LC-DAD-MS/MS	16–200 µg/L	[175]—2016
triazine herbicides	orange juice	in tube—poly(MAA-EDMA-SWNT)	DART-MS	0.1–50 µg/L	[28]—2014
triazoles	grape juice	fiber—MIP	GC-MS	100–2000 µg/L	[172]—2014
multiclass pesticides	grape juice, orange juice, cow milk	mesh—HLB/PAN	DART/MS	0.1–100 µg/L	[27]—2017
multiclass pesticides	grape juice, milk	mesh—HLB/PAN	DART/MS	5–500 µg/L	[170]—2017
organochlorine pesticides	juice, milk	fiber—PAF/IL	GC-ECD	1–500 µg/L	[173]—2016
bisphenol A	milk	fiber—$(Et_3NH)_2Zn_3(BDC)_4$ (E-MOF-5)	HPLC-SPD	1–200 µg/L	[177]—2016
PAHs	milk	home-made PDMS fiber	GC-MS	0.1–5 µg/L	[179]—2016
PCBs	milk	fiber—MoS_2/RGO	GC-MS	0.25–100 µg/L	[180]—2017
PCBs	milk	fiber—PIL 1-vinylbenzyl-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide [VBHDIM] [NTf_2]	GC-MS	2.5–100 ng/L	[181]—2014
perfluorinated compounds (PFCs)	milk	surface coated wooden-tip probe—n-octadecyldimethyl [3-(trimethoxysilyl)propyl]ammonium chloride	Orbitrap MS	0.5–100 ng/L	[29]—2014

Table 2. *Cont.*

Analytes	Matrix	SPME Approach and Coating Material	Instrumentation	Calibration Range	[Ref] Publishing Year
2-naphthol	pomelo and orange	fiber—MWCNTs-PILs	GC-FID	0.5–5000 µg/Kg	[143]—2014
carbamate pesticides	apple, lettuce	fiber—IL/CNT	GC-FID	0.05–250 µg/Kg	[144]—2016
organophosphorus pesticides	pear, grape, eggplant	fiber—CNTs@SiO_2	GC–corona discharge ion mobility spectrometric detection	0.5–15 µg/Kg	[147]—2016
organophosphorus pesticides	cucumber, lettuce, apple, tap water	fiber—polypyrrole/montmorillonite nanocomposites	GC-CD-IMS	0.05–10 µg/Kg	[148]—2014
BPA	canned beans, canned corn, canned peas	fiber—polypyrrole nanowire	ion mobility spectrometry	10–150 µg/Kg	[149]—2016
organophosphorous pesticides	fruits	fiber—molecularly imprinted polymer (MIP) with calixarene as template	GC-NPD	0.2–1000 µg/Kg	[150]—2016
multiclass pesticides	vegetables	fiber—Barley husk carbon	GC-MS	0.2–75 µg/Kg	[151]—2017
pyrethroids	vegetables, fruits	fiber—COF-PDA	GC-ECD	1–1000 µg/Kg	[152]—2016
organochlorine pesticides	cucumber	fiber—Covalent organic frameworks (COF)	GC-ECD	0.008–800 ng/kg	[153]—2016
triazole fungicides	vegetable, fruit	fiber—MOF-5/GO hybrid composite	GC-µECD	0.17–500 µg/Kg	[154]—2016
Organochlorine pesticides	vegetables	fiber—ZIF-67	GC-µECD	0.30–50 µg/Kg	[155]—2016
triazines	fruits, vegetables	fiber—ionic liquid (IL)-calixarene	GC-FID	25–5000 µg/Kg	[156]—2014
PAHs	potatoes	fiber—Bis(trifluoromethanesulfonyl)imide-based ionic liquids grafted on graphene oxide	GC-FID	0.05–50 µg/Kg	[158]—2016
parathion	apple, strawberry, celery	fiber—Halloysite nanotubes-titanium dioxide (HNTs-TiO_2)	negative corona discharge-ion mobility spectrometer	0.1–25 µg/Kg	[159]—2016
multiclass pesticides	cucumber, pear, green tea	fiber—C_3N_4 (ZnO/g-C_3N_4)	GC-MS	3–5000 ng/Kg	[160]—2016

Table 2. *Cont.*

Analytes	Matrix	SPME Approach and Coating Material	Instrumentation	Calibration Range	[Ref] Publishing Year
multiclass pesticides and contaminants	avocado puree	fiber—PDMS/DVB/PDMS	GCxGC-ToF/MS	-	[162]—2017
multiclass pesticides and contaminants	spinach, tomatoes, carrots	fiber—PDMS/DVB/PDMS	GC-MS	-	[163]—2016
multiclass pesticides	grapes	fiber—PDMS-modified PDMS/DVB	GC-ToFMS	1–1000 µg/Kg	[164]—2015
multiclass pesticide	fruits, vegetables	fiber—PDMS	GC-MS	1–500 µg/Kg	[168]—2015
Benzobenzo[a]pyrene	living fish	fiber—mixed-mode/PAN	LC-MS	-	[183]—2018
anesthetics	living fish	fiber—custom-made PDMS	GC-MS	10–5000 µg/Kg	[184]—2017
trihalomethanes	fish	fiber—DVB-CAR-PDMS	GC-ECD	0.35–8 µg/Kg	[185]—2017
PCBs	fish	SBSE—magnetic metal-organic frameworks—Fe_3O_4-MOF-5(Fe)	GC-MS	0.01–500 µg/Kg	[187]—2015
sudan dyes (I, II, III and IV), Rhodamine B	chili oil, chili powder	film—carbon nanotube	desorption corona beam ionization (DCBI)	100–20,000 µg/Kg	[200]—2015
Sudan dyes	chili powder	glass capillary—poly(BMA–EDMA–MAA)	DART-SVP-ToF MS	20–2000 µg/Kg	[201]—2016
PAHs, PCBs and pesticides	edible seaweeds	fiber—PDMS/DVB/PDMS	GC-MS	5–2000 µg/Kg	[202]—2018
triazine herbicides	vegetable oils	magnetic dispersive—1-hexyl-3-methylimidazolium tetrachloroferrate ([C_6mim] [$FeCl_4$]	HPLC-UV	5–1000 µg/L	[197]—2014
phthalates	drinking water, edible vegetable oil	fiber—graphene/polyvinylchloride	GC-FID	0.3–100 µg/L	[196]—2016
sulfonamides	butter	magnetic bar—1-octyl-3-methylimidazolium hexafluorophosphate ([C_8MIM][PF_6^-]	HPLC-UV	6–300 µg/Kg	[198]—2015
PAHs	smoked rice	hollow fiber—MWCNTs	GC-FID	0.02–1000 µg/Kg	[199]—2014

Table 2. *Cont.*

Analytes	Matrix	SPME Approach and Coating Material	Instrumentation	Calibration Range	[Ref] Publishing Year
phenols	honey	fiber—SNW-1	GC-MS	0.1–100 µg/Kg	[188]—2016
organochlorine pesticides, PAHs, PCBs	honey	fiber—PDMS	GC-MS/MS	10–3000 µg/Kg	[189]—2017
phenols	honey	fiber—COF-SNW-1	GC-MS	0.1–100 µg/Kg	[188]—2016
benzoylurea	honey, tea	dispersive ionic liquid (IL)-modified β-cyclodextrin/attapulgite (β-CD/ATP)	HPLC-DAD	5–500 µg/L	[190]—2016
phthalates	tea	fiber—C-NH_2-MIL-125	GC-MS	0.05–30 µg/L	[191]—2016
dicofol residues	tea	magnetic dispersive—magnetic molecular imprinted microspheres with DDT as template	GC-ECD	0.2–160 µg/L	[192]—2014
PAHs	tea	film—agarose-chitosan-C_{18}	HPLC-UV	1–500 µg/L	[193]—2017
acrylamide	brewed coffee and coffee powder	fiber—nine crosslinked PIL based coatings	GC-MS	0.5–200 µg/Kg	[194]—2016
phthalates	coffee	fiber—crosslinked PIL-based nitinol	GC-MS	-	[195]—2014

4. The Final Endpoint: Bio-Clinical Matrices

Human biomonitoring (HBM), that is the measurement of chemical and/or their metabolites in human tissues and fluids, is a significant means for assessing cumulative exposure to complex mixtures of chemicals and for monitoring chemical hazards in the population. It is also important for understanding the health effects of environmental pollutions and public susceptibility to these compounds. HBM can be used in epidemiological studies in combination with other medical data to show an association between the body burden of pollutants and their consequences on humans [208]. Besides, HBM is a powerful tool for tracking the effectiveness of public health interventions, such as, for example, restrictions on smoking in public places [209]. Considering its usefulness to perform an integrated assessment of environmental exposure, there is increasing awareness for HBM in developed countries that have already started national programs to improve the prevention of disease, injury, and harmful exposures in populations [209]. For these important screening programs, to develop simple, rapid, and reliable methods to quantify the markers of exposure in human body tissues and fluids represents an essential goal. Moreover, it is very necessary to realize automated procedures entailing the benefit of using a small quantity of toxic chemicals, which are not friendly to the environment. In this sense, microextraction approaches can provide a significant contribution to achieving this aim. In fact, many protocols developed in recent years involved the use of microextraction techniques, mainly SPME (Figure 6, Table 3).

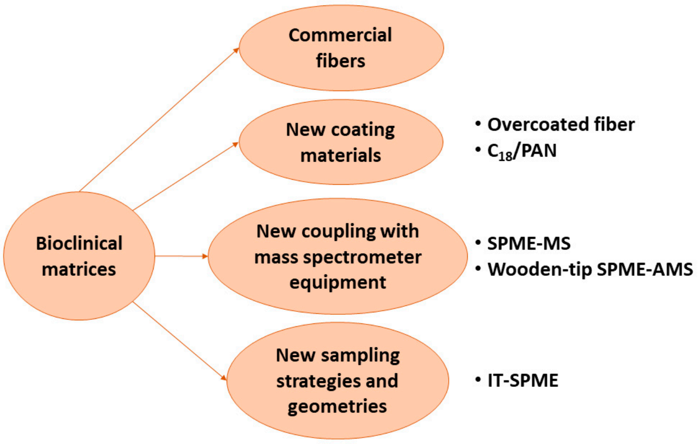

Figure 6. Main solid-phase microextraction geometries and strategies used in the analysis of bio-clinical matrices during the covered period (2014–2019).

Generally speaking, urine is undoubtedly the preferred matrix among the analyzed biological fluids because of its greater biological half-life and its less invasive sampling. This trend is confirmed in the last lustrum since most of the published works on this topic have been directed, as well as to the assay of markers of several pathological conditions [210–212], toward the determination of several contaminants in urine samples [14,74,83,213–219]. Few studies focused on hair [220–222], three papers were published about analysis in blood/serum [29,223,224], and one regarding meconium [225]. Some studies reporting the application of SPME for the analysis of urine have employed commercially available coatings such as Car/PDMS [214,216], PDMS/DVB [215], PDMS [217], and PA [14] for the extraction and further analysis of different contaminants such as VOCs [214,216], aromatic amines [215], organochlorine pesticides [217], and benzothiazoles, benzotriazoles, benzosulfonamides [14]. In all these works, except that regarding the analysis of the polar compounds benzothiazoles, benzotriazoles, benzosulfonamides, SPME was applied in headspace mode in order to minimize the coextraction of matrix interferences and extend the lifetime of employed coatings. In the DI-SPME application proposed by Naccarato et al. a six-fold dilution of urine sample was carried out to avoid the degradation of polyacrylate coating [14]. In another study by Naccarato et al., the overcoated fiber (i.e., PDMS/DVB/PDMS) was evaluated as an analytical sampling tool for the first time in human urine and urinary polycyclic aromatic hydrocarbons with 2–6 aromatic rings were considered as target compounds [74]. The satisfactory results achieved in terms of the lifetime of coatings and validation parameters created not only new alternatives for polycyclic aromatic hydrocarbon exposure assessment but also opened new perspectives for the application of direct immersion solid-phase microextraction to the analysis of bio-clinical matrices. As for food analysis, various coatings were proposed for the analysis of urine, such as C_{18}/PAN [213], layered double hydroxide/graphene (LDH-G) [218], inorganic-organic hybrid nanocomposite [219], and cross-linked PIL [83] for the determination of hydroxylated PAHs as metabolites of PAHs [213,219], organochlorine pesticides [218], and endocrine-disrupting chemicals [83]. In the study proposed by Yang et al. [213], an improved low-cost direct SPME-MS technique with glass capillary was further developed for the determination of five typical OH-PAHs in urine samples using a C18-SPME fiber, which then was inserted into a prefilled glass-capillary with spray solvent to generate ions for MS analysis.

Human hair as an indicator in assessing exposure to organic pollutants is less considered than urine. Recently, PAHs [221], multiclass pesticides, DDTs and PCBs [220,222] were determined in hair by commercial PDMS/DVB fiber [220,222] and a CP-Sil 19CB-based in-tube fiber [221].

As regards other biological fluids, the coupling of SPME with ambient mass spectrometry using a surface coated wooden-tip probe proposed by Deng for the analysis of PFCs in milk samples and already cited in the food section [29] was also employed for the analysis in whole blood. For this matrix, the porous structural surface together with the dual extraction mechanisms demonstrated that the SPME probe has an outstanding enrichment capacity, enhancing sensitivity by approximately 100–500 folds. In another application regarding the analysis in serum, a novel mesoporous graphitic carbon nitride@$NiCo_2O_4$ nanocomposite-based fiber was prepared and used for sensitive determination of PCBs and PAHs in headspace mode [224], whereas the commercial PDMS fiber was employed in order to analyze organochlorine pesticides and PCBs levels again in headspace mode [223]. To investigate fetal exposure to volatile organic compounds, a method was developed to identify and quantify BTEX and two chlorinated solvents (trichloroethylene and tetrachloroethylene) in meconium [225]. The protocol is based on SPME extraction in headspace mode carried out by commercial Car/PDMS fiber and following gas chromatography–mass spectrometry analysis.

Table 3. Selected SPME applications in bio-clinical matrices.

Analytes	Matrix	SPME Approach and Coating Material	Instrumentation	Calibration Range	[Ref] Publishing Year
PAHs	urine	fiber—PDMS/DVB/PDMS	GC-MS/MS	0.05–100 µg/L	[74]—2018
OH-PAHs	urine	fiber—C_{18}/PAN	nanoESI-MS/MS	0.1–5 µg/L	[213]—2017
endocrine disrupting chemicals (EDCs)	urine	multiple monolithic fiber—1-trimethyl-(4-vinylbenzyl) aminium chloride as monomer	HPLC-DAD	0.1–200 µg/L	[83]—2017
VOCs	urine	fiber—CAR/PDMS	GC-MS	2.9–1500 µg/L	[214]—2016
aromatic amines	urine	fiber—PDMS/DVB	GCxGC-qMS	1–500 ng/L	[215]—2015
VOCs	urine	fiber—CAR/PDMS	GC-MS	2.5–100 µg/L	[216]—2017
organochlorine pesticides	urine	fiber—PDMS	GC–MS	0.5–20 µg/L	[217]—2016
benzothiazoles, benzotriazoles, benzosulfonamides	urine	fiber—PA	GC-MS/MS	1–100 µg/L	[14]—2014
organochlorine pesticides	urine	stir bar—double hydroxide/graphene (LDH-G)	GC-MS	1–200 µg/L	[218]—2017
monohydroxy-PAHs	urine	in tube—inorganic–organic hybrid nanocomposite (zinc oxide/polypyrrole)	LC-MS/MS	0.2–100 µg/L	[219]—2016
multiclass pesticides, PCBs	hair	fiber—PDMS–DVB	GC–MS/MS	0.002–10 µg/Kg	[220]—2015
PAHs	hair	in tube—CP-Sil 19CB (14% cyanopropyl phenyl methylsilicone)	HPLC-FLD	0.02–1 µg/Kg	[221]—2015
DDTs, PCBs	hair	fiber—PDMS/DVB	GC-MS	2.5–50 ng/Kg	[222]—2014
perfluorinated compounds (PFCs)	blood	surface coated wooden-tip probe—n-octadecyldimethyl[3-(trimethoxysilyl)propyl]ammonium chloride	Orbitrap MS	0.5–100 ng/L	[29]—2014
PCBs, PAHs	Serum	fiber—mesoporous graphitic carbon nitride@$NiCo_2O_4$ nanocomposite	GC-FID	0.002–100 µg/L	[224]—2019
organochlorine pesticides, PCBs	Serum	fiber—PDMS	GC-MS	3–100 µg/L	[223]—2014
BTEX, chlorinated solvents	meconium	fiber—CAR/PDMS	GC-MS	0.08–9 (ng)	[225]—2014

5. Concluding Remarks and Future Directions

This review described the most impactful SPME applications in pollutant analysis published in the last five years (2014–2019). The goal of our paper is giving to the reader information about the ongoing research fields involving SPME and its potential future directions. The surveyed papers cover studies that focused on pollutant determination in the path that goes from the different environmental comparts to the bio-clinical matrices passing through the foods. We revised the studies aimed to determine different chemicals including persistent organic pollutants, pesticides, emerging pollutants, and personal care products. These applications underline the growing demands for green and sensitive analytical methods, which have also fostered the development of new SPME devices, coatings, and geometries. As a results, our paper points out how SPME is an analytical approach constantly evolving in multiple directions, that can satisfy the requirements of green analytical chemistry (GAC) [226], while providing ease of use, high-throughput, extraction efficiency for trace analysis, robustness, suitability for in vivo and on-site analysis, and easy coupling to various separation techniques and direct MS analysis.

Regarding the environmental field, the researchers have mainly focused their efforts on the analysis of environmental waters followed by a smaller number of applications on soil and air. In these areas, the SPME has not only been used to set-up new methods, but it was also used as a proper tool in the analyst's hands to carry out eco-biological and health control studies driven by its unique features such as the capability to determine the concentration of the analytes unbound to the matrix and the advancements in on-site sampling devices and modes.

In food analysis, SPME is a widely used technique particularly for drinking water and in other water matrices. The development in the last five years of new coatings that allow improving the fibers in terms of mechanical robustness, selectivity, and resistance to the matrix effect together with the possibility to perform in vivo and ex vivo analysis opened new research directions for pollutant analysis for the next years.

As for the monitoring of pollutants in bio-clinical matrices, SPME has not yet expressed its full potential. The bio-clinical matrices are very complex and although in the last 5 years the SPME was mainly used for pollutant monitoring in urine, the in vivo mode, and to a larger extent, the new direct couplings with the ambient mass spectrometry, are expected to open exciting scenarios in the near future.

Author Contributions: Conceptualization, A.N.; writing—original draft preparation, A.N. and A.T.; writing—review and editing, A.N. and A.T.; visualization, A.N. and A.T.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

Abbreviations

VOCs	volatile organic compounds
SVOCs	semivolatile organic compounds
DVB/CAR/PDMS	divinylbenzene/carboxen/polydimethylsiloxane
CAR/PDMS	carboxen/polydimethylsiloxane
PDMS	polydimethylsiloxane
PA	polyacrylate
PDMS/DVB	polydimethylsiloxane-divinylbenzene
PDMS/DVB/PDMS	polydimethylsiloxane-divinylbenzene-polydimethylsiloxane
PAHs	polycyclic aromatic hydrocarbons
THMs	trihalomethanes
PCBs	polychlorinated biphenyls

PFBHA	(pentafluorobenzyl)hydroxylamine
MtBSTFA	N-methyl-N-(tert.-butyldimethylsilyl) trifluoroacetamide
OPEs	organophosphate esters
BTEX	benzene, toluene, ethylbenzene and xylenes
PBDEs	polybrominated diphenyl ethers
PM	particulate matter
TWA	Time-Weighted Average sampling
MOF	metal-organic framework
COV	covalent organic frameworks
IL	Ionic liquids
PIL	polymeric ionic liquid
MMF-SPME	multiple monolithic fiber solid-phase microextraction
SPME-TM	Solid-Phase Micro Extraction-Transmission Mode
SPME-TM-DART/MS	Solid-Phase Micro Extraction-Transmission Mode Direct Analysis in Real-Time Mass Spectrometry

References

1. Carter, R.A.A.; West, N.; Heitz, A.; Joll, C.A. An analytical method for the analysis of trihalomethanes in ambient air using solid-phase microextraction gas chromatography-mass spectrometry: An application to indoor swimming pool complexes. *Indoor Air* **2019**, *29*, 499–509. [CrossRef] [PubMed]
2. Saucedo-Lucero, J.O.; Revah, S. Monitoring key organic indoor pollutants and their elimination in a biotrickling biofilter. *Environ. Sci. Pollut. Res.* **2018**, *25*, 9806–9816. [CrossRef] [PubMed]
3. Lucaire, V.; Schwartz, J.J.; Delhomme, O.; Ocampo-Torres, R.; Millet, M. A sensitive method using SPME pre-concentration for the quantification of aromatic amines in indoor air. *Anal. Bioanal. Chem.* **2018**, *410*, 1955–1963. [CrossRef] [PubMed]
4. Ghislain, M.; Beigbeder, J.; Plaisance, H.; Desauziers, V. New sampling device for on-site measurement of SVOC gas-phase concentration at the emitting material surface. *Anal. Bioanal. Chem.* **2017**, *409*, 3199–3210. [CrossRef] [PubMed]
5. Bourdin, D.; Desauziers, V. Development of SPME on-fiber derivatization for the sampling of formaldehyde and other carbonyl compounds in indoor air. *Anal. Bioanal. Chem.* **2014**, *406*, 317–328. [CrossRef]
6. Helin, A.; Rönkkö, T.; Parshintsev, J.; Hartonen, K.; Schilling, B.; Läubli, T.; Riekkola, M.-L. Solid phase microextraction Arrow for the sampling of volatile amines in wastewater and atmosphere. *J. Chromatogr. A* **2015**, *1426*, 56–63. [CrossRef]
7. Ruiz-Jimenez, J.; Zanca, N.; Lan, H.; Jussila, M.; Hartonen, K.; Riekkola, M.L. Aerial drone as a carrier for miniaturized air sampling systems. *J. Chromatogr. A* **2019**, *1597*, 202–208. [CrossRef]
8. Celeiro, M.; Dagnac, T.; Llompart, M. Determination of priority and other hazardous substances in football fields of synthetic turf by gas chromatography-mass spectrometry: A health and environmental concern. *Chemosphere* **2018**, *195*, 201–211. [CrossRef]
9. Baimatova, N.; Kenessov, B.; Koziel, J.A.; Carlsen, L.; Bektassov, M.; Demyanenko, O.P. Simple and accurate quantification of BTEX in ambient air by SPME and GC-MS. *Talanta* **2016**, *154*, 46–52. [CrossRef]
10. Sayed Mohamed Zain, S.M.; Shaharudin, R.; Kamaluddin, M.A.; Daud, S.F. Determination of hydrogen cyanide in residential ambient air using SPME coupled with GC–MS. *Atmos. Pollut. Res.* **2017**, *8*, 678–685. [CrossRef]
11. Van der Veen, I.; de Boer, J. Phosphorus flame retardants: Properties, production, environmental occurrence, toxicity and analysis. *Chemosphere* **2012**, *88*, 1119–1153. [CrossRef] [PubMed]
12. 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]
13. 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]

14. Naccarato, A.; Gionfriddo, E.; Sindona, G.; Tagarelli, A. Simultaneous determination of benzothiazoles, benzotriazoles and benzosulfonamides by solid phase microextraction-gas chromatography-triple quadrupole mass spectrometry in environmental aqueous matrices and human urine. *J. Chromatogr. A* **2014**, *1338*, 164–173. [CrossRef] [PubMed]
15. Raeppel, C.; Fabritius, M.; Nief, M.; Appenzeller, B.M.R.; Millet, M. Coupling ASE, sylilation and SPME-GC/MS for the analysis of current-used pesticides in atmosphere. *Talanta* **2014**, *121*, 24–29. [CrossRef] [PubMed]
16. Gutiérrez-Serpa, A.; Pacheco-Fernández, I.; Pasán, J.; Pino, V. Metal–Organic Frameworks as Key Materials for Solid-Phase Microextraction Devices—A Review. *Separations* **2019**, *6*, 47. [CrossRef]
17. Li, J.; Li, H.; Zhao, Y.; Wang, S.; Chen, X.; Zhao, R.S. A hollow microporous organic network as a fiber coating for solid-phase microextraction of short-chain chlorinated hydrocarbons. *Microchim. Acta* **2018**, *185*, 416. [CrossRef]
18. Jia, Y.; Su, H.; Wang, Z.; Wong, Y.L.E.; Chen, X.; Wang, M.; Chan, T.W.D. Metal-Organic Framework@Microporous Organic Network as Adsorbent for Solid-Phase Microextraction. *Anal. Chem.* **2016**, *88*, 9364–9367. [CrossRef]
19. Li, J.; Liu, Y.; Su, H.; Elaine Wong, Y.L.; Chen, X.; Dominic Chan, T.W.; Chen, Q. In situ hydrothermal growth of a zirconium-based porphyrinic metal-organic framework on stainless steel fibers for solid-phase microextraction of nitrated polycyclic aromatic hydrocarbons. *Microchim. Acta* **2017**, *184*, 3809–3815. [CrossRef]
20. Zhang, S.; Yang, Q.; Li, Z.; Wang, W.; Wang, C.; Wang, Z. Covalent organic frameworks as a novel fiber coating for solid-phase microextraction of volatile benzene homologues. *Anal. Bioanal. Chem.* **2017**, *409*, 3429–3439. [CrossRef]
21. Riboni, N.; Trzcinski, J.W.; Bianchi, F.; Massera, C.; Pinalli, R.; Sidisky, L.; Dalcanale, E.; Careri, M. Conformationally blocked quinoxaline cavitand as solid-phase microextraction coating for the selective detection of BTEX in air. *Anal. Chim. Acta* **2016**, *905*, 79–84. [CrossRef]
22. Heidari, M.; Bahrami, A.; Ghiasvand, A.R.; Shahna, F.G.; Soltanian, A.R.; Rafieiemam, M. Application of graphene nanoplatelets silica composite, prepared by sol-gel technology, as a novel sorbent in two microextraction techniques. *J. Sep. Sci.* **2015**, *38*, 4225–4232. [CrossRef] [PubMed]
23. Dias, C.M.; Menezes, H.C.; Cardeal, Z.L. Environmental and biological determination of acrolein using new cold fiber solid phase microextraction with gas chromatography mass spectrometry. *Anal. Bioanal. Chem.* **2017**, *409*, 2821–2828. [CrossRef] [PubMed]
24. Kenessov, B.; Koziel, J.A.; Baimatova, N.; Demyanenko, O.P.; Derbissalin, M. Optimization of time-weighted average air sampling by solid-phase microextraction fibers using finite element analysis software. *Molecules* **2018**, *23*, 2736. [CrossRef] [PubMed]
25. Tursumbayeva, M.; Koziel, J.A.; Maurer, D.L.; Kenessov, B.; Rice, S. Development of Time-Weighted Average Sampling of Odorous Volatile Organic Compounds in Air with Solid-Phase Microextraction Fiber Housed inside a GC Glass Liner: Proof of concept. *Molecules* **2019**, *24*, 406. [CrossRef]
26. Carasek, E.; Morés, L.; Merib, J. Basic principles, recent trends and future directions of microextraction techniques for the analysis of aqueous environmental samples. *Trends Environ. Anal. Chem.* **2018**, *19*, e00060. [CrossRef]
27. Gómez-Ríos, G.A.; Gionfriddo, E.; Poole, J.; Pawliszyn, J. Ultrafast Screening and Quantitation of Pesticides in Food and Environmental Matrices by Solid-Phase Microextraction-Transmission Mode (SPME-TM) and Direct Analysis in Real Time (DART). *Anal. Chem.* **2017**, *89*, 7240–7248. [CrossRef]
28. Wang, X.; Li, X.; Li, Z.; Zhang, Y.; Bai, Y.; Liu, H. Online coupling of in-tube solid-phase microextraction with direct analysis in real time mass spectrometry for rapid determination of triazine herbicides in water using carbon-nanotubes-incorporated polymer monolith. *Anal. Chem.* **2014**, *86*, 4739–4747. [CrossRef]
29. Deng, J.; Yang, Y.; Fang, L.; Lin, L.; Zhou, H.; Luan, T. Coupling solid-phase microextraction with ambient mass spectrometry using surface coated wooden-tip probe for rapid analysis of ultra trace perfluorinated compounds in complex samples. *Anal. Chem.* **2014**, *86*, 11159–11166. [CrossRef]
30. Grandy, J.J.; Lashgari, M.; Vander Heide, H.; Poole, J.; Pawliszyn, J. Introducing a mechanically robust SPME sampler for the on-site sampling and extraction of a wide range of untargeted pollutants in environmental waters. *Environ. Pollut.* **2019**, *252*, 825–834. [CrossRef]

31. Bu, Y.; Feng, J.; Sun, M.; Zhou, C.; Luo, C. Facile and efficient poly(ethylene terephthalate) fibers-in-tube for online solid-phase microextraction towards polycyclic aromatic hydrocarbons. *Anal. Bioanal. Chem.* **2016**, *408*, 4871–4882. [CrossRef] [PubMed]
32. Fu, M.; Xing, H.; Chen, X.; Zhao, R.; Zhi, C.; Wu, C.L. Boron nitride nanotubes as novel sorbent for solid-phase microextraction of polycyclic aromatic hydrocarbons in environmental water samples. *Anal. Bioanal. Chem.* **2014**, *406*, 5751–5754. [CrossRef] [PubMed]
33. Yin, L.; Hu, Q.; Mondal, S.; Xu, J.; Ouyang, G. Peanut shell-derived biochar materials for effective solid-phase microextraction of polycyclic aromatic hydrocarbons in environmental waters. *Talanta* **2019**, *202*, 90–95. [CrossRef] [PubMed]
34. Sun, S.; Huang, L.; Xiao, H.; Shuai, Q.; Hu, S. In situ self-transformation metal into metal-organic framework membrane for solid-phase microextraction of polycyclic aromatic hydrocarbons. *Talanta* **2019**, *202*, 145–151. [CrossRef] [PubMed]
35. Wang, G.; Lei, Y.; Song, H. Exploration of metal-organic framework MOF-177 coated fibers for headspace solid-phase microextraction of polychlorinated biphenyls and polycyclic aromatic hydrocarbons. *Talanta* **2015**, *144*, 369–374. [CrossRef]
36. Kong, J.; Zhu, F.; Huang, W.; He, H.; Hu, J.; Sun, C.; Xian, Q.; Yang, S. Sol–gel based metal-organic framework zeolite imidazolate framework-8 fibers for solid-phase microextraction of nitro polycyclic aromatic hydrocarbons and polycyclic aromatic hydrocarbons in water samples. *J. Chromatogr. A* **2019**. [CrossRef]
37. Hu, X.; Liu, C.; Li, J.; Luo, R.; Jiang, H.; Sun, X.; Shen, J.; Han, W.; Wang, L. Hollow mesoporous carbon spheres-based fiber coating for solid-phase microextraction of polycyclic aromatic hydrocarbons. *J. Chromatogr. A* **2017**, *1520*, 58–64. [CrossRef]
38. Bagheri, H.; Soofi, G.; Javanmardi, H.; Karimi, M. A 3D nanoscale polyhedral oligomeric silsesquioxanes network for microextraction of polycyclic aromatic hydrocarbons. *Microchim. Acta* **2018**, *185*, 418. [CrossRef]
39. Guo, M.; Song, W.; Wang, T.; Li, Y.; Wang, X.; Du, X. Phenyl-functionalization of titanium dioxide-nanosheets coating fabricated on a titanium wire for selective solid-phase microextraction of polycyclic aromatic hydrocarbons from environment water samples. *Talanta* **2015**, *144*, 998–1006. [CrossRef]
40. Gutiérrez-Serpa, A.; Napolitano-Tabares, P.I.; Pino, V.; Jiménez-Moreno, F.; Jiménez-Abizanda, A.I. Silver nanoparticles supported onto a stainless steel wire for direct-immersion solid-phase microextraction of polycyclic aromatic hydrocarbons prior to their determination by GC-FID. *Microchim. Acta* **2018**, *185*, 341. [CrossRef]
41. Wang, X.; Sheng, W.R.; Jiao, X.Y.; Zhao, R.S.; Wang, M.L.; Lin, J.M. Zinc(II)-based metal–organic nanotubes coating for high sensitive solid phase microextraction of nitro-polycyclic aromatic hydrocarbons. *Talanta* **2018**, *186*, 561–567. [CrossRef] [PubMed]
42. Liu, Y.L.; Chen, X.F.; Wang, X.; Zhou, J.B.; Zhao, R.S. Sensitive determination of polychlorinated biphenyls in environmental water samples by headspace solid-phase microextraction with bamboo charcoal@iron oxide black fibers prior to gas chromatography with tandem mass spectrometry. *J. Sep. Sci.* **2014**, *37*, 1496–1502. [CrossRef] [PubMed]
43. Sheng, W.R.; Chen, Y.; Wang, S.S.; Wang, X.L.; Wang, M.L.; Zhao, R.S. Cadmium(II)-based metal–organic nanotubes as solid-phase microextraction coating for ultratrace-level analysis of polychlorinated biphenyls in seawater samples. *Anal. Bioanal. Chem.* **2016**, *408*, 8289–8297. [CrossRef] [PubMed]
44. Cheng, H.; Wang, F.; Bian, Y.; Ji, R.; Song, Y.; Jiang, X. Co- and self-activated synthesis of tailored multimodal porous carbons for solid-phase microextraction of chlorobenzenes and polychlorinated biphenyls. *J. Chromatogr. A* **2019**, *1585*, 1–9. [CrossRef]
45. Li, Q.L.; Wang, X.; Liu, Y.L.; Chen, X.F.; Wang, M.L.; Zhao, R.S. Feasibility of metal-organic nanotubes [Cu3(μ3-O)(μ-OH)(triazolate)2]+-coated fibers for solid-phase microextraction of polychlorinated biphenyls in water samples. *J. Chromatogr. A* **2014**, *1374*, 58–65. [CrossRef]
46. Ling, X.; Chen, Z. Immobilization of zeolitic imidazolate frameworks with assist of electrodeposited zinc oxide layer and application in online solid-phase microextraction of Sudan dyes. *Talanta* **2019**, *192*, 142–146. [CrossRef]
47. Pei, M.; Zhu, X.; Huang, X. Mixed functional monomers-based monolithic adsorbent for the effective extraction of sulfonylurea herbicides in water and soil samples. *J. Chromatogr. A* **2018**, *1531*, 13–21. [CrossRef]

48. Zhang, Z.; Mei, M.; Huang, Y.; Huang, X.; Huang, H.; Ding, Y. Facile preparation of a polydopamine-based monolith for multiple monolithic fiber solid-phase microextraction of triazine herbicides in environmental water samples. *J. Sep. Sci.* **2017**, *40*, 733–743. [CrossRef]
49. Prieto, A.; Rodil, R.; Quintana, J.B.; Cela, R.; Möder, M.; Rodríguez, I. Evaluation of polyethersulfone performance for the microextraction of polar chlorinated herbicides from environmental water samples. *Talanta* **2014**, *122*, 264–271. [CrossRef]
50. Bagheri, H.; Amanzadeh, H.; Yamini, Y.; Masoomi, M.Y.; Morsali, A.; Salar-Amoli, J.; Hassan, J. A nanocomposite prepared from a zinc-based metal-organic framework and polyethersulfone as a novel coating for the headspace solid-phase microextraction of organophosphorous pesticides. *Microchim. Acta* **2018**, *185*, 62. [CrossRef]
51. Gutiérrez-Serpa, A.; Rocío-Bautista, P.; Pino, V.; Jiménez-Moreno, F.; Jiménez-Abizanda, A.I. Gold nanoparticles based solid-phase microextraction coatings for determining organochlorine pesticides in aqueous environmental samples. *J. Sep. Sci.* **2017**, *40*, 2009–2021. [CrossRef] [PubMed]
52. Zheng, J.; Liang, Y.; Liu, S.; Jiang, R.; Zhu, F.; Wu, D.; Ouyang, G. Simple fabrication of solid phase microextraction fiber employing nitrogen-doped ordered mesoporous polymer by in situ polymerization. *J. Chromatogr. A* **2016**, *1427*, 22–28. [CrossRef] [PubMed]
53. Wu, J.; Mei, M.; Huang, X. Fabrication of boron-rich multiple monolithic fibers for the solid-phase microextraction of carbamate pesticide residues in complex samples. *J. Sep. Sci.* **2019**, *42*, 878–887. [CrossRef] [PubMed]
54. Pang, J.; Liao, Y.; Huang, X.; Ye, Z.; Yuan, D. Metal-organic framework-monolith composite-based in-tube solid phase microextraction on-line coupled to high-performance liquid chromatography-fluorescence detection for the highly sensitive monitoring of fluoroquinolones in water and food samples. *Talanta* **2019**, *199*, 499–506. [CrossRef]
55. Peng, J.; Liu, D.; Shi, T.; Tian, H.; Hui, X.; He, H. Molecularly imprinted polymers based stir bar sorptive extraction for determination of cefaclor and cefalexin in environmental water. *Anal. Bioanal. Chem.* **2017**, *409*, 4157–4166. [CrossRef]
56. Barahona, F.; Albero, B.; Tadeo, J.L.; Martín-Esteban, A. Molecularly imprinted polymer-hollow fiber microextraction of hydrophilic fluoroquinolone antibiotics in environmental waters and urine samples. *J. Chromatogr. A* **2019**, *1587*, 42–49. [CrossRef]
57. Kazemi, E.; Haji Shabani, A.M.; Dadfarnia, S. Application of graphene oxide-silica composite reinforced hollow fibers as a novel device for pseudo-stir bar solid phase microextraction of sulfadiazine in different matrices prior to its spectrophotometric determination. *Food Chem.* **2017**, *221*, 783–789. [CrossRef]
58. Mei, M.; Huang, X.; Yu, J.; Yuan, D. Sensitive monitoring of trace nitrophenols in water samples using multiple monolithic fiber solid phase microextraction and liquid chromatographic analysis. *Talanta* **2015**, *134*, 89–97. [CrossRef]
59. Li, Q.L.; Huang, F.; Wang, X.L.; Wang, X.; Zhao, R.S. Multiple-helix cobalt(II)-based metal-organic nanotubes on stainless steel fibers for solid-phase microextraction of chlorophenol and nitrophenols from water samples. *Microchim. Acta* **2017**, *184*, 1817–1825. [CrossRef]
60. Gionfriddo, E.; Naccarato, A.; Sindona, G.; Tagarelli, A. Determination of hydrazine in drinking water: Development and multivariate optimization of a rapid and simple solid phase microextraction-gas chromatography-triple quadrupole mass spectrometry protocol. *Anal. Chim. Acta* **2014**, *835*, 37–45. [CrossRef]
61. Li, L.; Guo, R.; Li, Y.; Guo, M.; Wang, X.; Du, X. In situ growth and phenyl functionalization of titania nanoparticles coating for solid-phase microextraction of ultraviolet filters in environmental water samples followed by high performance liquid chromatography-UV detection. *Anal. Chim. Acta* **2015**, *867*, 38–46. [CrossRef] [PubMed]
62. Yang, Y.; Li, Y.; Liu, H.; Wang, X.; Du, X. Electrodeposition of gold nanoparticles onto an etched stainless steel wire followed by a self-assembled monolayer of octanedithiol as a fiber coating for selective solid-phase microextraction. *J. Chromatogr. A* **2014**, *1372*, 25–33. [CrossRef] [PubMed]
63. Zhou, S.; Wang, H.; Jin, P.; Wang, Z.; Wang, X.; Du, X. Electrophoretic deposition strategy for the fabrication of highly stable functionalized silica nanoparticle coatings onto nickel-titanium alloy wires for selective solid-phase microextraction. *J. Sep. Sci.* **2017**, *40*, 4796–4804. [CrossRef] [PubMed]

64. Li, Y.; Zhang, M.; Yang, Y.; Wang, X.; Du, X. Electrochemical in situ fabrication of titanium dioxide-nanosheets on a titanium wire as a novel coating for selective solid-phase microextraction. *J. Chromatogr. A* **2014**, *1358*, 60–67. [CrossRef]
65. Song, W.; Guo, M.; Zhang, Y.; Zhang, M.; Wang, X.; Du, X. Fabrication and application of zinc-zinc oxide nanosheets coating on an etched stainless steel wire as a selective solid-phase microextraction fiber. *J. Chromatogr. A* **2015**, *1384*, 28–36. [CrossRef]
66. Bu, Y.; Feng, J.; Wang, X.; Tian, Y.; Sun, M.; Luo, C. In situ hydrothermal growth of polyaniline coating for in-tube solid-phase microextraction towards ultraviolet filters in environmental water samples. *J. Chromatogr. A* **2017**, *1483*, 48–55. [CrossRef]
67. Wang, H.; Du, J.; Zhen, Q.; Zhang, R.; Wang, X.; Du, X. Selective solid-phase microextraction of ultraviolet filters in environmental water with oriented ZnO nanosheets coated nickel-titanium alloy fibers followed by high performance liquid chromatography with UV detection. *Talanta* **2019**, *191*, 193–201. [CrossRef]
68. 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]
69. Ma, M.; Wang, H.; Zhen, Q.; Zhang, M.; Du, X. Development of nitrogen-enriched carbonaceous material coated titania nanotubes array as a fiber coating for solid-phase microextraction of ultraviolet filters in environmental water. *Talanta* **2017**, *167*, 118–125. [CrossRef]
70. Wang, H.; Song, W.; Zhang, M.; Zhen, Q.; Guo, M.; Zhang, Y.; Du, X. Hydrothermally grown and self-assembled modified titanium and nickel oxide composite nanosheets on Nitinol-based fibers for efficient solid phase microextraction. *J. Chromatogr. A* **2016**, *1468*, 33–41. [CrossRef]
71. Yang, Y.; Guo, M.; Zhang, Y.; Song, W.; Li, Y.; Wang, X.; Du, X. Self-assembly of alkyldithiols on a novel dendritic silver nanostructure electrodeposited on a stainless steel wire as a fiber coating for solid-phase microextraction. *RSC Adv.* **2015**, *5*, 71859–71867. [CrossRef]
72. Li, Y.; Ma, M.; Zhang, M.; Yang, Y.; Wang, X.; Du, X. In situ anodic growth of rod-like TiO2 coating on a Ti wire as a selective solid-phase microextraction fiber. *RSC Adv.* **2014**, *4*, 53820–53827. [CrossRef]
73. Zhang, Y.; Song, W.; Yang, Y.; Guo, M.; Wang, X.; Du, X. Self-assembly of mercaptoundecanol on cedar-like Au nanoparticle coated stainless steel fiber for selective solid-phase microextraction. *Anal. Methods* **2015**, *7*, 7680–7689. [CrossRef]
74. 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] [PubMed]
75. Liu, S.; Pan, G.; Yang, H.; Cai, Z.; Zhu, F.; Ouyang, G. Determination and elimination of hazardous pollutants by exploitation of a Prussian blue nanoparticles-graphene oxide composite. *Anal. Chim. Acta* **2019**, *1054*, 17–25. [CrossRef] [PubMed]
76. Liu, S.; Xie, L.; Hu, Q.; Yang, H.; Pan, G.; Zhu, F.; Yang, S.; Ouyang, G. A tri-metal centered metal-organic framework for solid-phase microextraction of environmental contaminants with enhanced extraction efficiency. *Anal. Chim. Acta* **2017**, *987*, 38–46. [CrossRef]
77. Cen, J.; Wei, S.; Nan, H.; Xu, J.; Huang, Z.; Liu, S.; Hu, Q.; Yan, J.; Ouyang, G. Incorporation of carbon nanotubes into graphene for highly efficient solid-phase microextraction of benzene homologues. *Microchem. J.* **2018**, *139*, 203–209. [CrossRef]
78. Liu, S.; Hu, Q.; Zheng, J.; Xie, L.; Wei, S.; Jiang, R.; Zhu, F.; Liu, Y.; Ouyang, G. Knitting aromatic polymers for efficient solid-phase microextraction of trace organic pollutants. *J. Chromatogr. A* **2016**, *1450*, 9–16. [CrossRef]
79. Huang, Z.; Liu, S.; Xu, J.; Yin, L.; Zheng, J.; Zhou, N.; Ouyang, G. Porous organic polymers with different pore structures for sensitive solid-phase microextraction of environmental organic pollutants. *Anal. Chim. Acta* **2017**, *989*, 21–28. [CrossRef]
80. Xie, X.; Wang, J.; Zheng, J.; Huang, J.; Ni, C.; Cheng, J.; Hao, Z.; Ouyang, G. Low-cost Scholl-coupling microporous polymer as an efficient solid-phase microextraction coating for the detection of light aromatic compounds. *Anal. Chim. Acta* **2018**, *1029*, 30–36. [CrossRef]
81. Mei, M.; Huang, X.; Yuan, D. Multiple monolithic fiber solid-phase microextraction: A new extraction approach for aqueous samples. *J. Chromatogr. A* **2014**, *1345*, 29–36. [CrossRef] [PubMed]

82. Mei, M.; Huang, X.; Liao, K.; Yuan, D. Sensitive monitoring of benzoylurea insecticides in water and juice samples treated with multiple monolithic fiber solid-phase microextraction and liquid chromatographic analysis. *Anal. Chim. Acta* **2015**, *860*, 29–36. [CrossRef] [PubMed]
83. Pei, M.; Zhang, Z.; Huang, X.; Wu, Y. Fabrication of a polymeric ionic liquid-based adsorbent for multiple monolithic fiber solid-phase microextraction of endocrine disrupting chemicals in complicated samples. *Talanta* **2017**, *165*, 152–160. [CrossRef] [PubMed]
84. Huang, Y.; Lu, M.; Li, H.; Bai, M.; Huang, X. Sensitive determination of perfluoroalkane sulfonamides in water and urine samples by multiple monolithic fiber solid-phase microextraction and liquid chromatography tandem mass spectrometry. *Talanta* **2019**, *192*, 24–31. [CrossRef] [PubMed]
85. Mei, M.; Huang, X.; Luo, Q.; Yuan, D. Magnetism-Enhanced Monolith-Based In-Tube Solid Phase Microextraction. *Anal. Chem.* **2016**, *88*, 1900–1907. [CrossRef]
86. Kabir, A.; Furton, K.G. *Fabric Phase Sorptive Extractor (FPSE)*; US Patent and Trademark Office: Alexandria, VA, USA, 2014.
87. Racamonde, I.; Rodil, R.; Quintana, J.B.; Sieira, B.J.; Kabir, A.; Furton, K.G.; Cela, R. Fabric phase sorptive extraction: A new sorptive microextraction technique for the determination of non-steroidal anti-inflammatory drugs from environmental water samples. *Anal. Chim. Acta* **2015**, *865*, 22–30. [CrossRef]
88. Santana-Viera, S.; Guedes-Alonso, R.; Sosa-Ferrera, Z.; Santana-Rodríguez, J.J.; Kabir, A.; Furton, K.G. Optimization and application of fabric phase sorptive extraction coupled to ultra-high performance liquid chromatography tandem mass spectrometry for the determination of cytostatic drug residues in environmental waters. *J. Chromatogr. A* **2017**, *1529*, 39–49. [CrossRef]
89. Roldán-Pijuán, M.; Lucena, R.; Cárdenas, S.; Valcárcel, M.; Kabir, A.; Furton, K.G. Stir fabric phase sorptive extraction for the determination of triazine herbicides in environmental waters by liquid chromatography. *J. Chromatogr. A* **2015**, *1376*, 35–45. [CrossRef]
90. Lakade, S.S.; Borrull, F.; Furton, K.G.; Kabir, A.; Marcé, R.M.; Fontanals, N. Dynamic fabric phase sorptive extraction for a group of pharmaceuticals and personal care products from environmental waters. *J. Chromatogr. A* **2016**, *1456*, 19–26. [CrossRef]
91. Kenessov, B.; Koziel, J.A.; Bakaikina, N.V.; Orazbayeva, D. Perspectives and challenges of on-site quantification of organic pollutants in soils using solid-phase microextraction. *TrAC Trends Anal. Chem.* **2016**, *85*, 111–122. [CrossRef]
92. Bianchi, F.; Bedini, A.; Riboni, N.; Pinalli, R.; Gregori, A.; Sidisky, L.; Dalcanale, E.; Careri, M. Cavitand-based solid-phase microextraction coating for the selective detection of nitroaromatic explosives in air and soil. *Anal. Chem.* **2014**, *86*, 10646–10652. [CrossRef] [PubMed]
93. Yao, W.; Fan, Z.; Zhang, S. Preparation of metal-organic framework UiO-66-incorporated polymer monolith for the extraction of trace levels of fungicides in environmental water and soil samples. *J. Sep. Sci.* **2019**, *42*, 2679–2686. [CrossRef] [PubMed]
94. Gao, J.; Huang, C.; Lin, Y.; Tong, P.; Zhang, L. In situ solvothermal synthesis of metal-organic framework coated fiber for highly sensitive solid-phase microextraction of polycyclic aromatic hydrocarbons. *J. Chromatogr. A* **2016**, *1436*, 1–8. [CrossRef] [PubMed]
95. Zhang, X.; Zang, X.H.; Wang, J.T.; Wang, C.; Wu, Q.H.; Wang, Z. Porous carbon derived from aluminum-based metal organic framework as a fiber coating for the solid-phase microextraction of polycyclic aromatic hydrocarbons from water and soil. *Microchim. Acta* **2015**, *182*, 2353–2359. [CrossRef]
96. Zhang, N.; Huang, C.; Tong, P.; Feng, Z.; Wu, X.; Zhang, L. Moisture stable Ni-Zn MOF/g-C 3 N 4 nanoflowers: A highly efficient adsorbent for solid-phase microextraction of PAHs. *J. Chromatogr. A* **2018**, *1556*, 37–46. [CrossRef]
97. Zhang, N.; Huang, C.; Feng, Z.; Chen, H.; Tong, P.; Wu, X.; Zhang, L. Metal-organic framework-coated stainless steel fiber for solid-phase microextraction of polychlorinated biphenyls. *J. Chromatogr. A* **2018**, *1570*, 10–18. [CrossRef]
98. Wu, Y.Y.; Yang, C.X.; Yan, X.P. Fabrication of metal-organic framework MIL-88B films on stainless steel fibers for solid-phase microextraction of polychlorinated biphenyls. *J. Chromatogr. A* **2014**, *1334*, 1–8. [CrossRef]
99. Zhang, C.Y.; Yan, Z.G.; Zhou, Y.Y.; Wang, L.; Xie, Y.B.; Bai, L.P.; Zhou, H.Y.; Li, F.S. Embedment of Ag(I)-organic frameworks into silica gels for microextraction of polybrominated diphenyl ethers in soils. *J. Chromatogr. A* **2015**, *1383*, 18–24. [CrossRef]

100. Bakaikina, N.V.; Kenessov, B.; Ul'yanovskii, N.V.; Kosyakov, D.S. Quantification of transformation products of rocket fuel unsymmetrical dimethylhydrazine in soils using SPME and GC-MS. *Talanta* **2018**, *184*, 332–337. [CrossRef]
101. Peruga, A.; Beltrán, J.; López, F.; Hernández, F. Determination of methylisothiocyanate in soil and water by HS-SPME followed by GC-MS-MS with a triple quadrupole. *Anal. Bioanal. Chem.* **2014**, *406*, 5271–5282. [CrossRef]
102. Yegemova, S.; Bakaikina, N.V.; Kenessov, B.; Koziel, J.A.; Nauryzbayev, M. Determination of 1-methyl-1H-1,2,4-triazole in soils contaminated by rocket fuel using solid-phase microextraction, isotope dilution and gas chromatography-mass spectrometry. *Talanta* **2015**, *143*, 226–233. [CrossRef] [PubMed]
103. Škulcová, L.; Hale, S.E.; Hofman, J.; Bielská, L. Laboratory versus field soil aging: Impact on DDE bioavailability and sorption. *Chemosphere* **2017**, *186*, 235–242. [CrossRef] [PubMed]
104. Shen, H.; Li, W.; Graham, S.E.; Starr, J.M. The role of soil and house dust physicochemical properties in determining the post ingestion bioaccessibility of sorbed polychlorinated biphenyls. *Chemosphere* **2019**, *217*, 1–8. [CrossRef] [PubMed]
105. Ma, L.; Yates, S.R. Dissolved organic matter and estrogen interactions regulate estrogen removal in the aqueous environment: A review. *Sci. Total Environ.* **2018**, *640–641*, 529–542. [CrossRef] [PubMed]
106. Guo, M.; Gong, Z.; Allinson, G.; Tai, P.; Miao, R.; Li, X.; Jia, C.; Zhuang, J. Variations in the bioavailability of polycyclic aromatic hydrocarbons in industrial and agricultural soils after bioremediation. *Chemosphere* **2016**, *144*, 1513–1520. [CrossRef] [PubMed]
107. Kumar, R.; Gaurav; Kabir, A.; Furton, K.G.; Malik, A.K. Development of a fabric phase sorptive extraction with high-performance liquid chromatography and ultraviolet detection method for the analysis of alkyl phenols in environmental samples. *J. Sep. Sci.* **2015**, *38*, 3228–3238. [CrossRef]
108. Stanisz, E.; Werner, J.; Matusiewicz, H. Task specific ionic liquid-coated PTFE tube for solid-phase microextraction prior to chemical and photo-induced mercury cold vapour generation. *Microchem. J.* **2014**, *114*, 229–237. [CrossRef]
109. Psillakis, E. Vacuum-assisted headspace solid-phase microextraction: A tutorial review. *Anal. Chim. Acta* **2017**, *986*, 12–24. [CrossRef]
110. Wu, M.; Wang, L.; Zhao, F.; Zeng, B. Ionic liquid polymer functionalized carbon nanotubes-coated polyaniline for the solid-phase microextraction of benzene derivatives. *RSC Adv.* **2015**, *5*, 99483–99490. [CrossRef]
111. Sarafraz-Yazdi, A.; Rounaghi, G.; Vatani, H.; Razavipanah, I.; Amiri, A. Headspace solid phase microextraction of volatile aromatic hydrocarbons using a steel wire coated with an electrochemically prepared nanocomposite consisting of polypyrrole, carbon nanotubes, and titanium oxide. *Microchim. Acta* **2015**, *182*, 217–225. [CrossRef]
112. Song, X.L.; Chen, Y.; Yuan, J.P.; Qin, Y.J.; Zhao, R.S.; Wang, X. Carbon nanotube composite microspheres as a highly efficient solid-phase microextraction coating for sensitive determination of phthalate acid esters in water samples. *J. Chromatogr. A* **2016**, *1468*, 17–22. [CrossRef]
113. Di Pietro Roux, K.C.; Jasinski, É.F.; Merib, J.; Sartorelli, M.L.; Carasek, E. Application of a robust solid-phase microextraction fiber consisting of NiTi wires coated with polypyrrole for the determination of haloanisoles in water and wine. *Anal. Methods* **2016**, *8*, 5503–5510. [CrossRef]
114. Huang, S.; Xu, J.; Tao, X.; Chen, X.; Zhu, F.; Wang, Y.; Jiang, R.; Ouyang, G. Fabrication of polyaniline/ silver composite coating as a dual-functional platform for microextraction and matrix-free laser desorption/ionization. *Talanta* **2017**, *172*, 155–161. [CrossRef] [PubMed]
115. Li, Z.; Ma, R.; Bai, S.; Wang, C.; Wang, Z. A solid phase microextraction fiber coated with graphene-poly(ethylene glycol) composite for the extraction of volatile aromatic compounds from water samples. *Talanta* **2014**, *119*, 498–504. [CrossRef]
116. Sarafraz-Yazdi, A.; Yekkebashi, A. Development of a poly(ethylene glycol)-graphene oxide sol-gel coating for solid-phase microextraction of aromatic amines in water samples with a gas chromatography-flame ionization detector method. *New J. Chem.* **2015**, *39*, 1287–1294. [CrossRef]
117. De Toffoli, A.L.; Fumes, B.H.; Lanças, F.M. Packed in-tube solid phase microextraction with graphene oxide supported on aminopropyl silica: Determination of target triazines in water samples. *J. Environ. Sci. Health Part B Pestic. Food Contam. Agric. Wastes* **2018**, *53*, 434–440. [CrossRef] [PubMed]

118. Tan, F.; Zhao, C.; Li, L.; Liu, M.; He, X.; Gao, J. Graphene oxide based in-tube solid-phase microextraction combined with liquid chromatography tandem mass spectrometry for the determination of triazine herbicides in water. *J. Sep. Sci.* **2015**, *38*, 2312–2319. [CrossRef]
119. Li, S.; Lu, C.; Zhu, F.; Jiang, R.; Ouyang, G. Preparation of C18 composite solid-phase microextraction fiber and its application to the determination of organochlorine pesticides in water samples. *Anal. Chim. Acta* **2015**, *873*, 57–62. [CrossRef]
120. Jiang, H.; Li, J.; Jiang, M.; Lu, R.; Shen, J.; Sun, X.; Han, W.; Wang, L. Ordered mesoporous carbon film as an effective solid-phase microextraction coating for determination of benzene series from aqueous media. *Anal. Chim. Acta* **2015**, *888*, 85–93. [CrossRef]
121. Saraji, M.; Shahvar, A. Metal-organic aerogel as a coating for solid-phase microextraction. *Anal. Chim. Acta* **2017**, *973*, 51–58. [CrossRef]
122. Bagheri, H.; Javanmardi, H.; Abbasi, A.; Banihashemi, S. A metal organic framework-polyaniline nanocomposite as a fiber coating for solid phase microextraction. *J. Chromatogr. A* **2016**, *1431*, 27–35. [CrossRef] [PubMed]
123. Xie, L.; Liu, S.; Han, Z.; Jiang, R.; Zhu, F.; Xu, W.; Su, C.; Ouyang, G. Amine-functionalized MIL-53(Al)-coated stainless steel fiber for efficient solid-phase microextraction of synthetic musks and organochlorine pesticides in water samples. *Anal. Bioanal. Chem.* **2017**, *409*, 5239–5247. [CrossRef] [PubMed]
124. Zang, X.; Zhang, X.; Chang, Q.; Li, S.; Wang, C.; Wang, Z. Metal–organic framework UiO-67-coated fiber for the solid-phase microextraction of nitrobenzene compounds from water. *J. Sep. Sci.* **2016**, *39*, 2770–2776. [CrossRef]
125. Zang, X.; Zhang, G.; Chang, Q.; Zhang, X.; Wang, C.; Wang, Z. Metal organic framework MIL-101 coated fiber for headspace solid phase microextraction of volatile aromatic compounds. *Anal. Methods* **2015**, *7*, 918–923. [CrossRef]
126. Zhang, J.; Zhang, W.; Bao, T.; Chen, Z. Polydopamine-based immobilization of zeolitic imidazolate framework-8 for in-tube solid-phase microextraction. *J. Chromatogr. A* **2015**, *1388*, 9–16. [CrossRef] [PubMed]
127. Kang, H.; Mao, Y.; Wang, X.; Zhang, Y.; Wu, J.; Wang, H. Disposable ionic liquid-coated etched stainless steel fiber for headspace solid-phase microextraction of organophosphorus flame retardants from water samples. *RSC Adv.* **2015**, *5*, 41934–41940. [CrossRef]
128. Pacheco-Fernández, I.; Najafi, A.; Pino, V.; Anderson, J.L.; Ayala, J.H.; Afonso, A.M. Utilization of highly robust and selective crosslinked polymeric ionic liquid-based sorbent coatings in direct-immersion solid-phase microextraction and high-performance liquid chromatography for determining polar organic pollutants in waters. *Talanta* **2016**, *158*, 125–133. [CrossRef]
129. Pena-Pereira, F.; Marcinkowski, Ł.; Kloskowski, A.; Namieśnik, J. Ionogel fibres of bis(trifluoromethanesulfonyl) imide anion-based ionic liquids for the headspace solid-phase microextraction of chlorinated organic pollutants. *Analyst* **2015**, *140*, 7417–7422. [CrossRef]
130. Zhang, C.; Anderson, J.L. Polymeric ionic liquid bucky gels as sorbent coatings for solid-phase microextraction. *J. Chromatogr. A* **2014**, *1344*, 15–22. [CrossRef]
131. Yu, H.; Merib, J.; Anderson, J.L. Crosslinked polymeric ionic liquids as solid-phase microextraction sorbent coatings for high performance liquid chromatography. *J. Chromatogr. A* **2016**, *1438*, 10–21. [CrossRef]
132. Feng, J.; Wang, X.; Tian, Y.; Luo, C.; Sun, M. Basalt fibers grafted with a poly(ionic liquids) coating for in-tube solid-phase microextraction. *J. Sep. Sci.* **2018**, *41*, 3267–3274. [CrossRef] [PubMed]
133. Sun, M.; Feng, J.; Bu, Y.; Wang, X.; Duan, H.; Luo, C. Palladium-coated stainless-steel wire as a solid-phase microextraction fiber. *J. Sep. Sci.* **2015**, *38*, 1584–1590. [CrossRef] [PubMed]
134. Wang, X.; Feng, J.; Tian, Y.; Luo, C.; Sun, M. Co-Al bimetallic hydroxide nanocomposites coating for online in-tube solid-phase microextraction. *J. Chromatogr. A* **2018**, *1550*, 1–7. [CrossRef] [PubMed]
135. Feng, J.; Tian, Y.; Wang, X.; Luo, C.; Sun, M. Basalt fibers functionalized with gold nanoparticles for in-tube solid-phase microextraction. *J. Sep. Sci.* **2018**, *41*, 1149–1155. [CrossRef]
136. Pena-Pereira, F.; Marcinkowski, Ł.; Kloskowski, A.; Namieśnik, J. Silica-based ionogels: Nanoconfined ionic liquid-rich fibers for headspace solid-phase microextraction coupled with gas chromatography-barrier discharge ionization detection. *Anal. Chem.* **2014**, *86*, 11640–11648. [CrossRef]
137. Jiang, H.; Li, J.; Hu, X.; Shen, J.; Sun, X.; Han, W.; Wang, L. Ordered mesoporous silica film as a novel fiber coating for solid-phase microextraction. *Talanta* **2017**, *174*, 307–313. [CrossRef]

138. Bagheri, H.; Akbarinejad, A.; Aghakhani, A. A highly thermal-resistant electrospun-based polyetherimide nanofibers coating for solid-phase microextraction Microextraction Techniques. *Anal. Bioanal. Chem.* **2014**, *406*, 2141–2149. [CrossRef]
139. Bagheri, H.; Roostaie, A. Roles of inorganic oxide nanoparticles on extraction efficiency of electrospun polyethylene terephthalate nanocomposite as an unbreakable fiber coating. *J. Chromatogr. A* **2015**, *1375*, 8–16. [CrossRef]
140. Sarafraz-Yazdi, A.; Yekkebashi, A. A non-ionic surfactant-mediated sol-gel coating for solid-phase microextraction of benzene, toluene, ethylbenzene and o-xylene in water samples using a gas chromatography-flame ionization detector. *New J. Chem.* **2014**, *38*, 4486–4493. [CrossRef]
141. Saraji, M.; Mehrafza, N. A simple approach for the preparation of simazine molecularly imprinted nanofibers via self-polycondensation for selective solid-phase microextraction. *Anal. Chim. Acta* **2016**, *936*, 108–115. [CrossRef]
142. Mirabelli, M.F.; Wolf, J.C.; Zenobi, R. Direct Coupling of Solid-Phase Microextraction with Mass Spectrometry: Sub-pg/g Sensitivity Achieved Using a Dielectric Barrier Discharge Ionization Source. *Anal. Chem.* **2016**, *88*, 7252–7258. [CrossRef] [PubMed]
143. Feng, J.; Sun, M.; Li, L.; Wang, X.; Duan, H.; Luo, C. Multiwalled carbon nanotubes-doped polymeric ionic liquids coating for multiple headspace solid-phase microextraction. *Talanta* **2014**, *123*, 18–24. [CrossRef] [PubMed]
144. Wu, M.; Wang, L.; Zeng, B.; Zhao, F. Ionic liquid polymer functionalized carbon nanotubes-doped poly(3,4-ethylenedioxythiophene) for highly efficient solid-phase microextraction of carbamate pesticides. *J. Chromatogr. A* **2016**, *1444*, 42–49. [CrossRef] [PubMed]
145. Ai, Y.; Zhang, J.; Zhao, F.; Zeng, B. Hydrophobic coating of polyaniline-poly(propylene oxide) copolymer for direct immersion solid phase microextraction of carbamate pesticides. *J. Chromatogr. A* **2015**, *1407*, 52–57. [CrossRef] [PubMed]
146. Cavaliere, B.; Monteleone, M.; Naccarato, A.; Sindona, G.; Tagarelli, A. A solid-phase microextraction-gas chromatographic approach combined with triple quadrupole mass spectrometry for the assay of carbamate pesticides in water samples. *J. Chromatogr. A* **2012**, *1257*, 149–157. [CrossRef] [PubMed]
147. Saraji, M.; Jafari, M.T.; Mossaddegh, M. Carbon nanotubes@silicon dioxide nanohybrids coating for solid-phase microextraction of organophosphorus pesticides followed by gas chromatography-corona discharge ion mobility spectrometric detection. *J. Chromatogr. A* **2016**, *1429*, 30–39. [CrossRef]
148. Jafari, M.T.; Saraji, M.; Sherafatmand, H. Polypyrrole/montmorillonite nanocomposite as a new solid phase microextraction fiber combined with gas chromatography-corona discharge ion mobility spectrometry for the simultaneous determination of diazinon and fenthion organophosphorus pesticides. *Anal. Chim. Acta* **2014**, *814*, 69–78. [CrossRef]
149. Kamalabadi, M.; Mohammadi, A.; Alizadeh, N. Polypyrrole nanowire as an excellent solid phase microextraction fiber for bisphenol A analysis in food samples followed by ion mobility spectrometry. *Talanta* **2016**, *156–157*, 147–153. [CrossRef]
150. Li, J.W.; Wang, Y.L.; Yan, S.; Li, X.J.; Pan, S.Y. Molecularly imprinted calixarene fiber for solid-phase microextraction of four organophosphorous pesticides in fruits. *Food Chem.* **2016**, *192*, 260–267. [CrossRef]
151. Liang, W.; Wang, J.; Zang, X.; Dong, W.; Wang, C.; Wang, Z. Barley husk carbon as the fiber coating for the solid-phase microextraction of twelve pesticides in vegetables prior to gas chromatography–mass spectrometric detection. *J. Chromatogr. A* **2017**, *1491*, 9–15. [CrossRef]
152. Wu, M.; Chen, G.; Liu, P.; Zhou, W.; Jia, Q. Polydopamine-based immobilization of a hydrazone covalent organic framework for headspace solid-phase microextraction of pyrethroids in vegetables and fruits. *J. Chromatogr. A* **2016**, *1456*, 34–41. [CrossRef] [PubMed]
153. Wu, M.; Chen, G.; Ma, J.; Liu, P.; Jia, Q. Fabrication of cross-linked hydrazone covalent organic frameworks by click chemistry and application to solid phase microextraction. *Talanta* **2016**, *161*, 350–358. [CrossRef] [PubMed]
154. Zhang, S.; Yang, Q.; Wang, W.; Wang, C.; Wang, Z. Covalent Bonding of Metal-Organic Framework-5/Graphene Oxide Hybrid Composite to Stainless Steel Fiber for Solid-Phase Microextraction of Triazole Fungicides from Fruit and Vegetable Samples. *J. Agric. Food Chem.* **2016**, *64*, 2792–2801. [CrossRef] [PubMed]

155. Zhang, S.; Yang, Q.; Li, Z.; Wang, W.; Wang, C.; Wang, Z. Zeolitic imidazole framework templated synthesis of nanoporous carbon as a novel fiber coating for solid-phase microextraction. *Analyst* **2016**, *141*, 1127–1135. [CrossRef] [PubMed]
156. Tian, M.; Cheng, R.; Ye, J.; Liu, X.; Jia, Q. Preparation and evaluation of ionic liquid-calixarene solid-phase microextraction fibres for the determination of triazines in fruit and vegetable samples. *Food Chem.* **2014**, *145*, 28–33. [CrossRef]
157. Gionfriddo, E.; Naccarato, A.; Sindona, G.; Tagarelli, A. A reliable solid phase microextraction-gas chromatography-triple quadrupole mass spectrometry method for the assay of selenomethionine and selenomethylselenocysteine in aqueous extracts: Difference between selenized and not-enriched selenium potatoes. *Anal. Chim. Acta* **2012**, *747*, 58–66. [CrossRef]
158. Hou, X.; Guo, Y.; Liang, X.; Wang, X.; Wang, L.; Wang, L.; Liu, X. Bis(trifluoromethanesulfonyl)imide-based ionic liquids grafted on graphene oxide-coated solid-phase microextraction fiber for extraction and enrichment of polycyclic aromatic hydrocarbons in potatoes and phthalate esters in food-wrap. *Talanta* **2016**, *153*, 392–400. [CrossRef]
159. Saraji, M.; Jafari, M.T.; Mossaddegh, M. Halloysite nanotubes-titanium dioxide as a solid-phase microextraction coating combined with negative corona discharge-ion mobility spectrometry for the determination of parathion. *Anal. Chim. Acta* **2016**, *926*, 55–62. [CrossRef]
160. Zhang, N.; Gao, J.; Huang, C.; Liu, W.; Tong, P.; Zhang, L. In situ hydrothermal growth of ZnO/g-C3N4 nanoflowers coated solid-phase microextraction fibers coupled with GC-MS for determination of pesticides residues. *Anal. Chim. Acta* **2016**, *934*, 122–131. [CrossRef]
161. Souza Silva, É.A.; Pawliszyn, J. Optimization of fiber coating structure enables direct immersion solid phase microextraction and high-throughput determination of complex samples. *Anal. Chem.* **2012**, *84*, 6933–6938. [CrossRef]
162. De Grazia, S.; Gionfriddo, E.; Pawliszyn, J. A new and efficient Solid Phase Microextraction approach for analysis of high fat content food samples using a matrix-compatible coating. *Talanta* **2017**, *167*, 754–760. [CrossRef] [PubMed]
163. Naccarato, A.; Pawliszyn, J. Matrix compatible solid phase microextraction coating, a greener approach to sample preparation in vegetable matrices. *Food Chem.* **2016**, *206*, 67–73. [CrossRef] [PubMed]
164. Souza-Silva, É.A.; Pawliszyn, J. Direct immersion solid-phase microextraction with matrix-compatible fiber coating for multiresidue pesticide analysis of grapes by gas chromatography-time-of-flight mass spectrometry (DI-SPME-GC-ToFMS). *J. Agric. Food Chem.* **2015**, *63*, 4464–4477. [CrossRef] [PubMed]
165. Brereton, R.G. *Chemometrics: Data Analysis for the Laboratory and Chemical Plant*; John Wiley & Sons, Ltd.: Chichester, UK, 2003; ISBN 0471489778.
166. Naccarato, A.; Furia, E.; Sindona, G.; Tagarelli, A. Multivariate class modeling techniques applied to multielement analysis for the verification of the geographical origin of chili pepper. *Food Chem.* **2016**, *206*, 217–222. [CrossRef] [PubMed]
167. Di Donna, L.; Mazzotti, F.; Naccarato, A.; Salerno, R.; Tagarelli, A.; Taverna, D.; Sindona, G. Secondary metabolites of Olea europaea leaves as markers for the discrimination of cultivars and cultivation zones by multivariate analysis. *Food Chem.* **2010**, *121*, 492–496. [CrossRef]
168. Abdulra'uf, L.B.; Tan, G.H. Chemometric approach to the optimization of HS-SPME/GC-MS for the determination of multiclass pesticide residues in fruits and vegetables. *Food Chem.* **2015**, *177*, 267–273. [CrossRef]
169. Wang, X.; Li, X.; Bai, Y.; Liu, H. Just dip it: Online coupling of "dip-it" polymer monolith microextraction with plasma assisted laser desorption ionization mass spectrometry. *Chem. Commun.* **2015**, *51*, 4615–4618. [CrossRef]
170. Gómez-Ríos, G.A.; Vasiljevic, T.; Gionfriddo, E.; Yu, M.; Pawliszyn, J. Towards on-site analysis of complex matrices by solid-phase microextraction-transmission mode coupled to a portable mass spectrometer: Via direct analysis in real time. *Analyst* **2017**, *142*, 2928–2935. [CrossRef]
171. Asiabi, H.; Yamini, Y.; Seidi, S.; Esrafili, A.; Rezaei, F. Electroplating of nanostructured polyaniline-polypyrrole composite coating in a stainless-steel tube for on-line in-tube solid phase microextraction. *J. Chromatogr. A* **2015**, *1397*, 19–26. [CrossRef]

172. de Souza Freitas, L.A.; Vieira, A.C.; Mendonça, J.A.F.R.; Figueiredo, E.C. Molecularly imprinted fibers with renewable surface for solid-phase microextraction of triazoles from grape juice samples followed by gas chromatography mass spectrometry analysis. *Analyst* **2014**, *139*, 626–632. [CrossRef]
173. Wu, M.; Chen, G.; Liu, P.; Zhou, W.; Jia, Q. Preparation of porous aromatic framework/ionic liquid hybrid composite coated solid-phase microextraction fibers and their application in the determination of organochlorine pesticides combined with GC-ECD detection. *Analyst* **2016**, *141*, 243–250. [CrossRef] [PubMed]
174. Pelit, F.O.; Pelit, L.; Dizdaş, T.N.; Aftafa, C.; Ertaş, H.; Yalçinkaya, E.E.; Türkmen, H.; Ertaş, F.N. A novel polythiophene - ionic liquid modified clay composite solid phase microextraction fiber: Preparation, characterization and application to pesticide analysis. *Anal. Chim. Acta* **2015**, *859*, 37–45. [CrossRef] [PubMed]
175. Viñas, P.; Pastor-Belda, M.; Torres, A.; Campillo, N.; Hernández-Córdoba, M. Use of oleic-acid functionalized nanoparticles for the magnetic solid-phase microextraction of alkylphenols in fruit juices using liquid chromatography-tandem mass spectrometry. *Talanta* **2016**, *151*, 217–223. [CrossRef] [PubMed]
176. Mirabelli, M.F.; Gionfriddo, E.; Pawliszyn, J.; Zenobi, R. A quantitative approach for pesticide analysis in grape juice by direct interfacing of a matrix compatible SPME phase to dielectric barrier discharge ionization-mass spectrometry. *Analyst* **2018**, *143*, 891–899. [CrossRef]
177. Lan, H.; Pan, D.; Sun, Y.; Guo, Y.; Wu, Z. Thin metal organic frameworks coatings by cathodic electrodeposition for solid-phase microextraction and analysis of trace exogenous estrogens in milk. *Anal. Chim. Acta* **2016**, *937*, 53–60. [CrossRef]
178. Merib, J.; Nardini, G.; Carasek, E. Use of Doehlert design in the optimization of extraction conditions in the determination of organochlorine pesticides in bovine milk samples by HS-SPME. *Anal. Methods* **2014**, *6*, 3254–3260. [CrossRef]
179. Lin, W.; Wei, S.; Jiang, R.; Zhu, F.; Ouyang, G. Calibration of the complex matrix effects on the sampling of polycyclic aromatic hydrocarbons in milk samples using solid phase microextraction. *Anal. Chim. Acta* **2016**, *933*, 117–123. [CrossRef]
180. Lv, F.; Gan, N.; Cao, Y.; Zhou, Y.; Zuo, R.; Dong, Y. A molybdenum disulfide/reduced graphene oxide fiber coating coupled with gas chromatography–mass spectrometry for the saponification-headspace solid-phase microextraction of polychlorinated biphenyls in food. *J. Chromatogr. A* **2017**, *1525*, 42–50. [CrossRef]
181. Joshi, M.D.; Ho, T.D.; Cole, W.T.S.; Anderson, J.L. Determination of polychlorinated biphenyls in ocean water and bovine milk using crosslinked polymeric ionic liquid sorbent coatings by solid-phase microextraction. *Talanta* **2014**, *118*, 172–179. [CrossRef]
182. Pang, J.; Yuan, D.; Huang, X. On-line combining monolith-based in-tube solid phase microextraction and high-performance liquid chromatography- fluorescence detection for the sensitive monitoring of polycyclic aromatic hydrocarbons in complex samples. *J. Chromatogr. A* **2018**, *1571*, 29–37. [CrossRef]
183. Roszkowska, A.; Yu, M.; Bessonneau, V.; Bragg, L.; Servos, M.; Pawliszyn, J. Metabolome Profiling of Fish Muscle Tissue Exposed to Benzo[a]pyrene Using in Vivo Solid-Phase Microextraction. *Environ. Sci. Technol. Lett.* **2018**, *5*, 431–435. [CrossRef]
184. Huang, S.; Xu, J.; Wu, J.; Hong, H.; Chen, G.; Jiang, R.; Zhu, F.; Liu, Y.; Ouyang, G. Rapid detection of five anesthetics in tilapias by in vivo solid phase microextraction coupling with gas chromatography-mass spectrometry. *Talanta* **2017**, *168*, 263–268. [CrossRef] [PubMed]
185. Delvaux Júnior, N.A.; de Queiroz, M.E.L.R.; Neves, A.A.; Oliveira, A.F.; da Silva, M.R.F.; Faroni, L.R.A.; Heleno, F.F. Headspace solid phase microextraction-gas chromatography for the determination of trihalomethanes in fish. *Microchem. J.* **2017**, *133*, 539–544. [CrossRef]
186. Hashemi-Moghaddam, H.; Ahmadifard, M. Novel molecularly imprinted solid-phase microextraction fiber coupled with gas chromatography for analysis of furan. *Talanta* **2016**, *150*, 148–154. [CrossRef] [PubMed]
187. Lin, S.; Gan, N.; Qiao, L.; Zhang, J.; Cao, Y.; Chen, Y. Magnetic metal-organic frameworks coated stir bar sorptive extraction coupled with GC-MS for determination of polychlorinated biphenyls in fish samples. *Talanta* **2015**, *144*, 1139–1145. [CrossRef] [PubMed]
188. Wang, W.; Wang, J.; Zhang, S.; Cui, P.; Wang, C.; Wang, Z. A novel Schiff base network-1 nanocomposite coated fiber for solid-phase microextraction of phenols from honey samples. *Talanta* **2016**, *161*, 22–30. [CrossRef]

189. Al-Alam, J.; Fajloun, Z.; Chbani, A.; Millet, M. A multiresidue method for the analysis of 90 pesticides, 16 PAHs, and 22 PCBs in honey using QuEChERS–SPME. *Anal. Bioanal. Chem.* **2017**, *409*, 5157–5169. [CrossRef]
190. Yang, M.; Wu, X.; Xi, X.; Zhang, P.; Yang, X.; Lu, R.; Zhou, W.; Zhang, S.; Gao, H.; Li, J. Using β-cyclodextrin/attapulgite-immobilized ionic liquid as sorbent in dispersive solid-phase microextraction to detect the benzoylurea insecticide contents of honey and tea beverages. *Food Chem.* **2016**, *197*, 1064–1072. [CrossRef]
191. Liang, W.; Wang, J.; Zang, X.; Wang, C.; Wang, Z. A porous carbon derived from amino-functionalized material of Institut Lavoisier as a solid-phase microextraction fiber coating for the extraction of phthalate esters from tea. *J. Sep. Sci.* **2016**, *39*, 1331–1338. [CrossRef]
192. Cheng, X.; Yan, H.; Wang, X.; Sun, N.; Qiao, X. Vortex-assisted magnetic dispersive solid-phase microextraction for rapid screening and recognition of dicofol residues in tea products. *Food Chem.* **2014**, *162*, 104–109. [CrossRef]
193. Ng, N.T.; Sanagi, M.M.; Wan Ibrahim, W.N.; Wan Ibrahim, W.A. Agarose-chitosan-C18 film micro-solid phase extraction combined with high performance liquid chromatography for the determination of phenanthrene and pyrene in chrysanthemum tea samples. *Food Chem.* **2017**, *222*, 28–34. [CrossRef] [PubMed]
194. Cagliero, C.; Nan, H.; Bicchi, C.; Anderson, J.L. Matrix-compatible sorbent coatings based on structurally tuned polymeric ionic liquids for the determination of acrylamide in brewed coffee and coffee powder using solid-phase microextraction. *J. Chromatogr. A* **2016**, *1459*, 17–23. [CrossRef] [PubMed]
195. Ho, T.D.; Toledo, B.R.; Hantao, L.W.; Anderson, J.L. Chemical immobilization of crosslinked polymeric ionic liquids on nitinol wires produces highly robust sorbent coatings for solid-phase microextraction. *Anal. Chim. Acta* **2014**, *843*, 18–26. [CrossRef] [PubMed]
196. Amanzadeh, H.; Yamini, Y.; Moradi, M.; Asl, Y.A. Determination of phthalate esters in drinking water and edible vegetable oil samples by headspace solid phase microextraction using graphene/polyvinylchloride nanocomposite coated fiber coupled to gas chromatography-flame ionization detector. *J. Chromatogr. A* **2016**, *1465*, 38–46. [CrossRef]
197. Wang, Y.; Sun, Y.; Xu, B.; Li, X.; Jin, R.; Zhang, H.; Song, D. Magnetic ionic liquid-based dispersive liquid-liquid microextraction for the determination of triazine herbicides in vegetable oils by liquid chromatography. *J. Chromatogr. A* **2014**, *1373*, 9–16. [CrossRef]
198. Wu, L.; Song, Y.; Hu, M.; Xu, X.; Zhang, H.; Yu, A.; Ma, Q.; Wang, Z. Determination of sulfonamides in butter samples by ionic liquid magnetic bar liquid-phase microextraction high-performance liquid chromatography. *Anal. Bioanal. Chem.* **2015**, *407*, 569–580. [CrossRef]
199. Matin, A.A.; Biparva, P.; Gheshlaghi, M. Gas chromatographic determination of polycyclic aromatic hydrocarbons in water and smoked rice samples after solid-phase microextraction using multiwalled carbon nanotube loaded hollow fiber. *J. Chromatogr. A* **2014**, *1374*, 50–57. [CrossRef]
200. Chen, D.; Huang, Y.Q.; He, X.M.; Shi, Z.G.; Feng, Y.Q. Coupling carbon nanotube film microextraction with desorption corona beam ionization for rapid analysis of Sudan dyes (I-IV) and Rhodamine B in chilli oil. *Analyst* **2015**, *140*, 1731–1738. [CrossRef]
201. Li, X.; Li, Z.; Wang, X.; Nie, H.; Zhang, Y.; Bai, Y.; Liu, H. Monolith dip-it: A bifunctional device for improving the sensitivity of direct analysis in real time mass spectrometry. *Analyst* **2016**, *141*, 4947–4952. [CrossRef]
202. Zhang, L.; Gionfriddo, E.; Acquaro, V.; Pawliszyn, J. Direct immersion solid-phase microextraction analysis of multi-class contaminants in edible seaweeds by gas chromatography-mass spectrometry. *Anal. Chim. Acta* **2018**, *1031*, 83–97. [CrossRef]
203. Jian, J.M.; Guo, Y.; Zeng, L.; Liang-Ying, L.; Lu, X.; Wang, F.; Zeng, E.Y. Global distribution of perfluorochemicals (PFCs) in potential human exposure source–A review. *Environ. Int.* **2017**, *108*, 51–62. [CrossRef] [PubMed]
204. Monteleone, M.; Naccarato, A.; Sindona, G.; Tagarelli, A. A rapid and sensitive assay of perfluorocarboxylic acids in aqueous matrices by headspace solid phase microextraction-gas chromatography-triple quadrupole mass spectrometry. *J. Chromatogr. A* **2012**, *1251*, 160–168. [CrossRef] [PubMed]
205. Ouyang, G.; Oakes, K.D.; Bragg, L.; Wang, S.; Liu, H.; Cui, S.; Servos, M.R.; Dixon, D.G.; Pawliszyn, J. Sampling-rate calibration for rapid and nonlethal monitoring of organic contaminants in fish muscle by solid-phase microextraction. *Environ. Sci. Technol.* **2011**, *45*, 7792–7798. [CrossRef] [PubMed]
206. Ouyang, G.; Vuckovic, D.; Pawliszyn, J. Nondestructive sampling of living systems using in vivo solid-phase microextraction. *Chem. Rev.* **2011**, *111*, 2784–2814. [CrossRef]

207. Wang, H.; Sun, W.; Zhang, J.; Yang, X.; Lin, T.; Ding, L. Desorption corona beam ionization source for mass spectrometry. *Analyst* **2010**, *135*, 688–695. [CrossRef]
208. World Health Organization Regional Office for Europe. *Human Biomonitoring: Facts and Figures*; WHO: Geneva, Switzerland, 2015.
209. Centers for Disease Control and Prevention—National Biomonitoring Program. Available online: https://www.cdc.gov/biomonitoring/ (accessed on 1 November 2019).
210. Souza-Silva, É.A.; Reyes-Garcés, N.; Gómez-Ríos, G.A.; Boyaci, E.; Bojko, B.; Pawliszyn, J. A critical review of the state of the art of solid-phase microextraction of complex matrices III. Bioanalytical and clinical applications. *TrAC Trends Anal. Chem.* **2015**, *71*, 249–264. [CrossRef]
211. Naccarato, A.; Gionfriddo, E.; Elliani, R.; Sindona, G.; Tagarelli, A. A fast and simple solid phase microextraction coupled with gas chromatography-triple quadrupole mass spectrometry method for the assay of urinary markers of glutaric acidemias. *J. Chromatogr. A* **2014**, *1372*, 253–259. [CrossRef]
212. 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]
213. Yang, B.C.; Fang, S.F.; Wan, X.J.; Luo, Y.; Zhou, J.Y.; Li, Y.; Li, Y.J.; Wang, F.; Huang, O.P. Quantification of monohydroxylated polycyclic aromatic hydrocarbons in human urine samples using solid-phase microextraction coupled with glass-capillary nanoelectrospray ionization mass spectrometry. *Anal. Chim. Acta* **2017**, *973*, 68–74. [CrossRef]
214. Antonucci, A.; Vitali, M.; Avino, P.; Manigrasso, M.; Protano, C. Sensitive multiresidue method by HS-SPME/GC-MS for 10 volatile organic compounds in urine matrix: A new tool for biomonitoring studies on children. *Anal. Bioanal. Chem.* **2016**, *408*, 5789–5800. [CrossRef]
215. Lamani, X.; Horst, S.; Zimmermann, T.; Schmidt, T.C. Determination of aromatic amines in human urine using comprehensive multi-dimensional gas chromatography mass spectrometry (GCxGC-qMS). *Anal. Bioanal. Chem.* **2015**, *407*, 241–252. [CrossRef] [PubMed]
216. Song, H.N.; Kim, C.H.; Lee, W.Y.; Cho, S.H. Simultaneous determination of volatile organic compounds with a wide range of polarities in urine by headspace solid-phase microextraction coupled to gas chromatography/mass spectrometry. *Rapid Commun. Mass Spectrom.* **2017**, *31*, 613–622. [CrossRef] [PubMed]
217. Koureas, M.; Karagkouni, F.; Rakitskii, V.; Hadjichristodoulou, C.; Tsatsakis, A.; Tsakalof, A. Serum levels of organochlorine pesticides in the general population of Thessaly, Greece, determined by HS-SPME GC-MS method. *Environ. Res.* **2016**, *148*, 318–321. [CrossRef] [PubMed]
218. Sajid, M.; Basheer, C.; Daud, M.; Alsharaa, A. Evaluation of layered double hydroxide/graphene hybrid as a sorbent in membrane-protected stir-bar supported micro-solid-phase extraction for determination of organochlorine pesticides in urine samples. *J. Chromatogr. A* **2017**, *1489*, 1–8. [CrossRef]
219. Wang, S.L.; Xu, H. Inorganic–organic hybrid coating material for the online in-tube solid-phase microextraction of monohydroxy polycyclic aromatic hydrocarbons in urine. *J. Sep. Sci.* **2016**, *39*, 4610–4620. [CrossRef]
220. Hardy, E.M.; Duca, R.C.; Salquebre, G.; Appenzeller, B.M.R. Multi-residue analysis of organic pollutants in hair and urine for matrices comparison. *Forensic Sci. Int.* **2015**, *249*, 6–19. [CrossRef]
221. Yamamoto, Y.; Ishizaki, A.; Kataoka, H. Biomonitoring method for the determination of polycyclic aromatic hydrocarbons in hair by online in-tube solid-phase microextraction coupled with high performance liquid chromatography and fluorescence detection. *J. Chromatogr. B Anal. Technol. Biomed. Life Sci.* **2015**, *1000*, 187–191. [CrossRef]
222. Tzatzarakis, M.N.; Barbounis, E.G.; Kavvalakis, M.P.; Vakonaki, E.; Renieri, E.; Vardavas, A.I.; Tsatsakis, A.M. Rapid method for the simultaneous determination of DDTs and PCBs in hair of children by headspace solid phase microextraction and gas chromatography-mass spectrometry (HSSPME/GC-MS). *Drug Test. Anal.* **2014**, *6*, 85–92. [CrossRef]
223. Flores-Ramírez, R.; Ortiz-Pérez, M.D.; Batres-Esquivel, L.; Castillo, C.G.; Ilizaliturri-Hernández, C.A.; Díaz-Barriga, F. Rapid analysis of persistent organic pollutants by solid phase microextraction in serum samples. *Talanta* **2014**, *123*, 169–178. [CrossRef]
224. Zhang, J.; Li, W.; Zhu, W.; Qin, P.; Lu, M.; Zhang, X.; Miao, Y.; Cai, Z. Mesoporous graphitic carbon nitride@NiCo 2 O 4 nanocomposite as a solid phase microextraction coating for sensitive determination of environmental pollutants in human serum samples. *Chem. Commun.* **2019**, *55*, 10019–10022. [CrossRef]

225. Meyer-Monath, M.; Beaumont, J.; Morel, I.; Rouget, F.; Tack, K.; Lestremau, F. Analysis of BTEX and chlorinated solvents in meconium by headspace-solid-phase microextraction gas chromatography coupled with mass spectrometry. *Anal. Bioanal. Chem.* **2014**, *406*, 4481–4490. [CrossRef] [PubMed]
226. de la Guardia, M.; Garrigues, S. *Handbook of Green Analytical Chemistry*; John Wiley & Sons, Ltd.: Chichester, UK, 2012; ISBN 9780470972014.