Chromatography **2015**, *2*, 293-381; doi:10.3390/chromatography2030293

OPEN ACCESS

chromatography

ISSN 2227-9075

www.mdpi.com/journal/chromatography

Review

Recent Developments and Applications of Solid Phase Microextraction (SPME) in Food and Environmental Analysis—A Review

Sybille Merkle [1,†], Kim Karen Kleeberg [2,†] and Jan Fritsche [1,*]

[1] Faculty Life Sciences, Department Nutrition & Home Economics/Food Science, Hamburg University of Applied Sciences, Ulmenliet 20, 21033, Hamburg, Germany; E-Mail: sybille.merkle@haw-hamburg.de

[2] ODOCON Dr. Kim Kleeberg & Dr. Jan Streese-Kleeberg GbR, Amtsstraße 7, 22143, Hamburg, Germany; E-Mail: info@odocon.de

† These authors contributed equally to this work.

* Author to whom correspondence should be addressed; E-Mail: jan.fritsche@haw-hamburg.de; Tel.: +49-40-42875-6163; Fax: +49-40-42875-6205.

Academic Editor: Mary Boyce

Received: 1 April 2015 / Accepted: 11 June 2015 / Published: 30 June 2015

Abstract: Solid-phase microextraction (SPME) is a simple, sensitive, rapid and solvent-free technique for the extraction of analytes from gaseous, liquid and solid samples and takes a leading position among microextraction methods. Application of SPME in sample preparation has been increasing continuously over the last decade. It is most often used as an automatized fiber injection system coupled to chromatographic separation modules for the extraction of volatile and semivolatile organic compounds and also allows for the trace analysis of compounds in complex matrices. Since SPME was first introduced in the early 1990s, several modifications have been made to adapt the procedure to specific application requirements. More robust fiber assemblies and coatings with higher extraction efficiencies, selectivity and stability have been commercialized. Automation and on-line coupling to analytical instruments have been achieved in many applications and new derivatization strategies as well as improved calibration procedures have been developed to overcome existing limitations regarding quantitation. Furthermore, devices using tubes, needles or tips for extraction instead of a fiber have been designed. In the field of food analysis, SPME has been most often applied to fruit/vegetables, fats/oils, wine, meat products, dairy and

beverages whereas environmental applications focus on the analysis of air, water, soil and sediment samples.

Keywords: SPME; food analysis; environmental analysis; volatile compounds; aroma; off-flavor; GC; LC; SBSE

1. Introduction

The quality of trace analysis in food and environmental samples mainly depends on the selected sample treatment [1]. There is an increasing demand for strategies minimizing the analyte-matrix interferences, especially in case of volatile compounds occurring at low concentrations in complex matrices. These conditions require the reduction of final volumes of analytes to furnish higher concentrations of analytes at low quantification limits [2]. Moreover, there is a demand for environmentally sustainable procedures that apply reduced volumes of organic solvents [2]. Another aspect of analytical method development is automation [3]. There are numerous advantages of automation, e.g., lower time consumption, increase of simplicity, lower probability of sample contamination and higher repeatability. These are just a few reasons for the widespread application of solid phase microextration (SPME) techniques [3].

SPME is a relatively recent and easy to automate technique for the extraction of analytes from gaseous, liquid, and solid matrices. The simple, rapid and solvent-free technique was introduced in the early 1990s by Pawliszyn and coworkers [4–6]. The SPME process is composed of two basic steps: (i) partitioning of analytes between the extraction phase and the sample matrix and (ii) desorption of concentrated extracts into an analytical instrument [7]. Due to the combination of sampling, extraction, pre-concentration and sample introduction into an analytical instrument in one single step, SPME has gained popularity in many fields of application in recent years, especially in routine laboratories and industrial applications [8–10]. Areas of application have been steadily growing, including food packaging and environmental uses.

Automatised fiber injection systems hyphenated with gas chromatographic (GC) and gas chromatography-mass spectrometry (GC-MS) separation modules are the most popular instruments combined with SPME in use [11]. These instrumental assemblies have been successfully applied to a wide variety of compounds, especially for the extraction of volatile and semivolatile organic compounds from complex sample matrices [12]. Due to the inaccessibility of weakly volatile or thermally labile compounds to GC or GC-MS, SPME was also developed for direct coupling to high-performance liquid chromatography (HPLC) and liquid chromatography-mass spectrometry (LC-MS) [12].

A number of reviews on SPME have already been published, dealing with food analysis [12–15], environmental analysis [16–21], calibration methods [22], SPME coatings [11,23–26], drug analysis [12,27], the analysis of specific compounds [28,29] and specific SPME techniques [30]. In addition, general overviews of SPME techniques and contemporary developments are provided by others [2,6,17,31].

This review provides a comprehensive overview on latest trends of SPME method development including new techniques and new devices, as well as essential parameters in SPME processes. The latest development of fiber coating development and the application of nanotechnology in SPME

technology are also covered extensively by the present review. Moreover, this review reports for the first time simultaneously on two important life sciences SPME application areas—food and environmental applications published over the last decade (2005–2015).

2. SPME Techniques

The underlying principle of the SPME methodology is based on the partitioning of analytes between a coated fiber and a sample. The reusable fiber is coated with a stationary phase, which can be a liquid polymer, a solid sorbent, or a combination of both [9]. A mass transfer begins after exposure to the vapour phase above a solution (HS-SPME) or direct immersion in the solution (DI-SPME). This process is driven by the second law of thermodynamics. Thereby the chemical potential of each compound should be equal. Once equilibrium is reached, the extracted compounds on the fiber are desorbed and inserted into the injection port of a chromatograph. The release of the analytes is accomplished in GC by thermal desorption and in HPLC by dissolution and subsequent injection of the elution solvent [32]. Both methods lead to detection of the substances by the analytical instrument detector. The application of SPME-LC has lagged behind SPME-GC, which might be due to the small number of commercially available SPME sorbents for LC applications, the lack of commercially available interfaces, long equilibration times, and the lack of automation [2].

The aim of SPME is to reach the equilibrium between the sample matrix and the coating of the SPME device as rapidly as possible [33]. Further exposure of the fiber after equilibrium has been reached does not increase the concentration of extracted compounds. For that reason, sample extraction and pre-concentration could be carried out in one single step [34].

SPME has several advantages over traditional extraction methods. It is not just a rapid, simple and solvent-free method, but it is also sensitive, provides linear results for a wide range of concentrations and analytes [2]. Notwithstanding the low concentrations of analytes, quantitative or semi-quantitative data are provided and losses that can occur during the extraction, concentration and clean-up steps of traditional sample procedures are mostly avoidable [2].

One of the main drawbacks of SPME techniques is the limited number of commercially available stationary phases (fiber materials) only roughly covering the scale of polarity of target analytes. In particular, the extraction of polar analytes from samples with a polar matrix poses a problem [35–39]. Other challenges are the relatively low recommended operating temperature (240–280 °C), the instability and swelling in organic solvents, breakage of the fiber, stripping of coatings, bending of the needle, and the cost as well as the limited lifetime of the fiber [2,36]. Furthermore, sample carry-over may occur [40] and high molecular weight compounds cannot be analyzed in combination with GC [36]. In certain cases, low extraction efficiencies are reported, in particular in case of very volatile, polar, or thermally unstable analytes [2]. The early theoretical and practical aspects of SPME have undergone continuous technical development over the years.

SPME techniques cover a wide range of sampling techniques, including field, *in situ* and air sampling. The two different implementations fiber SPME and in-tube SPME are frequently used [9]. Detailed SPME theory has been explained in a number of reviews [6,15,41,42].

2.1. Fiber Solid-Phase Microextraction

"Fiber"-SPME devices have been developed and currently represent the widespread SPME technique which comprises a fiber holder and a fiber assembly [41]. The fiber assembly consists of a 1- to 2-cm long retractable SPME fiber [41] and a built-in coated fiber that looks like a modified syringe [6,33]. After the sample is placed in a vial sealed with a septum-type cap, the SPME needle is pierced through the septum and the fiber is extended into the vial. The analytes partition between the sample matrix and the extraction phase until equilibrium of concentrations is reached. The maximum sensitivity is achieved and a proportional relationship is obtained between the amount of the extracted analyte by the SPME fiber and its initial concentration in the sample [43,44].

2.2. In-tube Solid-Phase Microextraction

The more recent in-tube (IT) SPME was developed by Eisert and Pawliszyn [45] for application with HPLC or liquid chromatography (LC)-MS because fiber SPME could barely withstand aggressive HPLC solvent conditions [6,45]. In-tube SPME overcomes fiber-related drawbacks such as fragility, low sorption capacity and bleeding from thick-film coatings. It uses an open tubular fused-silica capillary in which the extraction phase is either an inner surface coating or a sorbent bed. Consequently, in-tube SPME devices exhibit considerably higher mechanical stability than fiber SPME devices. Another reason for the development of in-tube SPME was the lack of automation in the use of SPME coupled to HPLC [2]. By means of automation it is possible to perform extraction, desorption and injection simultaneously [6,12]. The advantages of automated systems compared to manual techniques are shorter total analysis times as well as higher accuracy and precision [2]. A drawback of in-tube SPME is the tendency of the capillary to clog up. This can be avoided by working with samples without interfering phases like particles or macromolecules [2]. Moreover, the enrichment factor is reduced compared to fiber SPME [2]. Kataoka [30] and Globig and Weickhardt [46] provided an overview of automated sample preparation using in-tube SPME and applications of this technique in environmental, clinical and food analysis, mainly for the determination of polar and thermolabile compounds.

In-tube SPME can be categorized into methods using *extraction coatings* where the coating is used as an internal extraction phase immobilized in the capillary wall and methods using *extraction fillings* where the extraction phase is a sorbent packing, as demonstrated in Figure 1 [47].

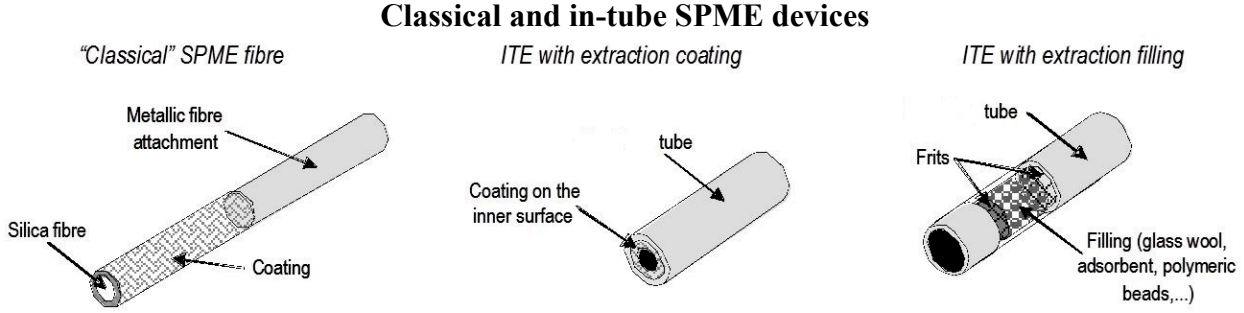

Figure 1. "Classical" solid-phase microextraction (SPME) fiber compared with in-tube fibers, adapted from Nerín *et al.* (2009) [2], reprinted with permission of Springer Verlag.

The latter techniques are particularly similar to the previously developed solid-phase extraction (SPE) and use different sorbent types. Both in-tube SPME techniques can be easily applied with existing autosampler systems. Several in-tube devices with extraction fillings have been developed, firstly in 2004 by Kubinek *et al.* [48], and are now commercially available, for example as in-tube extraction (ITEX) [2].

There are two modes of extraction in in-tube SPME. In the static mode, the analytes are transferred to the stationary phase by mere diffusion, while in the dynamic mode, the sample is actively drawn through the tube by repeated draw/eject cycles [49]. When the equilibrium is virtually reached, the extracted analytes are desorbed from the capillary either by direct transfer to the liquid chromatographic column or by a stream of the mobile phase. In case of a stronger attachment of the analytes to the capillary, desorption is achieved by a static desorption solvent which is subsequently injected into the chromatographic system [50]. The desorbed analytes are carried through the column and separated and detected by a mass selective detector [9].

Even though in-tube SPME was originally developed for HPLC applications, it can also be used with other instrumental equipment, for example capillary electrophoresis (CE) or GC [30]. On-line coupling to GC can be achieved by open-tubular trapping (OTT), which is mainly applied to HS samples [30]. In OTT, desorption of the analytes is carried out with a small amount of solvent or by thermal desorption. However, OTT is characterized by a complex instrumental setup and unfavorable sampling conditions, such as high pressure drop from long traps and limited flow rates [2].

In-tube SPME techniques have been developed further and modifications like *wire-in-tube and fiber-in-tube techniques* have emerged [51]. The wire-in-tube technique contains an additional stainless steel wire inserted into the extraction capillary. Thereby the surface of the coating material stay more or less the same, but the internal volume of the capillary is significantly reduced. A change in the phase ratio takes place which leads to preconcentration of the sample. This results in a more effective extraction [51]. In the fiber-in-tube technique, the extraction phase comprises several hundreds of delicate filaments of polymeric material packed longitudinally into a short capillary. This composition leads to enhanced pre-concentration of analytes [9].

2.3. Cooled Coated Fiber Device

Apart from in-tube SPME, procedures using a cooled fiber and other methods that do not necessarily rely on the use of a fiber have emerged. These new developments will be explained in the following section.

A recent development in the application of HS-SPME is an internally cooled coated fiber device (CCF) or cold fiber HS-SPME device. The main reason for developing this method was the improved release of analytes from the interfering phases in complex matrices [52,53].

For desorption of analytes from solid particles it is often useful to increase the extraction temperature. However absorption of analytes by the fiber coating is an exothermic process, therefore this process leads to a decrease of the partition coefficients [2]. The aim is to accelerate the mass transfer process and simultaneously increase the distribution constants of analytes [2]. For that purpose, an internally cooled coated fiber device was developed heating the sample matrix at the same time as the fiber coating is cooled down. Especially for matrices with high viscosity or for volatiles with low partition coefficients CCF is useful [2]. This technology was successfully employed for the first time to extract analytes from

various environmental matrices [52–54]. CCF was also successfully applied to food analysis, such as extracting volatiles and semivolatiles from tropical fruit pulps by Carasek and Pawliszyn (2006). They stated that the cold fiber was the most suitable fiber for the purpose of extracting volatile compounds from the five fruit pulps studied [55]. Additionally, it was reported that cold-fiber HS-SPME offers more sensitivity and higher sample throughput than conventional HS-SPME [56]. One drawback, however, of the increased fiber capacity through this cooled coated fiber is the loss of selectivity [2]. Not only the analytes but also the interferences are extracted exhaustively onto the coating [6]. CCF has been miniaturized and automated first by Chen and Pawliszyn (2006) [53] and is nowadays routinely used (see Figure 2) [2].

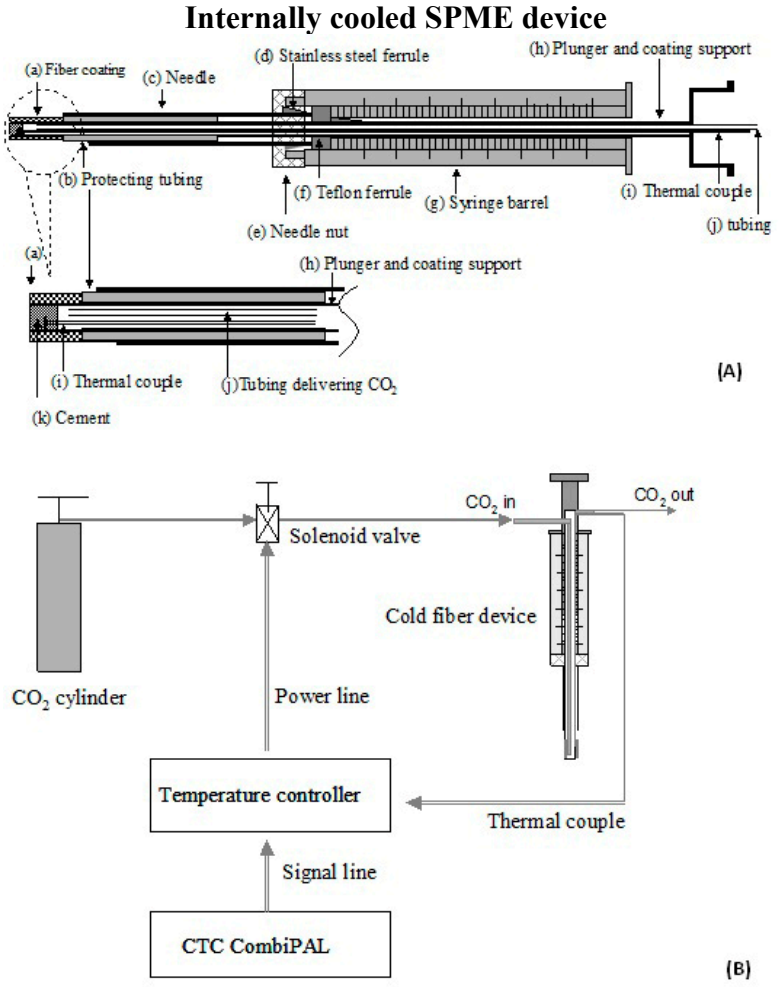

Figure 2. Internally cooled SPME device (**A**) and its automation (**B**) according to Chen and Pawliszyn (2006) [53], reprinted with permission of the American Chemical Society.

2.4. Non-fiber SPME Techniques

Non-fiber SPME techniques developed over the last two decades can be divided into static methods using sample stirring and dynamic techniques relying on the flow-through of the sample. The former include stir-bar sorptive extraction (SBSE) and thin-film microextraction (TFME). The latter can be classified as in-needle and in-tip SPME [21,47]. Figure 3 provides an overview of these new techniques.

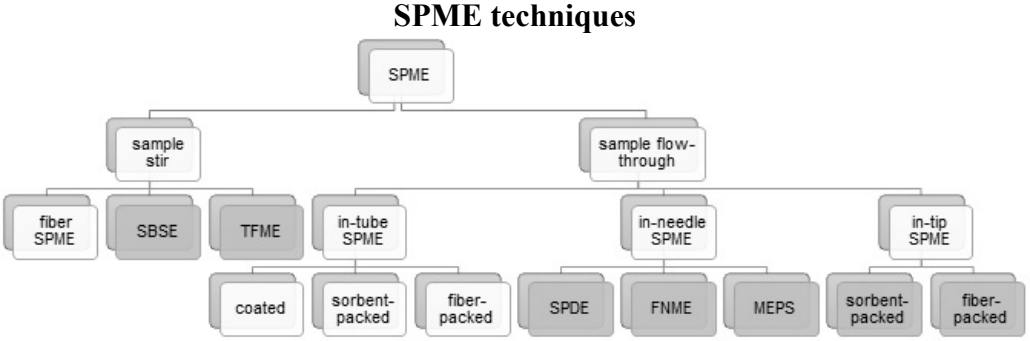

Figure 3. Overview of SPME techniques–techniques marked in grey are more recent developments (SBSE: stir-bar sorptive extraction; TFME: thin-film microextraction; SPDE: solid-phase dynamic extraction; FNME: fiber-packed needle microextraction; MEPS: microextraction by packed syringe).

In *stir-bar sorptive extraction* (SBSE), a magnetic stir bar coated with polydimethylsiloxane (PDMS) is stirred in or positioned above an aqueous sample [21,50]. After extraction, the stir bar is removed, which is usually done manually with tweezers. In case of a SBSE-GC coupling, desorption of the analytes is induced by inserting the bar into the heated GC injection port or by placing it in a small vial and back-extracting with a few microliters of an appropriate liquid solvent. In case of LC, the mobile phase can be added directly to the stir bar. Compared to fiber SPME, SBSE has a higher concentration capacity as the PDMS and the layer is 50 to 250 times thicker [21,50]. However, SBSE is not yet as widely accepted as fiber SPME due to the difficulty of achieving full automation and the limited number of commercially available coatings [21,50]. Dual-phase twisters using different carbon-based adsorbents in addition to PDMS are being developed at the moment as well as other phases covering a wide range of polarities and containing polymers like poly(methacrylic acid stearyl ester-ethylene dimethacrylate) and polypyrrole [21,50].

In *thin-film microextraction* (TFME), a flat film with a high surface area-to-volume ratio is used as the extraction phase [57,58]. This higher surface-to-volume ratio as well as an increased volume of extraction phase result in an enhanced sensitivity compared to conventional SPME without sacrificing the sampling time.The first step in TFME is the conditioning of the blades. Subsequently, the blades are exposed to the sample to extract the analytes [57,58]. A 96-well plate is placed on an orbital shaker for agitation. After washing with an appropriate solution to remove interfering substances, the blades can be transferred to a second 96-well plate containing the desorption solvent which is eventually injected into the chromatograph. A robotic workstation providing full automation of all the TFME steps including conditioning, extraction, washing and desorption may be used [57,58]. Moreover, coupling to liquid and gas chromatographic systems is possible [57,58]. TFME can be applied to gaseous, liquid and solid samples and is used in different sampling formats. In combination with liquid chromatography, it can be easily performed in a 96-well plate thus allowing for simultaneous analyses. The first TFME application used 96 pieces of small cut SPE disk membranes mounted on a stainless steel wire for support [57,58]. Nowadays, the extraction phase is coated onto a blade-shaped substrate and PDMS is the most common sorbent [57,58].

In case of coupling TFME to a gas chromatograph, desorption may also be achieved by direct thin-film injection inside a thermal desorption unit adapted to the special requirements of the thin-film with its particular geometry. The thermal desorption unit contains a large volume inlet and a programmed temperature vaporizer. The latter cryotraps the desorbed compounds. Once the thermal desorption process is completed, the cryotrap is heated and the trapped substances are transferred to the GC column [57,58]. In contrast to solvent desorption, direct thin-film injection allows for a complete introduction of the extracted analytes into the chromatograph [57,58]. As a thermal desorption unit is not always available and as solvent-desorption can be carried out in full automation, the latter is often used in practice [57,58].

In-needle SPME methods use a needle instead of a tube for extraction. In 2001, Koziel *et al*. [59] developed a needle trap (NT) device with quartz wool in order to trap particulate matter and aerosols in air. Wang *et al*. [60] used this development as a basis for the design of a sorbent-packed NT device for the analysis of VOCs in gaseous samples. The NT device was particularly robust because the quartz wool was protected by the needle. In 2006, Saito *et al*. [61] developed an in-needle extraction device for the analysis of VOCs using a copolymer of methacrylic acid and ethylene glycol dimethacrylate, which made the procedure more convenient [50,62–64]. This needle showed high extraction performance and thermal stability and was therefore suitable for typical GC applications. Also, the extracted analytes were very stable and could be analyzed even after several days of storage at room temperature [50,62–64].

Today, in-needle SPME methods can be classified as solid-phase dynamic extraction (SPDE), microextraction by packed syringe (MEPS) and fiber-packed needle microextraction (FNME). In SPDE, the analytes derived from a liquid or HS sample are concentrated onto a film of PDMS and 10% activated carbon coated on the inner wall of a stainless steel needle of a 2.5-mL gas-tight syringe by repeatedly moving the plunger of the syringe up and down [50,62–64]. Recovery of the trapped substances takes place by heat desorption directly into the GC injection port. Full automation is possible [50,62–64]. The first commercially available SPDE devices were developed in 2000 by Chromtech (Idstein, Germany) [50,62–64]. Lipinski [64] was the first who applied SPDE for the analysis of pesticides in water [50,62–64]. A significant advantage of SPDE over fiber SPME is the larger coating volume, which is approximately four to five times the volume of a 100-µm fiber and causes an increased in concentration capacity. Moreover, the extraction time is shorter, the repeatability better and the mechanical stability of the SPDE device higher [50,62–64]. On the other hand, carry-over may be an issue in SPDE as the analytes tend to remain on the inner surface of the needle after heat desorption [50,62–64].

Microextraction by packed syringe (MEPS) is a miniaturized form of the classical SPE where sample extraction takes place in a packed bed [50,62–64]. MEPS can be on-line coupled to liquid and gas chromatographic systems and is easily performed in automation. In contrast to SPE, the solid packing material is inserted directly into a needle coupled with a syringe and not into a separate column [50,62–64]. Furthermore, the sample preparation time as well as the volume of the sample and the organic solvents are considerably reduced and the MEPS sorbent can be used up to 100 times [50,62–64]. Sorbent materials include reversed phase (C2, C8 and C18), normal phase (silica), restricted access material (RAM) and molecular imprinted polymers (MIPs) [50,62–64]. After the packed bed has been conditioned, the sample solution is pumped several times through the syringe. The sorbent is then washed and the analytes are eluted either with an organic solvent which is injected into the chromatograph afterwards or with the LC mobile phase directly into the chromatographic injector [50,62–64]. Fiber-packed needle

microextraction (FNME) is an alternative technique using fiber instead of particle materials inside the needle [50,62–64].

In-tip SPME differs from MEPS in that the solid packing material is inserted into pipette tips rather than a needle. As extraction is generally done off-line, only parts of the sample are injected into the chromatograph resulting in a lower sensitivity compared to on-line MEPS [50]. On the other hand, a major benefit of in-tip SPME is that several samples can be handled in parallel. Automation is possible by commercially available systems using 96-well extraction plates and a rosdbot [50]. Sorbents used for in-tip SPME comprise silica and methacrylate monoliths. In contrast to fiber and in-tube SPME, in-tip SPME and MEPS provide quantitative recoveries [50]. On the other hand, these techniques exhibit only a moderate enrichment capacity and they have a tendency towards carry-over [50].

3. SPME Process

This section will provide an overview of the different available extraction and desorption techniques for SPME applications. The variety of these techniques is shown in Figure 4. Furthermore it will provide recent information on commercially available fiber coatings as well as current developments in fiber coating procedures. Finally, aspects of quantitation techniques applicable for SPME will be described.

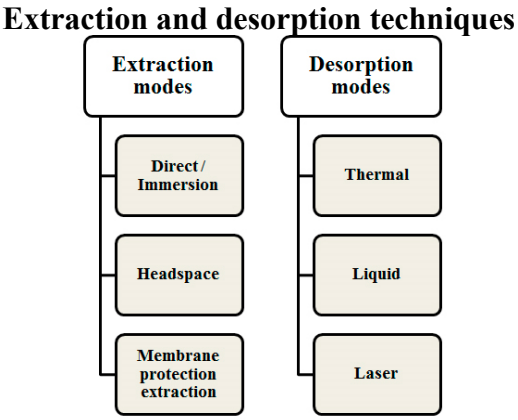

Figure 4. Extraction and desorption techniques for SPME applications.

3.1. Extraction and Desorption Techniques

The extraction process of fiber SPME can be conducted in three common ways: *direct or immersion extraction (DI)*, *headspace (HS) and membrane protection extraction* (see Figures 5 and 6). In *Direct SPME* the fiber is directly immersed in a gaseous or liquid sample. In case of a liquid sample certain agitation is required to reduce the extraction time. For volatile compounds in gaseous samples, the natural occurring air flow is often sufficient to reach the equilibrium [65].

In *HS-SPME* the fiber is exposed to the vapor phase above the liquid or solid sample [9]. The advantages are the protection of the fiber from damaging substances of the sample matrix and a possible adjustment of pH conditions. Only for very volatile compounds a significant difference between DI-SPME and HS-SPME techniques was observed [66]. The extraction kinetics are governed by Henry's law [67]. If the Henry's constant of a given substance is high, then the concentration of the compounds in the headspace is high, too. Under these conditions a rapid extraction from the headspace takes place.

In case of aqueous sample matrices, volatile and non-polar compounds are extracted faster than semi-volatiles and polar volatiles [65]. Moreover, increasing sample temperature and agitation efficacy may decrease the extraction time [65].

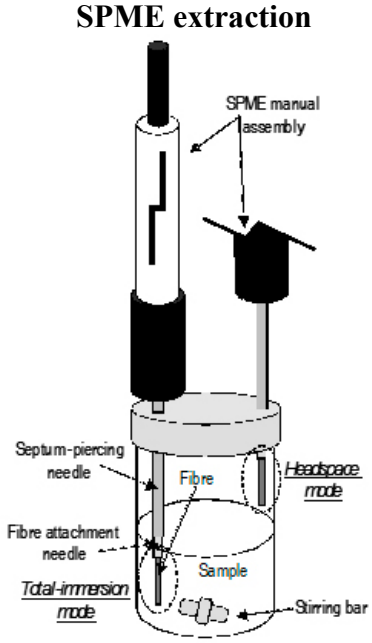

Figure 5. SPME procedure for total-immersion and headspace sampling according to Nerín *et al.* (2009) [2], reprinted with permission of Springer-Verlag.

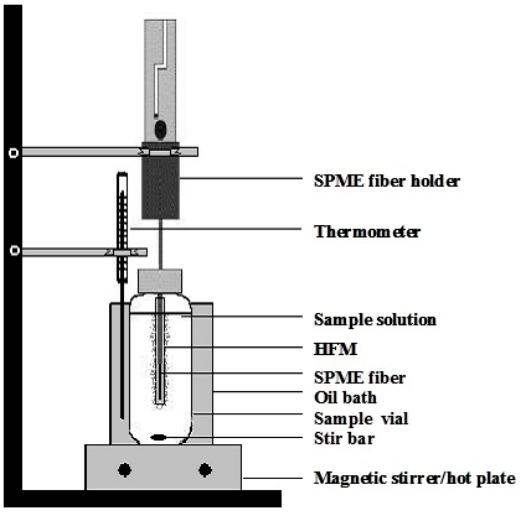

Figure 6. SPME procedure for membrane protection sampling according to Basheer and Lee (2004) [68], reprinted with permission of Elsevier B.V. (HFM: hollow fiber membrane).

In static headspace sampling, diffusion occurs between the fiber and the sample without any interference, whereas dynamic headspace sampling involves air movement devices like air sampling pumps that serve to move the headspace air [69]. To collect and pre-concentrate the headspace gas, the headspace air is transferred into another chamber where the SPME filament or another extraction trap is present [70].

An advantage of static headspace sampling in comparison with dynamic headspace sampling is that static headspace sampling does not require careful calibration processes and expensive air sampling pumps [71]. However, differences in temperature and pressure affect the efficiency of the static sampling process as well as wall effects from sampling containers that also play a role [69]. In summary static headspace sampling shows advantages of simplicity, sensitivity, selectivity and ease of automation over dynamic headspace sampling techniques [72].

The third extraction technique is the *membrane protection extraction*. Extraction which is typically applied to the analysis of samples containing interfering compounds such as proteins, humic acids and fatty material [68]. It is important to prevent the extraction of these high molecular weight compounds which potentially complicate, or even inhibit, sample analysis [68]. The extraction is conducted using a membrane which is selectively permeable for analytes of interest [68]. Membran protection extraction is slow in comparison with other extraction techniques, but effectively extracts compounds with low volatility [65].

All extraction procedures require an optimization of performing parameters in order to achieve good reproducibility, resulting from a compromise between sensitivity and extraction time. Method optimization parameters include agitation conditions, extraction time, extraction technique, temperature, headspace and sample volume vial shape, condition of fiber coating, depth of the SPME fiber inside the vial, geometry of the fiber, and pH conditions [33,73].

After extraction, target analytes are introduced into a suitable instrument for detection [74]. *Desorption* can be proceed in two different ways; static mode, by dipping the fiber into the mobile phase or solvent for a specified period, and dynamic mode, where the analytes are desorbed into a flowing mobile phase [65]. It is important to identify desorption solutions that completely remove the analytes from the fiber, eliminating carry over, but that do not damage the sorbent material or degrade the analytes of interest [74].

In the case of a GC coupling the analytes are released by *thermal desorption*, for which the SPME fiber is inserted into the GC inlet and heated to temperatures that increase analyte volatility sufficient for their release. The analytes are physically released from the sorbent through heating whereby the volatility of the target compounds is increased. The carrier gas flow rate and the injector temperature are critical factors for effective thermal desorption [75]. High desorption temperatures effect rapid transfer of the target analytes from the injector to the chromatographic column, but may reduce the stability of the sorbent and lead to bleeding of the polymeric material [73]. Therefore the thermal stability of the fiber coating determines the upper desorption temperature limit [74].

Combined with an HPLC interface desorption is performed by solvent extraction in the desorption chamber [12], namely *liquid desorption*. Liquid desorption is conducted using a small volume of suitable solvents to transfer the target analytes to the analytical instrumentation [74]. Desorption of the analytes can also be conducted using a polar organic solvent, such as methanol or acetonitrile [65]. This approach is often used in combination with liquid chromatography (LC) [65]. For thermally labile compounds liquid desorption has the advantage of not requiring elevated temperatures compared to thermal desorption [74]. Liquid desorption is the combination of SPME with HPLC where desorption is achieved using an appropriate extraction solvent in a desorption chamber. Individually designed desorption interfaces have been reported [51,76]. There is a commercially available device that enables desorption of all analytes directly into the LC injector [65].

Another form of desorption is conducted by means of *laser techniques*. SPME in combination with matrix-assisted laser desorption/ionization mass spectrometry was reported [74,77].

3.2. Derivatization

Under some conditions target analytes cannot be efficiently extracted or determined by the applied method due to the physicochemical properties of the analytes or the composition of the matrix. In these cases derivatization may modify the analytes and improve their extraction, desorption, or chromatography relative to matrix interferences. Derivatization might also improve the separation performance of analytes with poor chromatographic behavior [78]. Desired requirements for derivatization reactions are a fast and quantitatively formation at room temperature as well as a high stability and solubility in the applied solvent or phase [74].

There are different derivatization methods applicable for SPME (see Figure 7). The main difference of the various derivatisation approaches is the point of time when the derivatization reactions take place. Firstly, the derivatization reaction can be conducted by directly adding the derivatizing agent to the sample, named direct or pre-extraction derivatization. Furthermore, the reaction can take place during the extraction process (simultaneous derivatization and extraction) or immediately after that (derivatization following extraction or post-extraction derivatization). Under these conditions, the derivatization is performed by exposing the enriched SPME fiber to the derivatization agent solution after the extraction [74]. Another option is the post-extraction derivatization, which take place in the injection port of a gas chromatograph through thermal conversion (derivatization in GC Injector Port (see Figure 7).

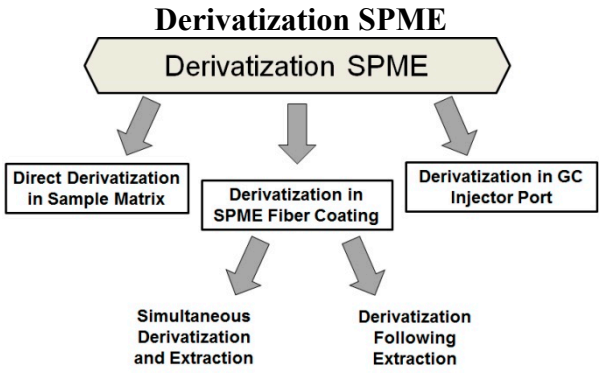

Figure 7. Classification of derivatization techniques in SPME, adapted from Pan and Pawliszyn (1997) [79].

In *direct derivatization* the chemical structure of the analyte is modified. Afterwards the common extraction and desorption procedures are performed. The obtained derivatives show better performance characteristics than the original analytes by respective extraction phases [79]. Direct derivatization is a simple derivatization technique and is frequently applied and easy to implement [74].

Another option for derivatization takes place *simultaneously with the extraction process* or *after the extraction process*. Due to the combination of extraction and derivatization this procedure is quite convenient to apply and the time needed for the analysis can be significantly reduced [74]. Barriers of this procedure are the compatibility of the derivatizing agent with the extraction phase and with the applied extraction method [74]. However, optimization of the composition of the derivatizing agent is

frequently required [74]. Therefore, post-extraction derivatization is preferred when extraction and derivatization cannot be conducted simultaneously or the partition coefficients of the derivative agents are lower than those of the analytes [74].

Injection port derivatization is a post-extraction derivatization procedure, for which analytes containingpolar functional groups such as –OH, –SH, –NH, and –COOH are thermally converted into derivatives.

Derivatization in food analysis for example has been applied for analysis of chlorophenols and chloroanisoles in wine [80] or formaldehyde in fish products [81]. Interesting fields of application of derivatization in environmental samples are, for example, the analysis of formaldehyde and other carbonyl compounds in indoor air [82], organometallic compounds (mercury, lead, tin) in river and seawater [83] or organotin compounds in sediment [84]. Further applications of derivatization in the fields of food [80,81,85,86] and environment [82–84,87–96] are provided in Section 3 and 4, respectively. Recently, commonly used derivatization agents were reviewed by Quintana and Rodriguez [97] and Stalikas and Fiamegos [78].

The main drawback of derivatization, however is the formation of artefacts or increased matrix interferences [74]. Furthermore, derivatization reactions favors the generation of waste and therefore, it is recommended to avoid them where possible [98].

3.3. Salt-addition

The addition of salting-out reagents, usually sodium chloride or sodium sulphate, increases the ionic strength of the solution. The extraction efficiency is improved by decreasing the solubility of analytes, thus increasing the amount of analyte sorbed on the fiber. However it should be realized that this effect depends on the particular analyte and salt concentration in the sample [99].

3.4. Fiber Coatings

The choice of the fiber coating mainly depends on the nature of the analytes. Before a sample is analyzed, the fiber should be cleaned in order to remove contaminants that might increase background noise in the chromatogram [65]. Frequently used commercially available fiber coatings for food and environmental analysis are polydimethylsiloxane (PDMS), polyacylate (PA), Carboxen (CAR; a carbon molecular sieve), divinylbenzene (DVB), and Carbowax (CW; polyethylene glycol). These fibers are available in various coating combinations, blends or copolymers, film thicknesses, and fiber assemblies. The variety is constantly growing increasing the number of applications [11]. The most widespread examples of absorption or liquid fiber coatings are PDMS and PA. Mixed coatings in which the primary extraction phase is a porous solid are also available [100]. CAR/PDMS and DVB/CAR/PDMS fibers provide the best extraction efficiencies for a wide range of analytes with different polarities and molecular weights [65]. PDMS has the ability to withstand high temperatures up to 300 °C and shows great stability [65]. PDMS fibers are better suited to the analysis of nonpolar analytes, whereas PA fibers are more useful to extract polar analytes [65]. DVB is also a polar porous solid coating and therefore efficient in extracting polar compounds such as disulfides and trisulfides [101]. Bipolar compounds like alcohols, aldehydes, ketones, ethers and carboxylic acids are often most efficiently extracted by fibers consisting of a combination of e.g., non-polar material (PDMS) and a polar material (DVB) [65].

Another appropriate choice to extract analytes with different polarities are coating mixtures consisting of CARB/PDMS or DVB/CARB/PDMS [65]. However, a disadvantage of this coating material is the displacement effect of analytes with a lower affinity to the coating [102]. Apart from commercially-available sorbents, different new coating procedures have been applied to expand coating types in the commercially applicable and reproducible SPME devices. These new approaches also address biocompatibility, on-site compatibility, selectivity and sensitivity limitations [103,104]. One can differentiate coating procedures based on the sorbent type into dipping and physical agglutinating methods, sol-gel technology, chemical grafting, electrochemical methods, electrospinning, liquid-phase deposition and the hydrothermal method [24]. Further new coatings are polypyrrole polymer coatings [105], molecularly imprinted polymers (MIPs) [106] and immunoaffinity systems [107].

The following section gives a brief overview of the variety of coating procedures. More detailed information, including advantages and disadvantages of various coatings, is available in other recent technology reviews [11,24].

Table 1 lists the different coating procedures, sorbent materials and examples of applications.

Physical coating processes were the first to be developed and constitute the most convenient procedures [11]. They are compatible with nearly all kinds of sorbent materials. Application of new coatings such as carbon nanomaterials (CNMs), ordered mesoporous materials, ionic liquids (ILs) and polymeric ionic liquids (PILs) is very simple. These coatings can be used for fused silica fibers as well as for metal wires. The Dipping process is conducted by placing a fiber in a concentrated organic solvent solution of the material to be deposited for a short time. Crosslinking of the deposited material can take place after evaporation of the solvent by drying. In case of a metal wire, support material can be attached using a sticky paste layer of the sorbent (epoxy or similar) [11,24].

An alternative to physical coating procedures is the sol-gel technology developed by Chong and co-workers (1997) [108]. Sol-gel process is based on the building of an inorganic network consisting of a colloidal suspension (sol) and gelation of this sol which forms a network in a continuous liquid phase (gel). The extraction phase can be chemically bonded to the silica thus producing highly cross-linked phase networks [2]. The precursors for the synthesis of the colloids consist of a metal or metalloid element (alkoxysilanes tetramethoxysilane or tetraethoxysilane (TMOS/TEOS) surrounded by various reactive ligands [109]. The sol-gel fibers therefore exhibit higher thermal stability, hydrolytic stability towards organic solvents as well as high and low pH solutions, and higher surface areas. Molecularly selective coatings can be prepared by using substances with specific functionalities such as crown ethers or ß-cyclodextrin derivatives [2]. Kumar *et al.* (2008) published a review on the development of sol-gel methods including various applications (e.g., PAHs, aromatic amines, phenols and pesticides) in environmental, pharmaceutical and food analysis [2,25]. A large number of new extraction phases with unique features have been introduced by application of the sol-gel technology. The most important advancements are summarized in Table 1. As there is no standardized sol-gel procedure, this new technology lacks inter-laboratory reproducibility [11]. Further disadvantages of the sol-gel technology are the large number of optimization factors and the fragility of the fused silica fiber used mostly as a support. Due to these limitations of the sol-gel procedures, simple chemical grafting has been developed. In this technique, the surface of the sorbents and supports are chemically modified in order to allow them to react with each other. Possible sorbents applicable to both metal wires and fused silica fibers are nanomaterials, antibodies, MIPs, ILs and PILs [24].

Electrochemical procedures are able to generate extraction films of variable thickness on an unbreakable metal support at a low cost and with a simple setup. Coatings show high thermal stability, have a long shelf life and some may provide higher capability to sorb polar compounds. Electrochemical procedures may be divided into electrodeposition, anodization and electrophoretic deposition (EPD) [110]. Electrodeposition can be used to create coatings with porous structure and refers to the deposition of a metallic or conductive polymer (CP) coating onto a base material by the electrochemical reduction of metal ions or electropolymerization of CPs from an electrolyte. This technique has been applied to the coating of metal supports with CPs, CPs nanocomposites, PIL composites and metal oxides [24]. Anodized metal wires were first developed by Djozan and co-workers in 2001 [111]. They anodized aluminum wires by direct current in sulfuric acid to obtain a porous layer of aluminum oxide on the aluminum surface [110]. Electrophoretic deposition (EPD) is a direct particle assembly method that is based on particle coagulation rather than an electrochemical reaction. Charged nanoparticles from a solution are deposited onto a substrate using an electric field [24]. Single-walled carbon nanotube (SWCNT) [112–114] and multi-walled carbon nanotube (MWCNT) [115] coatings have been prepared on the surfaces of platinum and stainless steel wires, respectively. In EPD, adsorption takes place in the spaces between the nanotubes and amorphous carbon in a three-dimensional network of nanotubes [24].

In electrospinning, a solution of a high molecular weight polymer with high viscosity is drawn into nanofibers by repulsive electrostatic forces. Zewe *et al.* (2010) were the first to prepare nanostructured polymeric based SPME coatings by electrospinning. They used a polymeric negative photoresist, SU-8 2100, which was converted to carbon by pyrolysis. The resultant SPME devices were used to extract both nonpolar and polar compounds [116].

Lin *et al.* (2008) employed liquid phase deposition (LPD) to produce a nanomaterial-based in-tube SPME coating with increased extraction efficiency [117]. Due to the chemical bonding between the substrate and the coating, LPD offers highly stable nanomaterial thin film coatings. It has been used to deposit thin films of SiO_2, TiO_2, SnO_2, ZrO_2 and the three dimensional transition metal oxides V, Cr, Mn, Fe, Co, Ni, Cu, Zn, In (individually or combined) [24].

The hydrothermal growth technique has been used to produce ZnO nanoparticles on the surface of fused silica fiber and stainless steel wire [118,119]. At first, the procedure consisted of two steps, seeding and growing [24]. A simplification to a single step was realized by Alizadeh *et al.* (2011) [118]. It is possible to coat 50 fibers at once. The hydrothermal method is used to produce organic framework (MOF) SPME coatings which offer high thermal and mechanical stability and exceptionally large surface areas [24].

In their review on procedures for the preparation of SPME coatings, Aziz-Zanjani and Mehdinia (2014) conclude that this variety of coatings forms a good basis for the development of more designable structures. Durable and stable SPME devices can be produced by metal supports and chemical bonding between support and sorbent. However, poor selectivity and limited applicability to samples with complex matrices remain problematic [24].

Table 1. Coating procedures and sorbent materials used [24].

Dipping and physical agglutinating methods	**Sol-gel technology**	**Chemical grafting**	**Electrochemical methods**	**Electro-spinning**	**Liquid-phase deposition**	**Hydro-thermal methods**
Carbon nanomaterials [26,120]	Functionalized or polymer-functionalized carbon nanomaterials [125,126,127]	Nanomaterials [138,139]	**<u>Electrodeposition</u>** Electropolymerized conductive polymers [88,145–147]	Electrospun epoxide polymer	SiO_2, TiO_2, SnO_2, ZrO2 [117]	ZnO nanoparticles
Ordered mesoporous materials [121,122]	Ionic liquid-mediated SPME coating [128,129]	Immunoaffinity SPME [140]	Electropolymerized conductive polymers nanocomposite [148,149]	Carbon nanofiber-based SPME [116,156,157]	Three dimensional transition metal oxides (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, In, individually or combined) [158]	Organic frameworks (MOFs) [118,119]
Ionic liquids and polymeric ionic liquids [123,124]	Sol-gel derived polymeric ionic liquid-based SPME coatings [130,131]	Molecularly imprinted polymers [141,142]	Conductive polymer-ionic liquid composites [150,151]			
	Sol-gel ordered mesoporous silica SPME coating [132,133]	Substrate-bonded ionic liquid coatings [143]	Metal oxides [152,153]			
	Sol-gel coating on metal wires [134,135]	Substrate-bonded polymeric ionic liquid coatings [144]	**<u>Anodized metal wires</u>** Metal oxides [154,155]			
	Sol-gel molecularly imprinted polymer coatings [113,136]		**<u>Electrophoretic deposition</u>** Carbon nanotubes (CNTs) [112–115]			
	Aptamer Sol-gel SPME [137]					

3.5. Quantitation

Contrary to traditional sample preparation methods such as liquid-liquid extraction, solid-phase extraction or Soxleth, SPME is a non-exhaustive technique where only a fraction of the target analyte is extracted from the sample [22]. Consequently SPME must be calibrated carefully for quantitative analysis.

Quantitation of analytes in complex food and environmental matrices is currently one of the major challenges of SPME procedures. Nevertheless, several international standards applying the SPME methodology have recently been implemented, proving that SPME has been accepted as a state-of-the-art analytical technique at least in some fields of application (e.g., environmental). Firstly, the International Standard ISO 27108 [159] "Water quality–Determination of selected plant treatment agents and biocide products–Method using solid-phase microextraction (SPME) followed by gas chromatography-mass spectrometry (GC-MS)" has been established. The described procedure is based on the German Standard DIN 38407-34 [160]. Another standard based on DIN 38407-41 [161] has been published as a Draft International Standard in 2014: "Water quality – Determination of volatile organic compounds in water–Method using headspace solid-phase microextraction (HS-SPME) followed by gas chromatography-mass spectrometry (GC-MS) (ISO/DIS 17943) [162]. In addition, two other standards applying SPME methods have been published: the Austrian OENORM A 1117 [163] (Determination of volatile compounds in cellulose based materials by SPME) and the American ASTM D 7363a [164] (Standard test method for determination of parent and alkyl polycyclic aromatics in sediment pore water using solid-phase microextraction and gas chromatography/mass spectrometry in selected ion monitoring mode).

Essential to developing quantitative SPME methods is the knowledge of fundamental principles governing the mass transfer of analytes in multiphase systems, such as thermodynamics and mass-transfer kinetics [5,43,44]. The current available SPME calibration methods can be categorized into traditional calibration methods including external standard, internal standard and standard addition as well as newer methods such as equilibrium extraction, exhaustive extraction and diffusion-based calibration (see Table 2). Ouyang and Pawliszyn [18,22] published a review giving more detailed information about the mentioned individual methods.

3.5.1. Traditional Calibration Methods

Traditional calibration methods include external standards (calibration curve), internal standard or standard addition method.

SPME calibration can be performed either by equilibrium or pre-equilibrium calibration, respectively. In equilibrium calibration a partitioning equilibrium between the sample matrix and extraction phase is reached. The convection conditions do not affect the amount of extracted analytes due to the present partitioning equilibrium [22]. In pre-equilibrium calibration the amount of extracted analytes is related to the extraction time [22]. The convection/agitation thereby is constant. Applying equilibrium calibration for quantitation purpose is more sensitive and does not depend on the time. However, if the equilibrium extraction is too long, the pre-equilibrium extraction is preferred [22].

The internal standard method is widely applied for quantitation in SPME methods. It has been applied for the quantitative analysis of environmental [165,166] and food [167,168] samples. For heterogeneous samples the standard addition calibration method is preferred [169,170]. Using an internal or a surrogate standard (preferably mass-labeled internal standards) compensates for matrix effects and instrumental or sample preparation variability [171–175]. In addition, external standards are widely used [22,176–180].

Table 2. SPME calibration methods [22].

Calibration method		Advantages	Disadvantages	Applications
Traditional	External standard	No extensive sample preparation	Need for availability of blank sample matrices	[176–178]
			Need for stable sampling procedure and chromatographic conditions	[169,170]
	Standard addition		Extensive sample preparation and analysis	[165–168,171,172]
	Internal standard	Correction of sample matrix effects	Limited availability of suitable internal standards	
		Compensation of matrix effects and losses of analytes during sample preparation and irreproducibility in parameters (injection in GC/LC)	High cost and limited availability of isotope-labelled standards	
Equilibrium extraction		Possibility to calculate concentration of analytes by amount of extracted analytes Independence of amount of extracted analytes of sample volume	Need for knowledge about distribution coefficients	[181,182]
Exhaustive extraction		Possibility to calculate concentration of analytes by amound of extracted analytes and sample volume	Suitable only for small sample volumes and large distribution coefficients or need for special devices	[56,183]

Table 2. *Cont.*

Calibration method		Advantages	Disadvantages	Applications
Diffusion-based	Fick's first law of diffusion	Suitability for TWA sampling Independency of sampling rate of face velocity	Sorbent should be zero sink for target analytes Very low sample rate for water sampling	[184,185]
	Interface model and cross-flow mode	Minimizing of competitive effects for solid coating through high sampling rate and short time Suitability for on-site sampling	Need for controlled or determined flow velocity of sampling matrix Application limited to linear sampling regime	[186,187]
	Kinetic calibration with standard	Suitability for TWA sampling	Need for determination of standard loading	[188,189]
	Standard-free kinetic calibration	No need for standard loading Possibility to calculate concentrations of all extracted analytes in sample	Need for stable sampling conditions Unsuitability for long-term monitoring	[190]

3.5.2. Equilibrium Extraction

The equilibrium extraction method is a widely applied method for quantitation [181,182]. A small part of the extraction phase is exposed to the sample until equilibrium is reached. The concentration of the extracted analyte in the extraction phase is not dependent on the sample volume but corresponds directly to its concentration in the sample [22]. Therefore in practice, there is no need to collect a defined sample prior to analysis. The fiber can be exposed directly to the sample. The analytical process can be accelerated by removing the sampling step. Errors related to analyte losses through the decomposition or adsorption on the sampling container walls will be prevented. In that case the concentration of the target analytes can be determined. However, the distribution coefficients of the analytes between the fiber coating and the sample matrix have to be determined by experimentations. The concentration then can be determined by the amount of the analytes on the fiber under extraction equilibrium.

This calibration method was successfully applied for on-site air [181] or water sampling [182]. For air sampling the extraction can be performed in static and dynamic model [22]. In dynamic model, extraction rates from air-samples can be increased significantly with an air pump [181].

3.5.3. Exhaustive Extraction

Exhaustive extraction calibration can be done by using an internally cooled fiber device [52]. The higher analyte recoveries achieved using internally cooled fiber extraction result in greater confidence in quantitation and reporting of analyte concentrations (see Section 2.3, Figure 2). Almost quantitative extraction of the analytes was reported [22].

3.5.4. Diffusion-based Calibration

The diffusion coefficient is essential for description of kinetic processes of SPME [22]. Recently various diffusion-based calibration methods have been developed [22]. They were developed based on Fick's first law of diffusion, the interface model, the cross-flow model and the kinetic process of absorption/adsorption and desorption [22]. Main applications are in on-site sampling, comprising grab sampling and long-term monitoring [22].

Fick's first law is applicable to calibration when diffusion paths are well-defined [22]. The main applications are air and water sampling. Fiber-retracted SPME devices are used in which the analyte molecules access the fiber coating only by means of diffusion through the static air/water gap between the needle opening and the fiber coating. In air, the diffusion of the molecules is fast and the length of the diffusion path can be adjusted [191]. These kinds of samplers were applied for time-weighted average (TWA) sampling of several analytes in air [56,184]. For water sampling, a commercially SPME fiber assembly was developed and used for monitoring polycyclic aromatic hydrocarbons (PAHs) in water [185].

In the case of a poorly defined or unknown diffusion path for on-site sampling (when the SPME fiber is inserted directly into the air or water sample , the interface model and cross-flow model can be used for calibration. However, these models are limited to the linear sampling regime and a constant convection of air/water [22]. Applying these calibration methods requires a controlled velocity of air/water [22]. The Interface model was developed by Koziel *et al*. [186] and applied for sampling of volatile organic compounds (VOC) in air. The cross-flow model was developed by Chen *et al*. [187].

Kinetic calibration is based on a diffusion-controlled mass transfer model proposed by Ai [43,44]. The underlying assumption of this dynamic model is that there is a linearly proportional relationship between the adsorbed analyte and its initial concentration in the sample matrix. Based on this model two calibration methods of SPME, the kinetic calibration with standard or in-fiber standardization technique [192] and the standard-free kinetic calibration [190] were proposed. The applicability of this technique for TWA water sampling was established by both theoretical derivations and field trials [188,189]. Furthermore this method has become more convenient and applicable through the single point calibration [193]. Kinetic calibration with standards in the extraction phase can be applied to grab sampling as well as long-term monitoring [22]. Due to the loss of the standard during sampling this calibration method may not work in some fast sampling situations. For fast on-site and *in vivo* analysis, a standard-free kinetic calibration method was developed [190]. With this calibration method, all analyes can be directly calibrated with only two samplings and can be quantified without bearing in mind of reaching equilibrium in the system. The method was validated for identification of PAHs and BTEX in a standard aqueous solution and a standard gas flow-through system [190]. Compared with the previous calibration methods for rapid on-site analysis by SPME this method does not require a standard to calibrate the extraction. The total amount of the extracted analytes can be quantified without bearing in mind of reaching equilibrium in the system [190].

4. Applications in Food Analysis

The research of aroma-active compounds in foods was developed simultaneously with the introduction of the first gas chromatographs in the early 1960s [194]. In the headspace of foodstuffs the occurrence of around 10,000 compounds was estimated [195]. When considering the choice of suitable methods for food analysis, it is essential to realize that food is a complex, heterogeneous mixture composed of a multitude of different compounds. The analysis of volatile target analytes requires the extraction from the food matrix. It is nearly impossible to analyse food samples without sample pretreatment even though advanced techniques of separation and identification have been made available. Therefore, sample extraction, removal of interferences and the pre-concentration of analytes are mandatory procedures [196].

Developing reliable and sensitive SPME methods for food analysis requires the selection and optimization of parameters like the fiber coating, sampling technique, agitation conditions, sample volume and extraction and desorption conditions [197]. Simultaneous variation of several control variables is possible by applying multivariate test designs reducing the experimental effort for SPME optimization [198]. Multivariate test designs such as full factorial design, Doehlert matrix, 2^4 experimental design and Design of Experiments are valid multivariate test designs for SPME method optimization [55,56,199].

SPME has been widely applied to the sampling and analysis of food matrices. Table 3 provides a comprehensive overview of SPME applications divided into different analyte classes; aroma, off-flavor (food products), off-Flavor (food packaging migrants) and volatile toxic compounds. Figure 8 shows the numbers of papers dealing with applications of SPME to the different types of analytes based on a ScienceDirect literature research for years 2005 to 2015. Hundreds of papers reporting SPME applications in the field of food analysis have been published in recent years (see Table 3). The vast majority of

which referred to aroma analysis (see Figure 8). The applications of SPME to different food matrices are shown in Figure 9. The majority of applications refer to the food classes fruits/vegetables, fats/oils, wine, meat, dairy and (non-) alcoholic-beverages. The results are comparable to those published by Jeleń *et al*. [13] derived from a Web of Knowledge search in food aroma analysis between 2006 and 2011.

The microextraction technology in greatest use second to SPME (91%) was SBSE (5%), followed by SDME and LLME. The advantage of SBSE is a particularly high sensitivity for semi volatiles. However, SBSE suffered for a long time due to only one available coating (PDMS). Due to the lack of automated versions of SDME and LLME, and also due to their lower popularity in the scientific community (compared to SPME and SBSE) their use in aroma analysis is yet not enough explored. The diversity of matrices for which microextraction methods other than SPME are used proves that these methods await broader applications in aroma analysis [13].

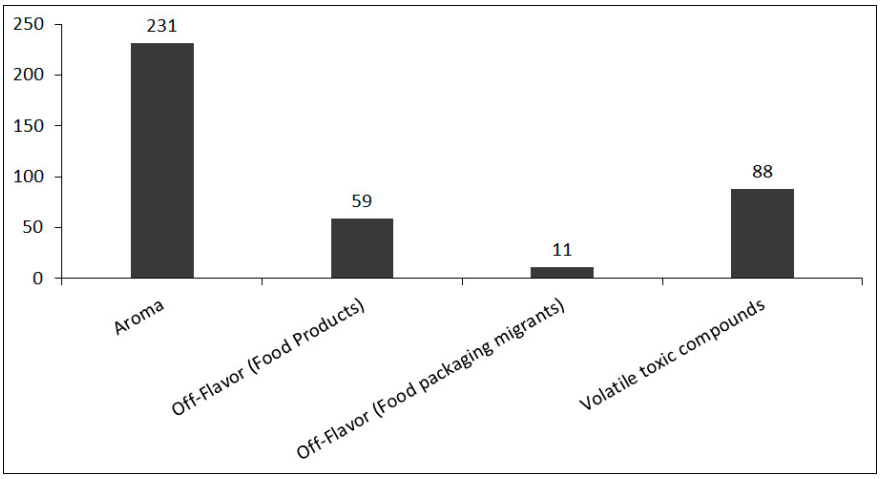

Figure 8. Application of SPME to different types of analytes. Number of papers based on ScienceDirect search for years 2005–2015.

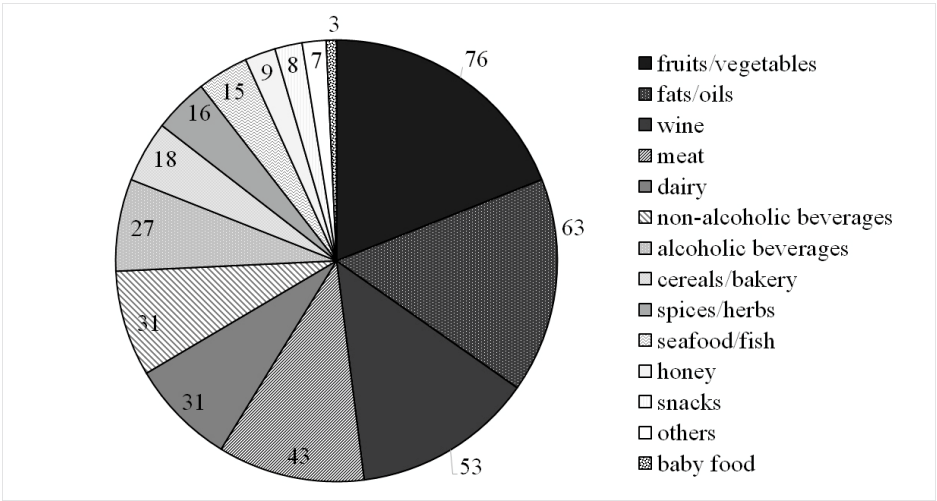

Figure 9. Application of SPME to different food matrices. Number of papers based on ScienceDirect search for years 2005–2015.

Table 3. SPME applications in food analysis.

			Extraction conditions					Desorption conditions					
Food Sample	**Analyte**	**Technique**	**Fiber**	**Time [min]**	**Temp. [°C]**	**Salt addition**	**Deriv.**	**Time [min]**	**Temp. [°C]**	**Detection**	**LOD**	**Recovery**	**Ref.**
Aroma													
Dairy products													
Butter	diacetyl	-	PDMS-DVB	5	37	-	-	1	250	GC-MS-MS	0.0078 ppm	-	[200]
European PDO hard cheeses	VVC	HS-SPME	DVB-CAR-PDMS	60	45	-	-	10	260	GC-MS / GC-FID	-	-	[201]
PDO Cheese, Oscypek	VVC	HS-SPME	CAR-PDMS	15	50	-	-	5	260	GC-MS	-	-	[202]
Van Herby Cheeses	esters, ketones, aldehydes, acids, alcohols, hydrocarbons, terpenes	HS-SPME	DVB-CAR-PDMS	30	40	-	-	5	250	GC-MS / GC-FID	-	-	[203]
Milk, cheese and whey powder	VVC	HS-SPME	DVB-CAR-PDMS	30	40	4 g NaCl	-	5	250	GC-MS	-	-	[204]
Meat and meat products													
Roasted pork of mini-pig	VVC	DI-SPME	CAR-PDMS	60	80	0.22 g salt	-	4	280	GC-MS / GO-O / GC-FID	-	-	[205]

Table 3. *Cont.*

Food Sample	Analyte	Technique	Fiber	Extraction conditions: Time [min]	Extraction conditions: Temp. [°C]	Extraction conditions: Salt addition	Extraction conditions: Deriv.	Desorption conditions: Time [min]	Desorption conditions: Temp. [°C]	Detection	LOD	Recovery	Ref.
Meat and meat products													
Traditional smoke-cured bacon (CSCB)	alkane, aldehydes, ketones, alcohols, thioethers, thiols, furans, phenols	-	CAR-PDMS / DVB-CAR-PDMS	30	60	-	-	5	280	GC-MS	-	-	[206]
Minced beef	VVC	HS-SPME	DVB-CAR-PDMS	30	40	25% NaCl	-	1	250	GC-MS	-	-	[207]
Cooked, cured pork ham	VVC	HS-SPME / SBSE	CAR-PDB-DVB / 0.5mm PDMS phase thickness stir bars	30 / 90	40 / RT	-	-	10	250 / 30	GC-MS	-	-	[208]
Slow fermented sausages	dimethyl trisulfide, 3-methyl thiophene, 2,3-butanedione, 2-nonanoneacetic acid	HS-SPME	CAR-PDMS	180	37	-	-	5	240	GC-MS / GC-O	-	-	[209]
Cooked, fermented sausage	VVC	SPME	CAR-PDMS	40	47	-	-	10	250	GC-MS	-	-	[210]
Cooked beef	VVC	HS-SPME	DVB–CAR–PDMS	25	40	6% NaCl	-	3	250	GC-MS	-	-	[211]

Table 3. *Cont.*

Food Sample	Analyte	Technique	Fiber	Extraction conditions: Time [min]	Temp. [°C]	Salt addition	Deriv.	Desorption conditions: Time [min]	Temp. [°C]	Detection	LOD	Recovery	Ref.
Juice and alcoholic beverages													
Whisky	fatty acid ethyl esters, higher alcohols, fatty acids, carbonyl compounds, monoterpenols, C13 norisoprenoids, volatile phenols	HS-SPME	CAR-PDMS	60	40	30% NaCl	-	6	220	GC-MS	-	-	[212]
Banana Terra spirit	3-methylbutan-1-ol, 3-methylbutan-1-ol acetate, 2-phenylethylacetate, phenylethyl alcohol	HS-SPME	PDMS-CAR-DVB	25	60	-	-	2	240	GC-MS / GC-O	-	-	[213]
Chinese Laobaigan liquor	VVC	HS-SPME	DVB-CAR-PDMS / CAR-PDMS	40	60	3 g NaCl	-	5	250	GC-MS	-	-	[214]
Ice wine	aroma compounds	HS-SPME	DVB-CAR-PDMS	5	45	1 g NaCl	-	2	260	GC-TOF-MS	trans-OL: 0.015 g/mL; cis-OL: 0.01 g/mL	-	[215,216]

Table 3. *Cont.*

			Extraction conditions					Desorption conditions					
Food Sample	**Analyte**	**Technique**	**Fiber**	**Time [min]**	**Temp. [°C]**	**Salt addition**	**Deriv.**	**Time [min]**	**Temp. [°C]**	**Detection**	**LOD**	**Recovery**	**Ref.**
Juice and alcoholic beverages													
Wine	2-methyl-3-furanthiol, 4-mercapto-4-methyl-2-pentanone, 3-mercaptohexanol, 2-furanmethane-thiol, 3-mercaptohexyl acetate	HS-SPME	PDMS–DVB	10	55	-	on-fiber deri-vatization	2	250	GC-NCI-MS	0.03–0.8 fg	-	[85]
Spanish white wines	VVC	HS-SPME	CAR-PDMS	60	46	-	-	2	280	GC-MS / GC-FID	0.1–900 ng/mL	97–110%	[217]
Cherry wines	VVC	HS-SPME	DVB-CAR-PDMS	45	50	2 g NaCl	-	5	230	GC-MS	0.03–7.27 µg/L	60.7–125.6%	[218]
China gingko wine	VVC	HS-SPME	CAR-PDMS	45	50	saturated NaCl solution	-	4	250	GC-MS	-	-	[219]
Black raspberry wines	VVC	HS-SPME	PDMS-DVB	30	60	-	-	5	230	GC-MS	-	-	[220]
Beer	alcohols, esters, organic acids, aldehydes, ketones, terpenes, sulfur com-pounds, amines, phenols	HS-SPME	TMSPMA-OH-TSO prepared by sol-gel technology	30	40	2 g NaCl	-	5	300	GC	0.01–35.2 µg/L	92.8–105.8%	[221]

Table 3. *Cont.*

			Extraction conditions					Desorption conditions					
Food Sample	**Analyte**	**Technique**	**Fiber**	**Time [min]**	**Temp. [°C]**	**Salt addition**	**Deriv.**	**Time [min]**	**Temp. [°C]**	**Detection**	**LOD**	**Recovery**	**Ref.**
Juice and alcoholic beverages													
Yellow passion fruit juice	VVC	HS-SPME	PDMS-DVB	20	50	17% NaCl	-	6	250	GC-MS	-	-	[222]
Grape juice	aroma compounds	HS-SBSE	PDMS	120	RT	-	-	5	-50	GC-MS	-	28.4%	[223]
Orange beverage emulsion	VVC	HS-SPME	CAR-PDMS	15	45	15% NaCl	-	8	250	GC-MS	0.06–2.27 mg/L	88.3–121.7%	[224]
Coffee	aroma compounds	HS-SPME	PDMS-DVB	20	60	-	-	1	270	GC-MS	-	-	[225]
Coffee	VVC	HS-SPME	PDMS	5	30	-	-	-	220	SAW	-	-	[226]
Coffee	VVC	HS-SPME	DVB-CAR-PDMS	30	60	-	-	5	230	GC	-	-	[227]
Coffee	furans, methoxyphenols, pyrazines, and ketones	HS-SPME	poly $[VC_{16}Im][NTf_2]$ with 50% $[VBIm_2C_{12}]2[Ntf_2]$	30	RT	-	-	5	175	GC-MS / GC-FID	-	-	[123]
Fruits and vegetables													
Various apricot varieties	ethyl acetate, hexyl acetate, limonene, b-cyclocitral, c-decalactone, 6-methyl-5-hepten-2-one, linalool, b-ionone, menthone and (E)-hexen-2-al	HS-SPME	CAR-PDMS	20	40	-	-	4	250	GC-MS / GC-O	-	-	[228]

Table 3. *Cont.*

Food Sample	Analyte	Technique	Fiber	Extraction conditions: Time [min]	Extraction conditions: Temp. [°C]	Extraction conditions: Salt addition	Deriv.	Desorption conditions: Time [min]	Desorption conditions: Temp. [°C]	Detection	LOD	Recovery	Ref.
Fruits and vegetables													
Apricot varieties	linalool, a-terpineol, b-ionone and c-decalactone	HS-SPME	CAR-PDMS	20	40	saturated NaCl solution	-	4	250	GC-MS	-	-	[229]
Apricot varieties	aldehydes, alcohols, acetates, esters, terpenes and acids	HS-SPME	CAR-PDMS	30	40	-	-	2	250	GC-MS	-	-	[230]
Jackfruit	ethyl isovalerate, 3-methylbutyl acetate, 1-butanol, propyl isovalerate, isobutyl isovalerate, 2-methyl-butanol, butyl isovalerate	HS-SPME	DVB-CAR-PDMS	30	10	-	-	5	250	GC-TOF-MS	-	-	[231]
Cooked peaches	VVC	HS-SPME	DVB-CAR-PDMS	20	40	-	-	10	270	GC-MS	-	-	[232]
Monstera deliciosa fruit	VVC	HS-SPME	PDMS-DVB	60	40	15% NaCl	-	6	250	GC–qMS	-	-	[233]
Pineapple fruit	VVC	HS-SPME	PDMS-DVB	30	40	-	-	2	240	GC×GC-qMS	-	-	[234]
Sweet cherry cultivars	VVC	HS-SPME	CAR-PDMS	20	45	0.2 g NaCl	-	10	260	GC-MS	-	-	[235]

Table 3. *Cont.*

			Extraction conditions					Desorption conditions					
Food Sample	**Analyte**	**Technique**	**Fiber**	**Time [min]**	**Temp. [°C]**	**Salt addition**	**Deriv.**	**Time [min]**	**Temp. [°C]**	**Detection**	**LOD**	**Recovery**	**Ref.**
Fruits and vegetables													
Air-dried raisins	free and glycosidically bound volatile compounds	HS-SPME	CAR-PDMS-DVB	40	60	1.3 g NaCl	-	8	-	GC-MS	-	-	[236]
Table grapes	alcohols, carbonyls, C6 compounds, terpenoids, esters	HS-SPME	PDMS-DVB	30	40	2 g $CaCl_2$, 20 g NaCl	-	3	220	GC-MS	-	-	[237]
Tomato	VVC	HS-SPME	DVB-CAR-PDMS	15	50	saturated $CaCl_2$ solution	-	10	250	GC-MS	-	-	[238]
Miscellaneous													
Thistle honey	VVC	HS-SPME	DVB-CAR-PDMS	40	60	30% NaCl	-	2	250	GC-MS	-	-	[239]
Croatian lime tree, fir honey-dew, sage honey	VVC	HS-SPME	DVB-CAR-PDMS	20	40	0.5 g an-hydrous Na_2SO_4	-	3	250	GC-MS	-	-	[240]
Honey	VVC	HS-SPME	PDMS-DVB	40	50	-	-	2	250	GC-QTOF-MS	-	-	[241]
Extra virgin olive oils	VVC	HS-SPME	DVB-CAR-PDMS	10	40	-	-	5	260	GC-FID	-	-	[242]
Extra virgin olive oils	VVC	HS-SPME	DVB-CAR-PDMS	360	30	-	-	4	270	GC-MS	-	-	[243]

Table 3. *Cont.*

		Extraction conditions						Desorption conditions					
Food Sample	**Analyte**	**Technique**	**Fiber**	**Time [min]**	**Temp. [°C]**	**Salt addition**	**Deriv.**	**Time [min]**	**Temp. [°C]**	**Detection**	**LOD**	**Recovery**	**Ref.**
Miscellaneous													
Virgin olive oil	VVC	HS-SPME	DVB-CAR-PDMS	40	40	-	-	5	300	GC-MS	0.1–2.54 mg/kg	-	[244]
Black and white rice bran	terpenoid flavor odorants	HS-SPME	PDMS	30	100	-	-	0.2	250	GCxGC-MS	-	-	[245]
Italian rice cultivars	VVC	HS-SPME	DVB-CAR-PDMS	60	60	-	-	5	250	GC-MS	-	-	[246]
Palm sugar	N-heterocyclic and O-heterocyclic compounds	HS-SPME	DVB-CAR-PDMS	10	50	-	-	5	240	GC-MS	-	-	[247]
Almond cultivars	VVC	HS-SPME	DVB-CAR-PDMS	60	60	-	-	10	270	GC-MS	-	-	[248]
Saffron	VVC	HS-SPME	PDMS	20	36	-	-	0.4	250	GC-MS	-	-	[249]
Garlic	VVC	HS-SPME	CAR-PDMS	30	30	-	-	3	220	GC-MS	-	-	[250]
Atlantic shellfish species	VVC	HS-SPME	CAR-PDMS	30	80	10 mL saturated NaCl solution	-	10	260	GC-MS	0.12–1.19 ppb	59.3–119.6%	[251]

Table 3. *Cont.*

			Extraction conditions					Desorption conditions					
Food Sample	**Analyte**	**Technique**	**Fiber**	**Time [min]**	**Temp. [°C]**	**Salt addition**	**Deriv.**	**Time [min]**	**Temp. [°C]**	**Detection**	**LOD**	**Recovery**	**Ref.**
Off-Flavor													
Food products													
Beer and beverage	sulfur compounds	HS-SDME / DI-SPME / HS-SDME	PDMS	5	25	2.0 g NaCl / 20% NaCl solution	-	5	250	GC-FPD	0.5 ng/mL for DPrDS -208.1 ng/mL	beer: 85.5–106.9%; bevera-ges: 95.2–110.8%	[252]
Beer	esters and vicinal diketones	HS-SPME	DVB-CAR-PDMS	30	60	3.0 g NaCl	-	-	260	GC-MS	-	-	[253]
Wine	volatile sulfur compouds	HS-SPME	CAR-PDMS	20	35	-	-	7	300	GC-pFPD	0.5 µg/L	0–100%	[254]
Chardonnay and Pinot gris wines	2-aminoacetophenone	DI-SPME	DVB-CAR-PDMS	30	30	-	-	-	250	GC-MS	-	70–80%	[255]
Orange juice	guaiacol and halogenated phenol	HS-SPME	DVB-CAR-PDMS	30	40	-	-	5	220	GC-MS / GC-O	-	-	[256]
Water and apple juice	geosmin	HS-SPME	PDMS synthesized as coated fiber by sol-gel technology	25	40	37% NaCl	-	4	250	GC-MS	1–1.000 ng/L	95–102%	[257]
Coffee beverage	volatile compounds produced by fungi	HS-SPME	DVB-CAR	30	65	-	-	0.7	270	GC-MS	-	-	[258]

Table 3. *Cont.*

Food Sample	Analyte	Technique	Fiber	Extraction conditions: Time [min]	Extraction conditions: Temp. [°C]	Extraction conditions: Salt addition	Extraction conditions: Deriv.	Desorption conditions: Time [min]	Desorption conditions: Temp. [°C]	Detection	LOD	Recovery	Ref.
Off-Flavor													
Food products													
Rapeseed oil	hexanal, 2,4-heptadienal, 2-heptenal and 1-pentene-3-ol	HS-SPME	CAR-DVB-PDMS	35	50	-	-	-	150	MS	-	-	[259]
Conventional and high-oleic sunflower oil	hexanal, (E)-2-heptenal, (E)-2-decenal, (E,E)-2,4-nonadienal	HS-SPME	CAR-DVB-PDMS	60 / 90 / 120	40 / 60 / 80	-	-	5	270	MS	0.4–4.3 mg/L	-	[260]
Conventional and high-oleic rapeseed oil	octanal, 3-octanone, propanal, (E,E)-2,4-hexa-dienal, (E)-2-heptenal	HS-SPME	CAR-DVB-PDMS	90	40	-	-	5	270	MS	3.7–816.5 µg/L	-	[261]
Various frying oils	(E,E)-2,4-decadienal, heptanal, (E,E)-2,4-heptadienal, (E)-2-decenal	HS-SPME	CAR-DVB-PDMS	90	40	-	-	5	270	MS	0.03–47.2 µg/L	-	[262]
Almond oils	hexanal, (E)-2-heptenal, (E)-2-octenal, nonanal, (E)-2-nonenal, (E,E)-2,4-nonadienal, (E,E)-2,4-decadienal	HS-SPME	DVB-CAR-PDMS	60	60	-	-	10	270	GC-MS	-	-	[263]

Table 3. *Cont.*

Food Sample	Analyte	Technique	Fiber	Extraction conditions: Time [min]	Temp. [°C]	Salt addition	Deriv.	Desorption conditions: Time [min]	Temp. [°C]	Detection	LOD	Recovery	Ref.
Off-Flavor													
Food products													
Butter	hexanal	HS-SPME	CAR-PDMS	180	4	-	-	5	250	GC-MS	-	97.37%	[264]
Soymilk	aldehydes, alcohols, ketones, aromatic compounds, esters, furans	HS-SPME	CAR-PDMS	20	40	-	-	3	300	GC-MS	-	-	[265]
Fresh chilled pasteurised milk	microbially induced changes in volatile constituents	HS-SPME	CAR-PDMS	30	40	-	-	2	240	GC-MS / PTR-MS	-	-	[266]
Full fat bovine milk	volatile compounds (pentanal, pentanol, hexanal) produced by photooxidation	HS-SPME	CAR-PDMS	30	50	-	-	0.02	250	GC-MS	-	-	[267]
Chicken breast	sulfides methanethiol, dimethyl disulfide, di-methyl trisulfide, ethanol, 1- and 2-butanol, 1-butanol isomers, free fatty acids	HS-SPME	PDMS	15	50	-	-	3	200	GC-MS-FASST	-	-	[268]

Table 3. *Cont.*

			Extraction conditions					Desorption conditions					
Food Sample	**Analyte**	**Technique**	**Fiber**	**Time [min]**	**Temp. [°C]**	**Salt addition**	**Deriv.**	**Time [min]**	**Temp. [°C]**	**Detection**	**LOD**	**Recovery**	**Ref.**
Off-Flavor													
Food products													
Whiting	trimethylamine, 3-methyl-butanal, 2-methyl-butanal, 3-hydroxy-2-butanone, 3-methyl-1-butanol, 2-methyl-1-butanol	HS-SPME	CAR-PDMS	40	50	saturated NaCl solution	-	0.16	250	GC-MS	-	-	[269]
Rainbow trout	geosmin	HS-SPME	DVB-PDMS	20	65	3.0 g NaCl	-	3	270	GC-MS	-	-	[270]
Potato crisps	VVC	HS-SPME	CAR-PDMS	20	50	-	-	3	300	MS e-nose / GS e-nose	-	-	[271]
Food packaging migrants													
Cork	chloroanisoles	CF-HS-SPME	PDMS	10	130 / 10	-	-	3	260	GC-TOF-MS	-	>90%	[56]
Wine	chlorophenols and chloroanisoles	MHS-SPME	DVB-CAR-PDMS	60	70	-	$KHCO_3$ and acetic acid anhy-dride	5	280	GC-MS-MS	0.004–0.077 ng	-	[80]
Wine	4-ethylphenol, 4-ethylguaiacol	SPME	PDMS-CAR	30	60	-	-	15	220	GC-MS	-	-	[272]

Table 3. *Cont.*

		Extraction conditions						Desorption conditions					
Food Sample	**Analyte**	**Technique**	**Fiber**	**Time [min]**	**Temp. [°C]**	**Salt addition**	**Deriv.**	**Time [min]**	**Temp. [°C]**	**Detection**	**LOD**	**Recovery**	**Ref.**
Food packaging migrants													
Wine	2,4,6-trichloroanisole, 2,3,4,6-tetrachloroanisole, pentachloroanisole, 2,4,6-tribromoanisole, 4-ethylphenol (4-EP), 4-ethylguaiacol, 4-vinyl-phenol, 4-vinylguaiacol	MHS-SPME	DVB-CAR-PDMS	60	70	-	-	5	270	GC-MS-MS	4-EP: 1800 g/L; others: 1000 g/L	93.85–101.27%	[273]
Wine	haloanisoles	MHS-SPME	DVB-CAR-PDMS	35	60	99.8% NaCl	-	4	250	GC-ion-trap MS	120.70–150 pg	88.8%	[274]
Water and honey	chlorophenols	DMSPE-HS-SPME	PVC/MWCNTs nanocomposite	15	60	5 mol/L NaCl solution	-	4	215	GC-ECD	0.08–0.6 ng/mL	91–109%	[120]
Volatlile toxic compounds													
Contaminants													
Milk	diethylstilbestrol	DI-SPME	CNT reinforced hollow fiber	30	60	-	-	10	-	HPLC	5.1 mg/L	57.50%–120.42%	[125]
Milk	enzyme-generated volatile organic compounds associated with *Listeria monocytogenes*	HS-SPME	PA	10	37	-	-	2	230	GC-MS	-	-	[275]

Table 3. *Cont.*

Food Sample	Analyte	Technique	Fiber	Extraction conditions: Time [min]	Extraction conditions: Temp. [°C]	Extraction conditions: Salt addition	Extraction conditions: Deriv.	Desorption conditions: Time [min]	Desorption conditions: Temp. [°C]	Detection	LOD	Recovery	Ref.
Volatlile toxic compounds													
Contaminants													
Milk	PAHs	DI-SPME	diethoxydiphenyl-silane prepared by sol-gel technology	60	60	-	-	2	330	GC-MS	0.01–0.08 µg/L	-	[276]
Milk and honey	benzimidazole	DI-SPME	MEMF	70	-	-	-	20	-	HPLC-DAD	0.11–0.30 µg/L	72.3–121%; 83.1–119%	[277]
Chicken muscle and milk	tetracyclines (antibiotic)	SPME	molecularly imprinted polymer	30	-	-	-	10	-	HPLC	1.0 - 2.3 µg/L	-	[141]
Baby formula	furfural and hydroxymethylfurfural	HS-SPME	dodecylbenzene-sulfonate-doped polypyrrole	30	50	2 mol/L NaCl	-	-	200	IMS	6 ng/g; 5 ng/g	95% / 92%	[278]
Baby food and fruit juice	furan	HS-SPME	PEG and PEG/CNTs fibers prepared by sol-gel technology		25 / 30	3 g NaCl	-	0.25	230	GC-FID	0.001 ng/mL; 0.00025 ng/mL	92–98.5%	[126]
Fruit juices	carbamate and phenylurea pesticide residues	DI-SPME	PDMS-DVB and CW-TPR	90	20	0.3 g 30% NaCl	-	15	250	LC/QIT-MS	0.001–0.01 mg/kg	0–82%	[279]

Table 3. *Cont.*

			Extraction conditions					Desorption conditions					
Food Sample	**Analyte**	**Technique**	**Fiber**	**Time [min]**	**Temp. [°C]**	**Salt addition**	**Deriv.**	**Time [min]**	**Temp. [°C]**	**Detection**	**LOD**	**Recovery**	**Ref.**
Volatlile toxic compounds													
Contaminants													
Soft drinks	4-methylimidazole	HS-SPME	PDMS-DVB	50	110	saturated NaCl solution	-	-	270	GC-MS / LC-MS/MS	1.9 µg/L	-	[280]
Brazilian sugarcane juice	pesticide and benzo[a]pyrene	SBSE and MASE	-	180 / 30	280 / 45	saturated NaCl solution	-	11	250	TD-GC-MS / LVI-GC-MS	0.002–0.4 µg/L; 0.004 - 0.56 µg/L	0.2–55.3%; 13.6–103.1%	[281]
Carbonated drink, juice drink, sauce, jam, succade	benzoic and sorbic acids	in-tube SPME	diethylamine-modified poly(GMA-co-EDMA) monolithic capillary	5	-	-	-	7	-	HPLC-UV	1.2; 0.9 ng/mL	84.4–106%	[282]
Water and juice	benzoylurea insecticides	MMF-SPME	MMF/MAED	70	-	-	-	-	-	HPLC-DAD	water: 0.026–0.075 mg/L; juice: 0.053–0.29 mg/L	65.1–118%	[283]

Table 3. *Cont.*

			Extraction conditions					Desorption conditions					
Food Sample	**Analyte**	**Technique**	**Fiber**	**Time [min]**	**Temp. [°C]**	**Salt addition**	**Deriv.**	**Time [min]**	**Temp. [°C]**	**Detection**	**LOD**	**Recovery**	**Ref.**
Volatlile toxic compounds													
Contaminants													
Drinking water	organic micro-pollutants	DI-SPME	PDMS-DVB	30	60	-	-	-	280	GC-MS	0.5–10 µg/L	-	[284]
Apple, apple juice, tomato	organophosphorus pesticides	HS-SPME	PDMS-DVB including B15C5 prepared by sol-gel technology	45	70	5 g NaCl	-	5	270	GC-FPD	0.003–0.09 ng/g	apple juice: 71.5–01.6% apple: 83.3–97.7% tomato: 55.3–105.3% (spiked 5 ng/g)	[285]
Apples	polycyclic aromatic hydrocarbons, benzene, toluene, ethylbenzene, xylene	HS-SPME	CAR-PDMS	45	60	-	-	5	250	GC-MS	0.02 mg < LOD < 0.26 mg	0.012–0.140 µg	[286]
Fruit and vegetables	pesticide residues	HS-SPME	PDMS	34	62	10% NaCl	-	7	270	GC-MS	0.35–8.33 µg/kg	73–118%	[287]
Packaged fresh vegetables	volatiles derived from *Salmonella typhimurium*	HS-SPME	CAR-PDMS	15	20	-	-	3	-	GC-MS	-	-	[288]

Table 3. *Cont.*

Food Sample	Analyte	Technique	Fiber	Extraction conditions: Time [min]	Temp. [°C]	Salt addition	Deriv.	Desorption conditions: Time [min]	Temp. [°C]	Detection	LOD	Recovery	Ref.
Volatlile toxic compounds													
Contaminants													
Vegetables	PAHs	HS-SPME	benzoxy-C[6]/OH-TSO prepared by sol-gel technology	40	60	NaCl	-	10	280	GC-FID	0.04–2.32 ng/g	81.07–107.5%	[289]
Vegetables	organophosphorus pesticide residues	DI-SPME	PA	30	RT	10% NaCl	-	11	260	GC-FPD	0.01–0.14 µg/L	-	[290]
Radish	organochlorine pesticides	HS-SPME	calix[4]arene/hydroxy-terminated silicone oil prepared by sol-gel technology	30	70	1.0 g K_2SO_4	-	2	270	GC-ECD	1.27–174 ng/kg	83.05–119.3%	[291]
Roasted coffee	furan	HS-SPME	CAR-PDMS	30	35	-	-	-	-	GC-MS	3–10 µg/kg	76–101%	[292]
Wine	2,4,6-trichloroanisole, dibutyl phthalate	SR-SPME	graphene and graphene oxide prepared by sol-gel technology	20	45	20% NaCl	-	5	250	GC-MS	0.3 ng/L	96.96% / 98.20%	[293]
Still and fortified wines	fungicides captan, chlorthalonil, folpet, iprodione, procymidone and vinclozolin, acaricide dicofol	DI-SPME	PDMS	60	35	-	-	3	250	GC-MS/MS	-	70–120%	[294]

Table 3. *Cont.*

Food Sample	Analyte	Technique	Fiber	Extraction conditions: Time [min]	Temp. [°C]	Salt addition	Deriv.	Desorption conditions: Time [min]	Temp. [°C]	Detection	LOD	Recovery	Ref.
Volatlile toxic compounds													
Contaminants													
Breaded fish products	furanic compounds	HS-SPME	CAR-PDMS	40	37 ± 1	3 g NaCl	-	10	280	GC-MS	-	-	[295]
Fresh, deep frozen, canned, boiled, roasted fish	formaldehyde	HS-SPME	CAR-PDMS	30	80	-	PFBHA	3	310	GC-MS	17 µg/kg	94.8 ± 1.7%	[81]
Cooked, peeled tropical shrimps	3-methyl-1-butanal, 2,3-butanedione, 2-methyl-1-butanal, 2,3-heptanedione and trimethylamine induced by isolated bacteria	HS-SPME	CAR-PDMS	25	40	-	-	5	280	GC-MS	-	-	[296]
Packaged, aged, fresh beef	VOCs associated with Salmonella	HS-SPME	CAR-PDMS	30	23±2℃	-	-	10	270	GC-MS	-	-	[297]

Table 3. *Cont.*

Food Sample	Analyte	Technique	Fiber	Extraction conditions: Time [min]	Extraction conditions: Temp. [°C]	Extraction conditions: Salt addition	Deriv.	Desorption conditions: Time [min]	Desorption conditions: Temp. [°C]	Detection	LOD	Recovery	Ref.
Volatlile toxic compounds													
Contaminants													
Smoked meat products	PAHs	DI-SPME	PDMS	60	25	-	-	30	250	GC-MS	0.008–0.138 ng/mL	-	[298]
Meat roasted in plastic bags	plasticisers (phthalates)	DI-CF-SPME	PA	30	45	-	-	0.02	250	GC-MS	0.01–0.18 µg/kg	-	[134]
Fruit leathers	carbonyl compounds generated from ozone-based food colorants decomposition	HS-SPME	PDMS-DVB	15	60	-	PFBHA methanol	-	250	GC-MS	0.016–0.030 µg/L	-	[86]

CF: cold fiber; CNT: carbon nanotube; CSCB: Chinese traditional smoke-cured bacon; DAD: diode array detector; deriv.: derivatization; DI: direct immersion; DPrDS: dipropyl disulphide; ECD: electron capture detector; EDMA: ethylene dimethacrylate; FASST: Fast Automated Scan/SIM Type; FID: flame ionization detector; FPD: flame photometric detector; GC-O: gas chromatography-olfactometry; GMA: glycidyl methacrylate; GS: gas sensor; IMS: ion mobility spectrometry; LOD: limit of detection; LVI: large volume injection; MAED: methacrylic acid-co-ethylene dimethacrylate; MASE: membrane assisted solvent extraction; MEMF: methacrylic acid-co-ethylene dimethacrylate monolithic fiber; MHS: multiple headspace; MMF: multiple monolithic fiber; MW: multi-walled; NCI: negative chemical ionization; OH-TSO: hydroxyl-terminated silicone oil; OL: oak lactone; PAHs: polycyclic aromatic hydrocarbons; PDO: protected designation of origin; PEG: polyethylene glycol; PFBHA: pentafluorobenzyl-hydroxylamine hydrochloride; pFPD: pulsed flame photometric detector; PTR: Proton-transfer-reaction; PVC: polyvinyl chloride; QIT: quadrupole ion trap; qMS: quadrupole mass spectrometry; QTOF: quadrupole time-of-flight; ref.: reference; RT: room temperature; SAW: surface acoustic wave; SIM: selected ion monitoring; SR: space-resolved; TD: thermal desorption; temp.: temperature; TMSPMA: 3-(trimethoxysylil)propyl methacrylate; TOF: time-of-flight; TPR: template resin; VVC: various volatile compounds.

4.1. Aroma

The verification of taste and fragrance attributed to specific foods has become an important part of consumer demand. For this purpose SPME methods can serve as a valuable tool to examine the presence or absence of desired aroma compounds in food products [65]. SPME has gained increasing popularity for aroma analysis in recent years (see Figure 8). A collection of recently published studies in the field of applications of SPME in food, non-food, and fragrance analysis, *etc.* are listed in the Handbook of Solid Phase Microextraction [75].

Various food components like proteins, lipids, and sugars affect the chemical composition found in the headspace above food items. Page and Lacroix (1993) reported that the presence of a large quantity of lipid material in food products led to a lower extraction of volatiles from the headspace [299]. To prevent this decrease it is recommended to carefully raise the extraction temperature that will increase the number of volatile constituents present in the headspace. Thereby the number of volatile constituents present in the headspace increase. Raw meat for example had no strong aroma [300], but cooking increased meat aroma [300]. Xie *et al*. (2008) studied compounds that have a real impact on meat aroma. Volatiles of the roasted Mini-pig pork were determined by both SPME and SDE combined with GC-MS. Additionally GC-O was applied to identify potent contributors to the special meat aroma. A total of 86 different volatile compounds have been identified, whereas only 45 odor active regions could be recognized by olfactometry. Aldehydes from lipid oxidation followed by spice components were among the highest contributors to the volatile chemical profile [205].

Another study on meat aroma was performed with Chinese traditional smoke-cured bacon (CSCB) by Yu *et al*. [206]. The aim of the study was to work out the substances responsible for the characteristic aroma of CSCB. In total, 48 volatile compounds (alkanes, aldehydes, ketones, alcohols, thiolethers and thiols, furans and phenol compounds) were identified and quantified using SPME coupled to GC-MS [206]. Chemical processes like smoking, oxidation and the Maillard reaction (reaction between reducing sugars and amino acids, usually under the influence of heat) are largely responsible for the occurrence of these compounds.

Another approach in aroma analysis is to verify the origin and authenticity of foods. For example, Majcher *et al*. [202] developed a SPME method in combination with chemometrics for the determination of volatile compounds derived from traditional Polish cheese Oscypek and its imitations [202]. Sostaric *et al.* (2000) used SPME-GC-MS to differentiate between natural vanilla extracts and nature-identical and synthetic vanilla flavorings [301].

The extraction of aromatic volatile compounds from alcoholic and non-alcoholic beverages by SPME was recently extensively investigated (see table 3). Câmara *et al*. [212] investigated aroma compounds in whisky samples. Classical analytical methods such as LLE, simultaneous extraction or distillation show relatively low reproducibility or possible contamination with solvents. Further the lengh of time required for the analysis and the selectivity of the results are such a few drawbacks, which can be overcome selectivity can be overcome by dynamic headspace SPME and gas chromatography coupled to GC-MS. In this study the use of five different SPME fibers PDMS, PA, CAR-PDMS, CW-DVB and CAR-PDMS-DVB were compared. Optimized results were achieved by saturating the samples with salt solutions and using a CAR-PDMS fiber. More than seventy compounds including ethylesters, long-chain alcohols, isoamyl acetates and fatty acids were identified [212].

Ong *et al*. [231] investigated volatile compounds derived from jackfruit applying SPME and gas chromatography-time-of-flight mass spectrometry (GCTOF-MS). In five jackfruit cultivars thirty-seven compounds were identified. Compounds responsible for the sweet and fruity aroma in jackfruit were identified as ethyl isovalerate, 3-methylbutyl acetate, 1-butanol, propyl isovalerate, isobutyl isovalerate, 2-methylbutanol, and butyl isovalerate [231].

Fruit origin and authenticity (species idenfication) can also be successfully investigated by means of SPME analysis of volatile compounds [229]. For example, the typical sensory expectations of apricot fruits are sweetness and juiciness, which are strongly related to the ripening stage apricots at harvest [302]. Aroma compounds of apricots from different regions of the world were extensively studied [303]. Major identified aroma compounds were ethyl acetate, hexyl acetate, limonene, 6-methyl-5-hepten-2-one, menthone, E-hexen-2-al, linalool, beta-ionone and cyclo-decalactone [228].

Recently the European Union established the research program Horizon 2020 to develop a validated analytical method for determination of volatiles resulting from virgin olive oils by means of SPME-GC/MS. Romero *et al*. [244] published a validated method including calibration curves for 29 volatile compounds. The analytical precision of 67% of these compounds had a relative standard deviation lower than 10% and accuracies were determined for 97% of the analyzed volatile compounds. The limits of detection ranged from 0.1 to 2.54 mg/kg for determined volatile compounds [244].

4.2. Off-Flavors

As described in Section 4.1, aroma belongs to the most important sensory characteristics of food. Food products with an inappropriate aroma impression are often rejected by consumers and may lead to a loss of consumer confidence [304]. The awareness of off-flavors in food relies mainly on their concentration occurring in the food matrix and odor threshold values. Off-flavors are defined as unpleasant odors or flavors transmitted to food through internal impairing changes [304]. Many volatile compounds are associated with unpleasant odor notes such, e.g., putrid, musty, rotten, skunk, *etc*. However, the received off-flavor impression often depends on the concentration of the related aroma compounds. The most common off-flavor compounds are those that cause musty, earthy off-flavors (haloanisoles, halophenols, geosmin and methylisoborneol) and medicinal off-flavors (phenolic compounds, sulfur-containing compounds and carbonyl compounds) [304]. Other off-flavor compounds are generally classified according to their origin, including microbially derived off-flavors, compounds originating from packaging materials, from cleaning agents, and compounds resulting from Maillard reactions [304].

The impact of the cork composition on the sensory properties of wines was investigated by means of SPME GC-MS [272]. Cork was shown to have an active role in the sorption of volatile phenols from wine. In particular, the sorption properties of 4-ethylphenol and 4-ethylguaiacol phenols in hydro-alcoholic medium were investigated by Gallardo-Chacón and Karbowiak [272]. Through the high sorption activity of corks the concentration of 4-ethylphenol and 4-ethylguaiacol was decreased. High concentration of these compounds can lead to the formation of off-flavor. Both, in models and real wine samples the tested cork leads to a significant reduction of the mentioned off-flavor compounds in wine [272].

The oxidative stability of conventional high-oleic sunflower oil and analytical and sensory lipid oxidation parameters in conventional and high-oleic rapeseed oil were reported by Petersen *et al*. [260,261].

It was concluded that the combination of volatile compound analysis with HS-SPME-GC and multivariate statistical methods provides a sensitive tool in differentiating conventional sunflower oil and high-oleic sunflower oil as by means of volatile lipid oxidation marker compounds. The same applies to differentiating rapeseed oil and high-oleic rapeseed oil.

4.3. Volatile Toxic Compounds

Various sources of microbiological and chemical hazardous compounds may occur in foods. The latter may include natural toxicants, such as mycotoxins [305–307], marine toxins [308], and environmental contaminants, such as mercury and lead [309–314].

Among these substances for example volatile toxic aldehydes like formaldehyde has recently received increased attention. Formaldehyde is formed post-mortem by the enzymatic reduction of trimethylamine-N-oxide to formaldehyde and dimethylamine [315,316]. Due to its high volatility, formaldehyde is captured well by SPME for subsequent measurement. Firstly, in 2005 Bianchi *et al*. [317] developed a SPME method with *in situ* derivatisation with pentafluorobenzyl-hydroxylamine hydrochloride (PFBHA). In 2007, Bianchi *et al*. [81] used a SPME-GC-MS method based on the same derivatization to evaluate the formaldehyde content of various fish products.

Additional non-flavor contaminants are polycyclic aromatic hydrocarbons (PAHs), identified as pollutants in the environment and food items [1–3]. Bianchi *et al*. [276] developed a SPME method with a coating based on the use of diethoxydiphenylsilane produced by sol-gel technology for determination of PAHs at trace levels in milk. For vegetables, a simple, sensitive and affordable method has been developed for the quantitation of eight PAHs by Lei *et al*. [289]. The method was based on HS-SPME connected with GC-FID. The sol-gel designed benzoxy-C[6]/OH-TSO proved to have a good capability to capture aromatic compounds such as phthalate acid esters. Compared to the tested PDMS fiber and C[4]/OH-TSO fiber, the benzoxy-C[6]/OH-TSO showed to have the highest affinity to PAHs [289].

The VOCs 2-nitrophenol and 3-fluoroaniline were extracted, separated and detected by headspace-solid phase microextraction coupled to gas chromatography–mass spectrometry (HS-SPME-GC-MS). It was stated to be a potential rapid method for future development [275].

Microorganisms can also be responsible for food contamination and spoilage. The metabolic activity of microorganisms through breakdown of compounds in food leads to the release of volatile organic compounds [41]. Extensive research was carried out in order to identify microbial activities in foods using SPME [275,288,297,318]. Siripatrawan and Harte [288] investigated the occurrence of *Salmonella typhimurium* present in packaged alfalfa sprouts. For that purpose CAR/PDMS fibers were compared to PDMS/DVB fibers which extracted lesser sulfur volatiles. Sulfur-containing compounds seem to be a major marker compound for spoiled food stuffs, off-flavor in milk, and the presence of pathogens [288]. Other volatile organic compounds such as 2-nitrophenol and 3-fluoroaniline may be associated with the presence of *Listeria monocytogenes* contamination in food [318].

Pesticides are not only contaminants, but are also non-flavor compounds occurring in food items. The simultaneous determination of fourteen multiclass pesticide residues in fruit and vegetable samples by means of HS-SPME coupled to GC-MS were reported by Abdulra'uf and Tan [287]. The method development was based on multivariate experimental designs (Plancket-Burman and central composite design) conducted in two stages. Internal standard calibration was applied for quantitation (detection

limits between 0.35 and 8.33 µg/kg). Compared to liquid-liquid extraction techniques and SPE, which are commonly used in pesticide analysis, SPME takes less time, is less labor-intensive, does not require any solvents and simplifies sample preparation to one single step and one device [41].

5. Environmental Applications

SPME has been widely applied to the sampling and analysis of environmental matrices including air, water, soil, and sediment samples, in on-site or off-site analysis [20,16,18]. Hundreds of papers reporting SPME applications in the field of environmental analysis have been published in recent years (see Table 4), the vast majority of which referred to aqueous samples (see Figure 10).

5.1. Air Samples

Applications of SPME in air sampling can be performed on-site [319,320] or in the laboratory after collecting air samples in suitable containers, e.g., bags [102,321], glass bulbs [181,322], or pre-evacuated vessels [323]. The analytes are extracted either by direct exposure of the fiber to the air sample or by headspace method after absorption in a suitable liquid medium [324,325] or adsorption on a solid material, e.g., Tenax TA [326]. Some authors use dynamic flux chambers for air sampling [133,327–329]. Most applications published on SPME analysis of gaseous samples involve the use of commercially available SPME fibers, although novel fiber coatings have already been developed for this purpose as well. For example, a sol-gel single-walled carbon nanotube/silica composite coated SPME has been developed for the analysis of organohalogen compounds in workplace air [133].

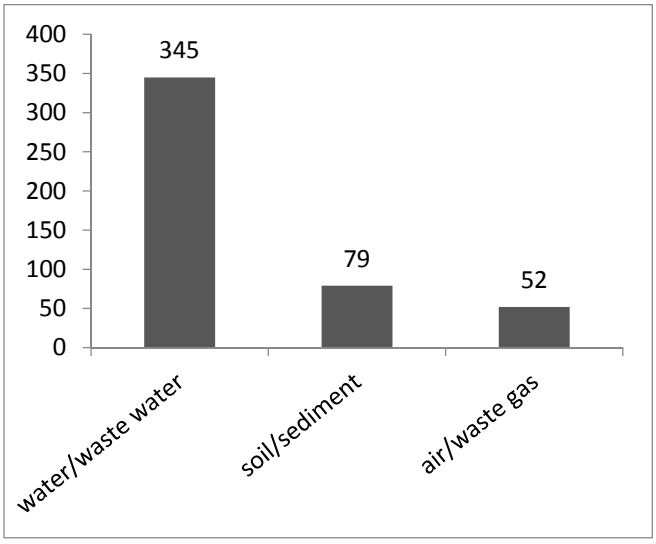

Figure 10. Applications of SPME to different environmental matrices. Number of papers based on ScienceDirect search for years 2005–2015.

Table 4. SPME applications in environmental analysis.

			Extraction conditions					Desorption conditions					
Analyte	**Environmental Sample**	**Technique**	**Fiber**	**Time [min]**	**Temp. [°C]**	**(Salt) Addition**	**Deriv.**	**Time [min]**	**Temp. [°C]**	**Detection**	**LOD**	**Recovery [%]**	**Ref.**
					Air								
					Pollutants								
Volatile organohalogen compounds	workplace air	SPME	sol-gel SWCNT / silica	15	RT	-	-	3	280	GC-MS	0.09–0.2 ng/mL	-	[127]
Formaldehyde and other carbonyl compounds	indoor air	SPME	PDMS-DVB	15	RT	-	PFBHA	4	250	GC-MS	0.002–0.032 µg/m³	-	[82]
Acetaldehyde, acetone, BTX, pinene, trichloroethylene, alkanes	indoor air (classrooms)	SPME	PDMS-CAR	240	RT	-	-	2.5	320	GC-MS	0.05–5.9 µg/m³	79–120	[181]
BTEX	indoor and outdoor air	SPME	PDMS-CAR	30	14–24	-	-	2	260	GC-MS	0.05–0.1 µg/m³ (benzene)	-	[319]
PAH	ambient air particulate matter (PM10, TPS), sampling on quarz filter disks and extraction with water/methylene chloride/acetone	DI-CF-SPME	PDMS	60	70	-	-	1	270	GC-MS	0.02–1.16 ng	88–98	[330]
Alkyl- and methoxy-phenolic compounds	biomass smoke, absorption in aqueous NaOH prior to SPME	HS-SPME	CW-DVB	90	-	35% NaCl, pH 2	-	3	250	GC-MS	1.13–4.60 ng/mL	-	[324]

Table 4. *Cont.*

			Extraction conditions					Desorption conditions					
Analyte	**Environmental Sample**	**Technique**	**Fiber**	**Time [min]**	**Temp. [°C]**	**(Salt) Addition**	**Deriv.**	**Time [min]**	**Temp. [°C]**	**Detection**	**LOD**	**Recovery [%]**	**Ref.**
					Air								
					Pollutants								
Organophosphate triesters	indoor air (lecture room, office)	dynamic SPME	PDMS	40–90 min / >18 h; air flow rate 10–35 cm/s	22	-	-	2	280	GC-NPD	-	-	[327]
					Volatile organic compounds								
VOC	indoor air	SPME	PDMS-CAR	10	RT	-	-	10	300	GC-MS / GC-FID	-	122 ± 24	[331]
VOC	indoor air	SPME	PDMS-CAR	1–45	-	-	-	2.5	320	GC-MS	-	-	[332]
VOC	air from volcanic and geothermal areas, landfill gas	SPME	PDMS-DVB-CAR	30	20	-	-	2	230	GC-MS	-	78–84	[323]
					Odorous compounds								
VOC and odorous compounds	air from swine barn, cattle feedlots	SPME	PDMS-CAR	60	RT	-	-	5	260	GC-MS-O	-	-	[320]
Volatile carbon, sulfur and nitrogen compounds	air from livestock operations	dynamic SPME	PDMS-DVB-CAR	5 min / air flow rate 16 cm/s	20	-	-	-	300	GC-MS	-	-	[328]

Table 4. *Cont.*

			Extraction conditions					Desorption conditions					
Analyte	**Environmental Sample**	**Technique**	**Fiber**	**Time [min]**	**Temp. [°C]**	**(Salt) Addition**	**Deriv.**	**Time [min]**	**Temp. [°C]**	**Detection**	**LOD**	**Recovery [%]**	**Ref.**
					Odorous compounds								
VOC and odorous compounds	swine barn particulate matter (TPS, PM10, PM2.5, PM1), adsorption on TEOM filters prior to SPME	HS-SPME	PDMS-CAR	180	25	-	-	40	260	GC-MS-O	-	-	[333]
Odorous compounds	waste gas from fat refinery	SPME	PDMS-CAR	30	RT	-	-	5	290	GC-MS / GC-FID-O	-	-	[102]
Odorous compounds	gaseous effluents from production of poultry feather and viscera meal, condensed prior to SPME	HS-SPME	PDMS-DVB-CAR	20	50	-	-	4	250	GC-MS	-	-	[325]
Volatile organic sulfur compounds	air from different areas of sewage treatment plant	SPME	PDMS-CAR	45	22 /RT	-	-	2	200	GC-MS	0.01–0.08 µg/m³	75–96	[322]
Synthetic musks	indoor air, adsorption on Tenax TA prior to SPME	HS-SPME	DVB-CAR-PDMS	20	100	100 µL acetone	-	5	270	GC-MS	0.029–0.380 ng/m³	85–103	[326]
Trimethylamine	ambient air	SPME	PDMS-DVB	10	22 / RT	-	-	3	210	GC-FID			[321]
Diacetyl	air	SPME	PDMS	2	RT	-	-	1	250	GC-MS	0.05 ppm	-	[200]
Monoterpenes	plant emissions, ambient air	SPME	PDMS-DVB	20	25 / RT	-	-	5	250	GC-MS	4–20 ppt	-	[329]

Table 4. *Cont.*

			Extraction conditions					Desorption conditions					
Analyte	**Environmental Sample**	**Technique**	**Fiber**	**Time [min]**	**Temp. [°C]**	**(Salt) Addition**	**Deriv.**	**Time [min]**	**Temp. [°C]**	**Detection**	**LOD**	**Recovery [%]**	**Ref.**
Water													
Odorous compounds													
Earthy-musty odorants	source, product, and tap water from different waterworks	HS-SPME	PDMS-DVB-CAR	30	60	25% NaCl	-	5	230	GC-MS	0.1–1.3 ng/L	83–112	[334]
Earthy-musty odorants	tap water, river water, lake water	HS-SPME	PDMS-DVB-CAR	30	90	-	-	-	-	GC-MS	0.25–0.61 ng/L	65–92	[335]
Earthy-musty odorants	tap water, lake water	HS-SPME	PDMS-DVB-CAR	30	50	30% NaCl	-	3	265	GC-MS	0.32–0.66 ng/L	86–113	[336]
Odorous trichlorobromo-phenols	tap water, river water	HS-SPME	PDMS-DVB-CAR	90	60	NaCl 6.5 g/ 30 mL	di-methyl sulfate / NaOH	1	270	GC-MS	0.22–0.95 ng/L	-	[337]
Algal taste and odor compounds	lake water	HS-SPME	PDMS-DVB-CAR	30	65	NaCl	-	3	250	GC-MS-O	sub to low ppt range	80–115	[87]
Volatile sulfur compounds	odorous freshwater lakes	HS-SPME	PDMS-CAR	30	45	-	-	3	250	GC-FPD	1.6–93.5 ng/L	87–112	[338]
Nitro musk fragrances	tap water, wastewater	HS-SPME	PDMS-CAR, PDMS-DVB	25	100	-	-	2	300 / 270	GC-µECD	0.25–3.6 ng/L	96–108	[339]
Volatile and semivolatile organic compounds													
VOC	surface water, wastewater from wastewater treatment plant and from municipal solid-waste treatment plant	HS-SPME	PDMS-CAR	30	50	10% NaCl	-	5	280	GC-MS-MS	0.005–2 µg/L	70–120	[340]

Table 4. *Cont.*

			Extraction conditions					Desorption conditions					
Analyte	**Environmental Sample**	**Technique**	**Fiber**	**Time [min]**	**Temp. [°C]**	**(Salt) Addition**	**Deriv.**	**Time [min]**	**Temp. [°C]**	**Detection**	**LOD**	**Recovery [%]**	**Ref.**
Volatile and semivolatile organic compounds													
Volatile and semivolatile organic compounds	landfill leachate	SBSE	PDMS	60–120	RT	-	none, acetate or BSTFA	30 °C to 280 °C at 60 °C/min, 5 min hold at 280 °C		GC-MS	-	-	[341]
Volatile and semivolatile organic compounds	snow	Di-SPME/ HS-SPME	PDMS-DVB	40 / 180	RT	-	-	5	250	GC-MS	0.11–1.93 µg/L	-	[342]
Pesticides													
Pyrethroid pesticides	tap water, waste water from sewage treatment plant, run-off water, water from container used for washing oranges	DI-SPME	PDMS	20	50	0.02% $Na_2S_2O_3$, 2% acetone	-	3	280	GC-MS	0.9–35 pg/mL	-	[343]
Pyrethroid pesticides	groundwater	DI-SPME	PDMS/DVB	30	65	-	-	5	-	LC-PIF-FD	0.003–0.009 µg/L	92–109	[344]
Benzimidazole fungicides	seawater, ground water, sewage	DI-SPME	PDMS-CAR	40	60	15% NaCl	-	10 (in metha-nol)	-	HPLC-FD	0.03–1.30 ng/mL	81–120	[345]
Organochlorine pesticides	lake water	HS-SPME	PMPVS	30	80	-	-	2	270	GC-ECD	0.84–13.0 ng/L	72–116	[346]
Organochlorine pesticides	groundwater	DI-SPME	PDMS-DVB-CAR	45	RT	-	-	2	260	GC-ECD	0.0013–0.45 ng/L	92–105	[347]

Table 4. *Cont.*

			Extraction conditions					Desorption conditions					
Analyte	**Environmental Sample**	**Technique**	**Fiber**	**Time [min]**	**Temp. [°C]**	**(Salt) Addition**	**Deriv.**	**Time [min]**	**Temp. [°C]**	**Detection**	**LOD**	**Recovery [%]**	**Ref.**
						Pesticides							
Organochlorine pesticides	seawater	HS-SPME	poly(3,4-ethylene dioxythio-phene)	15	70	-	-	2	270	GC-μECD	0.16–0.84 ng/L	63–127	[146]
Organochlorine pesticides and metabolites	seawater, sewage, groundwater	DI-SPME	PDMS-DVB, CW/TPR	40	50 /45	-	-	8 / 10	-	HPLC-UV-DAD	0.3–3.6 ng/mL	90–104	[348]
Pesticides tebuthiuron and diuron	water	DI-SPME	PA	50	-	-	-	15	-	LC-DAD	10–50 μg/L	-	[349]
Pesticides	surface and groundwater	DI-SPME	PA	30	50	-	-	5	280	GC-MS	0.02–0.3 ng/mL	78–109	[350]
Organo-phosphorus pesticides	river water	DI-SPME	sol-gel based amino fiber	40	30	20% NaCl	-	4	250	GC-MS	0.05–1.0 ng/L	80–115	[351]
Organochlorine (OCP), organo-phosphorus (OPP), triazine, pyrethroid, and miscellaneous pesticides	groundwater	HS-SPME	PDMS-DVB	60	60	-	-	-	-	GC-ECD-TSD / GC-MS / GC-MS-MS	<0.1 μg/L	-	[352]

Table 4. *Cont.*

			Extraction conditions					Desorption conditions					
Analyte	**Environmental Sample**	**Technique**	**Fiber**	**Time [min]**	**Temp. [°C]**	**(Salt) Addition**	**Deriv.**	**Time [min]**	**Temp. [°C]**	**Detection**	**LOD**	**Recovery [%]**	**Ref.**
PAH and related compounds													
PAH	tap water, surface water, underground water, rainwater	HS-SPME	PDMS	30	60	10% NaCl	-	2	280	GC-FID	0.06–0.5 µg/L	71–109	[353]
PAH	rainwater, strom water	DI-SPME	PDMS	60	65	0.5 M sodium mono-chloro-acetate	-	-	-	GC-MS	0.001–0.041 µg/L	72–111	[354]
PAH	wastewater from scrubber of pilot-scale fluidized bed incinerator system	MA-HS-SPME	PDMS-DVB	30	20	-	-	5	290	GC-FID	0.3–1.0 µg/L	88–103	[355]
PAH	surface waters, leaching waters of contaminated soils	HS-SPME	PA	60	50	-	-	2	250	GC-FID	0.08–0.20 µg/L	-	[356]
Hydroxy metabolites of PAH	mini pore water, minimal salts medium, soil extract culture medium	DI-SPME	PA	40	40	8% NaCl	BSTFA	3	280	GC-MS	0.002–0.134 µg/L	-	[357]

Table 4. *Cont.*

			Extraction conditions					Desorption conditions					
Analyte	**Environmental Sample**	**Technique**	**Fiber**	**Time [min]**	**Temp. [°C]**	**(Salt) Addition**	**Deriv.**	**Time [min]**	**Temp. [°C]**	**Detection**	**LOD**	**Recovery [%]**	**Ref.**
					Phenols								
Volatile phenols	well water, drinking water	HS-SPME	PANI	60	80	30% NaCl, pH 2	-	5	275	GC-FID	1.3–12.8 ng/mL	88–103	[88]
Phenols	real-life water samples	HS-SPME	PANI	50	50	NaCl, pH 2	-	5	200	GC-FID	0.69–3.7 ng/mL	69–112	[147]
Phenols	river water, waste water	DI-SPME	oxidized MWCNTs	30	20	36% NaCl	-	3 (in ACN / water 70:30)	RT	HPLC-DAD	0.25–3.67 ng/L	86–119	[138]
Phenols and nitrophenols	rainwater	SPME	PA	40	RT	NaCl, pH 3.0	MDBSTFA	5	280	GC-MS	0.2–99 µg/L	-	[358]
Chlorophenols	landfill leachate	IL-HS-SPME	1-butyl-3-methylimida-zolium hexafluoro-phosphate	4	25	pH 2	-	4	240	GC-MS	0.008–0.026 µg/L	87–99	[124]
Chlorophenols	landfill leachate	purge-assisted HS-SPME	PA	30	75	-	-	3	130 °C (0.05 min) to 300 °C at 8 °C/s, 4 min hold	GC-MS	0.1–0.4 pg/mL	83–114	[359]

Table 4. *Cont.*

			Extraction conditions					Desorption conditions					
Analyte	**Environmental Sample**	**Technique**	**Fiber**	**Time [min]**	**Temp. [°C]**	**(Salt) Addition**	**Deriv.**	**Time [min]**	**Temp. [°C]**	**Detection**	**LOD**	**Recovery [%]**	**Ref.**
					Miscellaneous								
Organometallic compounds (mercury, lead, tin)	river water, seawater	HS-SPME	PDMS-DVB-CAR	15	40	-	sodium tetra-ethyl-borate	2	260	GC-MS-MS	4–33 ng/L	50–109	[360]
Organo-phosphorus fire retardants and plasticizers	wastewater, MAE prior to SPME	DI-SPME	PDMS	30	65	10% NaCl	-	0.5	250	GC-ICP-MS / GC-TOF-MS	29–50 ng/L	38–43	[83]
Non-halogenated solvents	textile wastewater	HS-SPME	PDMS	10	35	-	-	5	240	GC-MS	0.1–300 µg/L	-	[361]
Acetone	seawater	SPME	PDMS-DVB	30	RT	NaCl, pH 3.7	PFBHA	5	250	GC-MS	3.0 nM	-	[362]
BTEX	waste water	HS-SPME	PDMS-DVB	1	RT	35% NaCl	-	0.16	200	portable GC-µFID	0.4–1.4 µg/L	98–111	[89]
BTEX	groundwater	HS-SPME	PDMS-CAR	15	25	267 g/L NaCl	-	2	290	cryo-trap-GC-MS	0.01–0.05 ng/L	-	[363]
Acrolein	surface water, drinking water	HS-SPME	PDMS-CAR	50	60	saturated NaCl solution	2,2,2-trifluo-roethyl-hydra-zine	-	220	GC-MS	0.06 µg/L	91–104	[364]

Table 4. *Cont.*

			Extraction conditions					Desorption conditions					
Analyte	**Environmental Sample**	**Technique**	**Fiber**	**Time [min]**	**Temp. [°C]**	**(Salt) Addition**	**Deriv.**	**Time [min]**	**Temp. [°C]**	**Detection**	**LOD**	**Recovery [%]**	**Ref.**
Miscellaneous													
Pharmaceutical compounds	wastewater	dSPME	CW-TPR	30	75	300 g/L NaCl, pH 3/11	-	10	-	LC-MS-MS	LOQ: 0.005–0.05 µg/L	89–110	[90]
Endocrine disrupting chemicals and steroid hormones	river water	DI-SPME	PA	90	45	10 g/L NaCl 10, pH 5	BSTFA	5	290	GC-MS	0.002–0.378 µg/L	-	[365]
Bisphenol A	landfill leachate	HS-SPME	PA	60	25	100 g/L NaCl, pH 2	BSTFA	5	280	GC-MS	0.03 µg/L	-	[91]
Estrogens	surface water, wastewater	IT-SPME	DVB	20 cycles à 40 µL (100 µL/min)	-	-	-	-	-	LC-MS-MS	2.7–11.7 pg/mL	86–107	[92]
Organic pollutants (pesticides, octyl/nonyl phenols, pentachloro-benzene, PAHs)	wastewater, landfill leachate	DI-SPME	CW-DVB	45	RT	NaCl 10%	-	5	250	GC-TOF-MS	-	-	[366]
Organochlorine pesticides and polychlorinated bisphenyls	river water	HS-SPME	PDMS	60	80	-	-	5	250	GC-MS-MS	0.4–26 pg/L	75–105	[367]

Table 4. *Cont.*

			Extraction conditions					Desorption conditions					
Analyte	**Environmental Sample**	**Technique**	**Fiber**	**Time [min]**	**Temp. [°C]**	**(Salt) Addition**	**Deriv.**	**Time [min]**	**Temp. [°C]**	**Detection**	**LOD**	**Recovery [%]**	**Ref.**
						Miscellaneous							
Volatile halogenated hydrocarbons, benzene	groundwater from waste-oil recycling facility	HS-SPDE	PDMS-AC	15 cycles à 1 mL (50 µL/s)	60	5% NaCl	-	1 mL (10 µL/s)	300	GC-MS	12–870 ng/L	-	[368]
BTEX and halocarbons	contaminated water	HS-SPME	PAC	20	40–45	25% NaCl	-	1	260	GC-FID-ECD	LOQ: 0.01–0.94 µg/L	88–113	[369]
Chlorobenzene	tap water, river water	HS-SPME	nanofiber coated by electrospun PU	5	30	25% NaCl	-	2	200	GC-MS	10 ng/L	94–102	[370]
1,2-cis-dichloroethylene, trichloroethylene	effluent from soil column experiments	HS-SPME	PDMS	5	25	-	-	1	250	GC-FID	2.4–4.2 µg/L	-	[371]
1,3-dichloro-2-propanol	tap water, river water, paper mill sewage	HS-SPME	PDMS-DVB-CAR	30	25	NaCl	BSTFA	5	260	GC-MS-MS	0.4 ng/mL	93–103	[318]
Epichlorohydrin	water and sewage	HS-SPME	PDMS-CAR	15	50	-	-	1	240	GC-MS, GC-ECD	water: 1.0 ng/L	-	[93]
Polybrominated diphenyl ethers	river water, waste water	DI-SPME	MWCNT	30	RT	-	-	2	295	GC-ECD	3.6–8.6 ng/L	90–119	[372]

Table 4. *Cont.*

			Extraction conditions					Desorption conditions					
Analyte	**Environmental Sample**	**Technique**	**Fiber**	**Time [min]**	**Temp. [°C]**	**(Salt) Addition**	**Deriv.**	**Time [min]**	**Temp. [°C]**	**Detection**	**LOD**	**Recovery [%]**	**Ref.**
Soil / Sediment and other Solid Matrices													
Odorous compounds													
VOC and odorous compounds	dairy manure	HS-SPME	PDMS-DVB-CAR	30	30	-	-	-	230	MD-GC-MS-O	-	-	[373]
Odorous volatile compounds	compost	HS-SPME	PDMS-CAR	60	20	-	-	40	250	GC-MS	0.06–2.38 ppb	-	[374]
Volatile and semivolatile organic compounds													
VOC	soil, manure, compost, biochar	HS-SPME	PDMS-DVB-CAR	20	20	-	-	5	230	GC-MS	0.01–310 ng/g	-	[375]
VOC	cow slurry	HS-SPME	PDMS-DVB-CAR / PDMS-CAR	15	35	NaCl	-	3	300	GC-MS	0.02–1441 µg/L	-	[376]
Volatile and semivolatile organic compounds	urban landfill soil	HS-SPME	PDMS-DVB	30	50	NaCl	-	-	250	GC-MS	-	-	[377]
Pesticides													
Pyrethroids, organochlorine pesticides	agricultural soils	HS-SPME	PA	30	100	-	-	5	290	GC-µECD	0.004–1.2 ng/g	71–147	[378]
Pyrethroids	sediment pore water	SPME	PDMS	20	-	-	-	3	260	GC-ECD	-	-	[379]

Table 4. *Cont.*

				Extraction conditions				Desorption conditions					
Analyte	**Environmental Sample**	**Technique**	**Fiber**	**Time [min]**	**Temp. [°C]**	**(Salt) Addition**	**Deriv.**	**Time [min]**	**Temp. [°C]**	**Detection**	**LOD**	**Recovery [%]**	**Ref.**
PAH and related compounds													
PAH	sediment pore water, sediments	SPME	PDMS	500 h	18	1 mL 10 mM NaN_3	-	15		50 °C to 250 °C at 200 °C /min	-	-	[380]
PAH	coastal sediments, MAE with acetone prior to SPME	DI-SPME	PDMS	60	60	-	-	-	270	GC-MS	0.07–0.76 µg/kg	70–110	[381]
PAH	sand, sediment	CF-HS-SPME	PDMS	40	150 (fiber: 5)	-	-	2	300	GC-FID	0.3–3 pg/g	-	[54]
Parent and alkyl PAH	sediment pore water	HS-SPME	PDMS	30	-	-	-	5	320	GC-MS	0.002–0.6 ng/mL	-	[382]
Miscellaneous													
4-*t*-octylphenol, nonylphenol, bisphenol A	activated sludge	nd-SPME	PA	-	20	-	-	5	2800	GC-MS	-	-	[383]
Phenols and indoles	cow slurry	HS-SPME	PDMS-DVB-CAR	15	35	NaCl	MTBSTFA	9	300	GC-MS	0.004–707 µg/L	>64	[94]
Polybrominated diphenyl ethers	soil	HS-SPME	sol-gel M-β-CD-OH-TSO	60	95	methanol	-	12	300	GC-MS	13.0–78.3 pg/g	78–99	[384]
Perfluoro-carboxylic acids	harbour sediments, PFE prior to SPME	HS-SPME	PDMS	30	30	saturated NaCl solution	boron trifluo-ride	3	300	GC-MS	0.5–0.8 ng/g	99–103	[95]

Table 4. *Cont.*

		Extraction conditions						Desorption conditions					
Analyte	**Environmental Sample**	**Technique**	**Fiber**	**Time [min]**	**Temp. [°C]**	**(Salt) Addition**	**Deriv.**	**Time [min]**	**Temp. [°C]**	**Detection**	**LOD**	**Recovery [%]**	**Ref.**
Miscellaneous													
Organotin compounds	sediment	HS-SPME	PDMS	30	80	ethanol, pH 5.3	sodium tetra-ethyl-borate	1	250	GC-MS	1.0–6.3 µg/kg	98–117	[84]
Mono-, di- and tri-butyltin	sediment, extraction with hydrochloric acid/ethanol prior to SPME	HS-SPME	PDMS	30	40	pH 4	sodium tetra-ethyl-borate	2	250	GC-MS-MS	0.03–1.0 pg/g	-	[96]
Cyclopentadienyl-manganese tricarbonyl, (methylcyclo-penta-di-enyl)manganese tricarbonyl	seawater, soil	HS-SPME	PDMS-DVB	20	60	5% NaCl	-	0,25	250	GC-MIP-AED	0.62–0.65 pg Mn/g	76–113	[385]
Nitrous oxide	estuarine soils and sediments	HS-SPME	PDMS-CAR	2	50	-	-	1	200	GC-MS	18 ppb	-	[386]

ACN: acetonitrile; CF: cold fiber; BSTFA: N,O-bis(trimethylsily)trifluoroacetamide; BTEX: benzene, toluene, ethyl benzene, ortho-xylene and meta- and para-xylene; BTX: benzene, toluene and xylene; DAD: diode array detector; deriv.: derivatization; DI: direct immersion; dSPME: dual SPME; ECD: electron capture detector; FID: flame ionization detector; FPD: flame photometric detector; IL: ionic liquid; IT: in-tube; FD: fluorescence detection; LOD: limit of detection; LOQ: limit of quantification; MA: microwave assisted; MAE: microwave assisted extraction; M-β-CD/OH-TSO: permethylated-β-cyclodextrin/hydroxyl-termination silicone oil; MD: multidimensional; MDBSTFA: N-(t-butyldimethylsilyl)-N-methyltrifluoroacetamide; MIP-AED: microwave-induced plasma atomic emission detection; MS-O: mass spectrometry-olfactometry; MTBSTFA: N-methyl-N-t-butyldimethylsilyltrifluoroacetamide; MW: multi-walled; nd-SPME: negligible depletion-SPME; NPD: nitrogen–phosphorus detector; PAC: powered activated carbon; PAHs: polycyclic aromatic hydrocarbons; PANI: polyaniline; PDMS-AC: PDMS mixed with activated C; PFBHA: pentafluorobenzyl-hydroxylamine hydrochloride; PFE: pressurized fluid extraction; PIF: postcolumn photochemically induced fluorimetry derivatization; PMPVS: polymethylphenylvinylsiloxane; PU: polyurethane; ref.: reference; RT: room temperature; SW: single-walled; temp.: temperature; TOF: time-of-flight; TPR: template resin; TPS: total suspended particulate; TSD: thermoionic specific detection.

Typical fields of applications are the analysis of VOC, odorous compounds, or micro-pollutants in indoor air, atmospheric air, or gaseous effluents from industrial or agricultural operations. For example, Bourdin and Desauziers [82] developed a simple and fast method based on on-fiber derivatization using BSTFA for the analysis of formaldehyde and other carbonyl compounds in indoor air. For a 5 min fiber exposure time, the limits of detection were below 0.5 μg/m^3, the average reproducibility was 15%, and the linearity of the calibration curves was satisfactory. Of the micro-pollutants, formaldehyde is of particular concern as it was recognized as "carcinogenic to humans" (class 1) by the International Agency for Research on Cancer. It is found in nearly every indoor atmosphere because of its numerous sources, such as furniture, human activity (tobacco), glues, and varnishes [82]. Several authors used SPME as a screening method for the characterization of odorous compounds in gaseous effluents, e.g., livestock operations [320] or production of poultry feather and viscera meal [325] in order to develop suitable abatement strategies. SPME can also be used for analysis of airborne particulate matter after collection on filters [330,333].

5.2. Aqueous Samples

Aqueous sampling by SPME can be performed by direct immersion, the HS method, or the IT SPME method. Most of the papers reported HS-SPME applications to aqueous samples and subsequent GC separation combined with different detectors (see Table 4). In recent years DI-SPME followed by LC has gained popularity [21]. Derivatization techniques have been used for example for analysis of PAH and related compounds [357], phenols [337,358], organometallic compounds [360], endocrine disruptors and steroid hormones [91,365], acetone [362], and acrolein [364] in aqueous samples. In addition to commercially available SPME fibers, fibers with new coating materials have been used. They include poly(3,4-ethylene dioxythiophene) [146] and a sol-gel based amino fiber [351] for analysis of pesticides. Polyaniline [88,147], oxidized multiwalled carbon nanotubes [138], and 1-butyl-3-methylimidazolium hexafluorophosphate [124] have been applied to the analysis of phenols. Furthermore, a nanofiber coated by electrospun PU [370] was utilized for analysis of chlorobenzene.

SPME has been used for the analysis of a wide variety of water pollutants including pesticides, PAHs, and phenols. Several publications on SPME analysis of many classes of pesticides in groundwater, lake, river and seawater, and waste water are available [146,343–347]. Results showed good performance of the methods with high recovery rates >70% and very low LOD, often in the range of ng/L. For example, Raposo *et al*. [347] applied a GC/ECD method using DI-SPME for the analysis of organochlorine pesticides in groundwater with recovery rates between 92 and 105% and LOD between 0.0013 and 0.45 ng/L [347]. Furthermore, SPME has been used to determine PAH, a large group of molecules widely distributed in the environment, and their metabolites in tap, rain, and surface waters as well as scrubber water with high recoveries (>71%) [353–357]. SPME has also been successfully applied to other classes of pollutants in environmental water samples, e.g., phenols [88,124,138,147,358,359], pharmaceuticals [90], endocrine disrupting chemicals and hormones [97,98,365] and organometallic compounds of mercury, lead and tin [360].

Other fields of SPME application are the analysis of volatile and semivolatile organic compounds in waste water and landfill leachate [340] and the analysis of odorous compounds like earthy-musty odorants [334–336] and volatile sulfur compounds [338] in tap, river, or lake water.

5.3. Solid Samples

Sampling of soil and sediments as well as other solid materials like manure, activated sludge, and biochar by SPME is usually performed by HS methods. In some applications extraction of analytes has been assisted by heating of the sample [84,377,378,384–386] or cooling the fiber [54], use of microwaves [381]; use of pressurized fluid extraction [95], or addition of small amounts of organic solvents prior to SPME [84,384]. Most applications published on SPME analysis of solid environmental samples involve the use of commercially available SPME fibers. A novel sol-gel permethylated-β-cyclodextrin/hydroxyl-termination silicone oil coated fiber has been used to extract polybrominated diphenyl ethers from soil [384]. With this coating, improved fiber stability has been achieved at analytical characteristics similar to commercially available fibers (RSD < 10%, LOD 13.0–78.3 pg/g, recovery > 78%, r > 0.999).

The main fields of SPME applications to solid environmental samples are analysis of pesticides [378,379], PAH and related compounds [380–382], phenols [94,383], perfluorocarboxylic acids [95], and organotin compounds [84] in contaminated soils and sediments (see Table 4). Since SPME is generally organic solvent free, rapid, and sensitive, it allows the detection of trace amounts of substances that are short-lived during biotransformation, thus, providing insight into degradation pathways. For example, Shen *et al*. [383] developed a negligible depletion-SPME (nd-SPME) method to measure free concentrations of 4-t-octylphenol, nonylphenol and bisphenol A in order to determine aerobic biodegradation kinetics in activated sludge [383]. In nd-SPME, the extracted amount of analytes is so small that the depletion (*i.e*., change of concentrations) of the analytes does not lead to a change in reaction kinetics or other relevant conditions in the sample. Further applications of SPME to solid environmental samples are characterization of VOC and odorous compounds in soil, manure, compost, and biochar samples [373–377].

6. Prospects and Trends

Recent trends in sample preparation techniques comprise miniaturization, automation, high-throughput performance, on-line coupling with analytical instruments as well as low-cost operation through extremely low or no solvent consumption. Among other techniques mentioned in this review, SPME has the potential to meet these challenges [50]. Through miniaturization of sample preparation steps time and operation costs can be saved. The main advantage however is the possibility to determine trace and ultratrace analytes in complex matrices.

In addition to SPME techniques, further selective extraction procedures have been developed. They all show clear trends toward simplification of sampling and sample preparation methods, an increase in reliability and precision, and the elimination of the cleanup step. The development of more sensitive and selective phases may be a step towards further miniaturization of these techniques. Increasing interest also lies in the field of automating sample preparation. Automation can result in faster procedures as well as improved precision and cost-effectiveness. Over the last decade, sample preparation devices have been automated and coupled to separation and detection systems specifically designed for automation.

Due to the lack of automation, SPME tends to be coupled more often to GC than to LC. Moreover, more recent techniques such as SBSE are not yet as widely accepted as SPME due to the difficulty of

achieving full automation. Another challenge related to new SPME techniques that has to be overcome is the carry-over effect occurring for example in SPDE, in-tip SPME and MEPS techniques due to the remaining of analytes on the inner surface of the needle after heat desorption [50,63,64,387]. Another aspect that should be considered for optimization is the moderate enrichment capacity of these techniques [50].

Research regarding SPME is not only based on the development of new devices but also on the study of derivatization strategies, new coatings with higher extraction efficiencies, selectivity and stability, and the study of novel calibration processes [2]. During the SPME process there are many different parameters that can be applied to achieve specific methods. Derivatization for example is a valuable tool in many cases to achieve efficient extraction. With regard to chemical consumption and waste generation, a recent trend however is to avoid derivatization techniques where possible [98].

The variety of commercially available fiber coatings is constantly growing which open up the range for further applications. However, in addition to these commercially available sorbents, further promising coating procedures have been developed. This approach opens up new fields of application. Furthermore, efforts are made to overcome limitations in biocompatibility, on-site compatibility, selectivity and sensitivity of currently available SPME coatings [103,104]. Besides physical coating processes which are compatible with nearly all kinds of sorbent materials there is a clear trend towards procedures developed for specific components. Most attention in past years has been given to the application of nanomaterials [115,370]. Nanostructured MIP-based coatings will continue to be of particular interest. Great attention is currently given to such specific SPME coatings as a basis for development of more designable structures. Even when issues like selectivity for target analytes and applicability for samples with complex matrix compositions have to be solved [24].

Quantitation is currently the major challenge for SPME procedures to gain wider application. This review showed that calibration techniques are still under development [22]. The model calculation methods laid down in chapter 2.5 provide a meaningful approach to overcome these challenges. A better understanding of SPME processes will be the basis of further improvements. Nonetheless, a number of norms have already been implemented and indicate that the application of calibration methods in SPME is possible. In the field of aroma analysis of food, the main quantification barrier is the high complexity of volatile compounds [388,389].

Food safety and quality control is mainly responsible for the development of further rapid and automated procedures aimed to raise the sample throughput and minimize sources of error [3]. Since 2006 there has been a strong and still valid trend towards SPME application for the analysis of wine, fruit/vegetables, dairy and meat products and other foods. In this field, SPME seems to have a leading role followed by SBSE and liquid microextraction methods such as SDME and LLME [13].

In the field of environmental analysis, further improvement of rapid techniques suitable for on-site, on-line and *in situ* measurements of pollutants and their transformation products will be an important future challenge. These methods will provide insight into natural environmental processes, such as natural attenuation and uptake by plants as well as toxic effects and toxicity mechanisms of emerging chemicals.

Microextraction techniques represent a step towards the miniaturization of the analytical laboratory which is one of the major challenges and directions of future method development acitivites. Applications of SPME in different fields apart from environmental and food analysis such as pharmaceutical, process monitoring, clinical, forensic or drugs are continuously increasing [2].

7. Conclusions

Solid-phase microextraction (SPME) techniques take a leading position among microextraction methods due to their simplicity and the possibility of automation. SPME is a very useful technique for analyzing volatiles occurring in very low concentrations in various foods and environmental applications occurring in very low concentrations. A reliable tool for the identification and quantitation widely applied in the analysis of chemical compounds and biological substances needs a high-quality sample preparation. In this context, SPME may provide very good solutions. The development of new rapid SPME techniques might further increase its credibility. However, the challenges of this method in handling complex sample matrices must be taken into consideration. Additionally, limitations regarding quantitation of target analytes need to be reduced. The selection of an appropriate SPME fiber requires knowledge of the sample matrix properties. Nowadays, there is a large variety of different fiber coatings, extraction and desorption techqniues as well as derivatization procedures available, enabling the development of selective, sensitive and repeatable SPME methods for food and environmental analysis.

Author Contributions

Sybille Merkle reviewed the food applications and recent SPME developments together with Dr. Kim Karen Kleeberg who wrote to the environmental applications under the supervision of Prof. Jan Fritsche.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Nerín, C. Focus on sample handling. *Anal. Bioanal. Chem.* **2007**, *388*, 1001–1002.
2. Nerín, C.; Salafranca, J.; Aznar, M.; Batlle, R. Critical review on recent developments in solventless techniques for extraction of analytes. *Anal. Bioanal. Chem.* **2009**, *393*, 809–833.
3. Mondello, L.; Costa, R.; Tranchida, P.Q.; Dugo, P.; Presti, M.L.; Festa, S.; Fazio, A.; Dugo, G. Reliable characterization of coffee bean aroma profiles by automated headspace solid phase microextraction-gas chromatography-mass spectrometry with the support of a dual-filter mass spectra library. *J. Sep. Sci.* **2005**, *28*, 1101–1109.
4. Arthur, C.L.; Pawliszyn, J. Solid Phase Microextraction with Thermal Desorption Using Fused Silica Optical Fibers. *Anal. Chem.* **1990**, *62*, 2145−2148.
5. Pawliszyn, J. *Solid Phase Microextraction: Theory and Practice*; Wiley, VCH: New York, NY, USA, 1997.
6. Lord, H.; Pawliszyn, J. Evolution of solid-phase microextraction technology. *J. Chromatogr. A* **2000**, *885*, 153−193.
7. Adahchour, M.; Beens, J.; Vreuls, R.J.J.; Batenburg, A.M.; Rosing, E.A.E.; Brinkman, U.A.T. Application of Solid-Phase Micro-Extraction and Comprehensive Two-Dimensional Gas Chromatography (GC x GC) for Flavour Analysis. *Chromatographia* **2002**, *55*, 361–367.

8. Chai, M.; Pawliszyn, J. Analysis of Environmental Air Samples by Solid-Phase Microextraction and Gas Chromatography/lon Trap Mass Spectrometry. *Environ. Sci. Technol.* **1995**, *29*, 693−701.
9. Kleeberg, K.K.; Dobberstein, D.; Hinrichsen, N.; Müller, A.; Weber, P.; Steinhart, H. Sampling Procedures with Special Focus on Automatization. In *Advances in Food Diagnostics*, 1st ed.; Nollet, L.M.L., Toldrá, F., Eds.; Blackwell Publishing: Ames, IA, USA, 2007; pp. 253−293.
10. Pawliszyn, J. Method and Device for Solid Phase Microextraction and Desorption. US Patent 5691206 A, 1997.
11. Dietz, C.; Sanz, J.; Cámara, C. Recent developments in solid-phase microextraction coatings and related techniques. *J. Chromatogr. A* **2006**, *1103*, 183–192.
12. Kataoka, H.; Lord, H.L.; Pawliszyn, J. Applications of solid-phase microextraction in food analysis. *J. Chromatogr. A* **2000**, *880*, 35–62.
13. Jeleń, H.H.; Majcher, M.; Dziadas, M. Microextraction techniques in the analysis of food flavor compounds: A review. *Anal. Chim. Acta* **2012**, *738*, 13–26.
14. Pillonel, L.; Bosset, J.O.; Tabacchi, R. Rapid Preconcentration and Enrichment Techniques for the Analysis of Food Volatile. A Review. *Lebensm.-Wiss. Technol.* **2002**, *35*, 1–14.
15. Wardencki, W.; Michulec, M.; Curylo, J. A review of theoretical and practical aspects of solid-phase microextraction in food analysis. *Int. J. Food Sci. Technol*. **2004**, *39*, 703–717.
16. Alpendurada, M.F. Solid-phase microextraction: A promising technique for sample preparation in environmental analysis. *J. Chromatogr. A* **2000**, *889*, 3−14.
17. Buchberger, W.; Zaborsky, P. Sorptive Extraction Techniques for Trace Analysis of Organic Pollutants in the Aquatic Environment. *Acta Chim. Slov*. **2007**, *54*, 1–13.
18. Ouyang, G.; Pawliszyn, J. Recent developments in SPME for on-site analysis and monitoring. *TrAC Trends Anal. Chem.* **2006**, *25*, 692–703.
19. Ribeiro, C.; Ribeiro, A.R.; Maia, A.S.; Gonçalves, V.M.; Tiritan, M.E. New Trends in Sample Preparation Techniques for Environmental Analysis. *Crit. Rev. Anal. Chem*. **2014**, *44*, 142−185.
20. Wardencki, W.; Curyło, J.; Namieśnik, J. Trends in solventless sample preparation techniques for environmental analysis. *J. Biochem. Biophys. Methods* **2007**, *70*, 275–288.
21. Padrón, M.E.; Afonso-Olivares, C.; Sosa-Ferrera, Z.; Santana-Rodríguez, J.J.; Microextraction Techniques Coupled to Liquid Chromatography with Mass Spectrometry for the Determination of Organic Micropollutants in Environmental Water Samples. *Molecules* **2014**, *19*, 10320−10349.
22. Ouyang, G.; Pawliszyn, J. A critical review in calibration methods for solid-phase microextraction. *Anal. Chim. Acta* **2008**, *627*, 184–197.
23. Aziz-Zanjani, M.O.; Mehdinia, A. Electrochemically prepared solid-phase microextraction coatings—A review. *Anal. Chim. Acta* **2013**, *781*, 1–13.
24. Aziz-Zanjani, M.O.; Mehdinia, A. A review on procedures for the preparation of coatings for solid phase microextraction. *Microchim. Acta* **2014**, *181*, 1169–1190.
25. Kumar, A.; Gaurav; Malik, A.K.; Tewary, D.K.; Singh, B. A review on development of solid phase Microextraction fibers by sol–gel methods and their applications. *Anal. Chim. Acta* **2008**, *610*, 1–14.
26. Luo, J.; Wu, Y.; Lin, S. Review: Recent developments of carbon nanotubes hybrid assemblies for sensing. *Am. J. Nano Res. Appl.* **2015**, *3*, 23−28.
27. Moein, M.M.; Said, R.; Bassyouni, F.; Abdel-Rehim, M. Solid Phase Microextraction and Related Techniques for Drugs in Biological Samples. *J. Anal. Methods Chem*. **2014**, doi: 10.1155/2014/921350.

28. Aulakh, J.S.; Malik, A.K.; Kaur, V.; Schmitt-Kopplin, P. A Review on Solid Phase Micro Extraction—High Performance Liquid Chromatography (SPME-HPLC) Analysis of Pesticides. *Crit. Rev. Anal. Chem*. **2005**, *35*, 71−85.
29. Turner, N.W.; Subrahmanyam, S.; Piletsky, S.A. Analytical methods for determination of mycotoxins: A review. *Anal. Chim. Acta* **2009**, *632*, 168–180.
30. Kataoka, H. Automated sample preparation using in-tube solid-phase microextraction and its application—A review. *Anal. Bioanal. Chem*. **2002**, *373*, 31–45.
31. Smith, R.M. Before the injection—Modern methods of sample preparation for separation techniques. *J. Chromatogr. A* **2003**, *1000*, 3–27.
32. Nerín, C.; Philo, M.R.; Salafranca, J.; Castle, L. Determination of bisphenol-type contaminants from food packaging materials in aqueous foods by solid-phase microextraction–high-performance liquid chromatography. *J. Chromatogr. A* **2002**, *963*, 375–380.
33. Zhang, Z.; Pawliszyn, J. Headspace solid-phase microextraction. *Anal. Chem.* **1993**, *65*, 1843–1852.
34. Tuduri, L.; Desauziers, V.; Fanlo, J.L. A simple calibration procedure for volatile organic compounds sampling in air with adsorptive solid-phase microextraction fibers. *Analyst* **2003**, *128*, 1028–1032.
35. Spietelun, A.; Pilarczyk, M.; Kloskowski, A.; Namieśnik, J. Current trends in solid-phase microextraction (SPME) fibre coatings. *Chem. Soc. Rev.* **2010**, *39*, 4524.
36. Namieśnik, J.; Zygmunt, B.; Jastrzebska, A. Application of solid-phase microextraction for determination of organic vapours in gaseous matrices. *J. Chromatogr. A* **2000**, *885*, 405–418.
37. Souza-Silva, E.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.
38. Aulakh, J.S.; Malik, A.K.; Kaur, V.; Schmitt-Kopplin, P. A Review on Solid Phase Micro Extraction—High Performance Liquid Chromatography (SPME-HPLC) Analysis of Pesticides. *Crit. Rev. Anal. Chem.* **2005**, *35*, 71–85.
39. Spietelun, A.; Marcinkowski, Ł.; Kloskowski, A.; Namieśnik, J. Application of green sample preparation techniques for the isolation, preconcentration and gas chromatographic determination of organic environmental pollutants. Proceeedings of the 6th Shanghai International Symposium on Analytical Chemistry, Shanghai, China, 16−18 October 2012.
40. Gan, J.; Bondarenko, S. Determination of Pesticides in Water. In *Analysis of Pesticides in Food and Enviromental Samples*; Tadeo, J.L., Ed.; CRC Press: Boca Raton, FL, USA, 2008; Volume 3, pp. 231–256.
41. Vas, G.; Vékey, K. Solid-phase microextraction: A powerful sample preparation tool prior to mass spectrometric analysis. *J. Mass Spectrom*. **2004**, *39*, 233–254.
42. Prosen, H.; Zupančič-Kralj, L. Solid-phase microextraction. *TrAC Trends Anal. Chem*. **1999**, *18*, 272–282.
43. Ai, J. Solid Phase Microextraction for Quantitative Analysis in Nonequilibrium Situations. *Anal. Chem*. **1997**, *69*, 1230–1236.
44. Ai, J. Headspace Solid Phase Microextraction. Dynamics and Quantitative Analysis before Reaching a Partition Equilibrium. *Anal. Chem*. **1997**, *69*, 3260–3266.

45. Eisert, P.; Pawliszyn, J. Automated In-Tube Solid-Phase Microextraction Coupled to High-Performance Liquid Chromatography. *Anal. Chem.* **1997**, *69*, 3140–3147.
46. Globig, D.; Weickhardt, C. Fully automated in-tube solid-phase microextraction for liquid samples coupled to gas chromatography. *Anal. Bioanal. Chem*. **2005**, *381*, 656−659.
47. Silva, C.; Cavaco, C.; Perestrelo, R.; Pereira, J.; Câmara, J.S. Microextraction by Packed Sorbent (MEPS) and Solid-Phase Microextraction (SPME) as Sample Preparation Procedures for the Metabolomic Profiling of Urine. *Metabolites* **2014**, *4*, 71−97.
48. Kubinec, R.; Berezkin, V.G.; Górová, R.; Addová, G.; Mracnová, H.; Soják, L. Needle concentrator for gas chromatographic determination of BTEX in aqueous samples. *J. Chromatogr. B* **2004**, *800*, 295–301.
49. Jochmann, M.A. Solventless extraction and enrichment methods for compound-specific isotope analysis. Ph.D. Thesis, University of Tubingen, Germany, 19 December 2006.
50. Kataoka, H. Recent developments and applications of microextraction techniques in drug analysis. *Anal. Bioanal. Chem*. **2010**, *396*, 339–364.
51. Saito, Y.; Jinno, K. Miniaturized sample preparation combined with liquid phase Separations. *J. Chromatogr. A* **2003**, *1000*, 53–67.
52. Zhang, Z.; Pawliszyn, J. Quantitative Extraction Using an Internally Cooled Solid Phase Microextraction Device. *Anal. Chem*. **1995**, *67*, 34–43.
53. Chen, Y.; Pawliszyn, J. Miniaturization and Automation of an Internally Cooled Coated Fiber Device. *Anal. Chem*. **2006**, *78*, 5222–5226.
54. Ghiasvand, A.R.; Hosseinzadeh, S.; Pawliszyn, J. New cold-fiber headspace solid-phase microextraction device for quantitative extraction of polycyclic aromatic hydrocarbons in sediment. *J. Chromatogr. A* **2006**, *1124*, 35–42.
55. Carasek, E.; Pawliszyn, J. Screening of Tropical Fruit Volatile Compounds Using Solid-Phase Microextraction (SPME) Fibers and Internally Cooled SPME Fiber. *J. Agric. Food Chem.* **2006**, *54*, 8688–8696.
56. Carasek, E.; Cudjoe, E.; Pawliszyn, J. Fast and sensitive method to determine chloroanisoles in cork using an internally cooled solid-phase microextraction fiber. *J. Chromatogr. A* **2007**, *1138*, 10–17.
57. Mirnaghi, F.S.; Hein, D.; Pawliszyn, J. Thin-Film Microextraction Coupled with Mass Spectrometry and Liquid Chromatography–Mass Spectrometry. *Chromatographia* **2013**, *76*, 1215–1223.
58. Jiang, R.; Pawliszyn, J. Thin-film microextraction offers another geometry for solid-phase microextraction. *TrAC Trends Anal. Chem*. **2012**, *39*, 245–253.
59. Koziel, J.A.; Odziemkowski, M.; Pawliszyn, J. Sampling and Analysis of Airborne Particulate Matter and Aerosols Using In-Needle Trap and SPME Fiber Devices. *Anal. Chem*. **2001**, *73*, 47–54.
60. Wang, A.; Fang, F.; Pawliszyn, J. Sampling and determination of volatile organic compounds with needle trap devices. *J. Chromatogr. A* **2005**, *1072*, 127−135.
61. Saito, Y.; Ueta, I.; Kotera, K.; Ogawa, M.; Wada, H.; Jinno, K. In-needle extraction device designed for gas chromatographic analysis of volatile organic compounds. *J. Chromatogr. A* **2006**, *1106*, 190–195.

62. SPDE^{TM}: The Magic Needle. flyer; CHROMTECH GmbH: Idstein, Germany, 2006. Available online: http://www.chromtech.de/download/20130130160105/CT-ProduktblattSPDE-231205.pdf (accessed on 31 March 2015).
63. Ampuero, S.; Bogdanov, S.; Bosset, J.O. Classification of unifloral honeys with an MS-based electronic nose using different sampling modes: SHS, SPME and INDEX. *Eur. Food Res. Technol.* **2004**, *218*, 198–207.
64. Lipinski, J. Automated solid phase dynamic extraction—Extraction of organics using a wall coated syringe needle. *Fresenius. J. Anal. Chem.* **2001**, *369*, 57–62.
65. Balasubramanian, S.; Panigrahi, S. Solid-Phase Microextraction (SPME) Techniques for Quality Characterization of Food Products: A Review. *Food Bioprocess Technol.* **2011**, *4*, 1–26.
66. Nilsson, T.; Ferrari, R.; Facchetti, S. Inter-laboratory studies for the validation of solid-phase microextraction for the quantitative analysis of volatile organic compounds in aqueous samples. *Anal. Chim. Acta* **1997**, *356*, 113–123.
67. Bene, A.; Luisier, J.L.; Fornage, A. Applicability of a SPME method for the rapid determination of VOCs. *Chimia* **2002**, *56*, 289–291.
68. Basheer, C.; Lee, H.K. Hollow fiber membrane-protected solid phase microextraction of triazine herbicides in bovine milk and sewage sludge samples. *J. Chromatogr. A* **2004**, *1047*, 189–194.
69. Razote, E.; Jeon, I.; Maghirang, R.; Chobpattana, W. Dynamic air sampling of volatile organic compounds using solid phase microextraction. *J. Environ. Sci. Health Part B* **2002**, *37*, 365–378.
70. Razote, E.B.; Maghirang, R.G.; Seitz, L.M.; Jeon, I.J. Characterization of volatile organic compounds on airborne dust in a swine finishing barn. *Transac. ASAE* **2004**, *47*, 1231–1238.
71. Parreira, F.V.; de Carvalho, C.R.; Cardeal, Z.L. Evaluation of indoor exposition to benzene, toluene, ethylbenzene, xylene and styrene by passive sampling with a solid-phase microextraction device. *J. Chromatogr. Sci*. **2002**, *40*, 122–126.
72. Jung, D.M.; Ebeler, S.E. Headspace solid-phase microextraction method for the study of the volatility of selected flavor compounds. *J. Agric. Food Chem*. **2003**, *51*, 200–205.
73. Pawliszyn, J. Solid phase Microextraction. In *A century of Separation Science*; Issaq, H.J., Ed.; Marcel Dekker, Inc: New York, NY, USA, 2002; pp. 399–419.
74. Costas-Rodriguez, M.; Pena-Pereira, F. Method Development with Miniaturized Sample Preparation Techniques. In *Miniaturization in Sample Preparation*; Pena-Pereira, F., Ed.; De Gruyter Open: Warsaw, Poland, 2014; pp. 276−307.
75. Pawliszyn, J. *Handbook of solid phase Microextraction*, 1st ed.; Elsevier Inc: Waltham, MA, USA, 2012.
76. Lord, H.L. Strategies for interfacing solid-phase microextraction with liquid chromatography. *J. Chromatogr. A* **2008**, *1152*, 2–13.
77. Tong, H.; Sze, N.; Thomson, B.; Nacson, S.; Pawliszyn, J. Solid phase microextraction with matrix assisted laser desorption/ionization introduction to mass spectrometry and ion mobility spectrometry. *Analyst* **2002**, *127*, 1207–1210.
78. Stalikas, C.D.; Fiamegos, Y.C. Microextraction combined with derivatization. *TrAC Trends Anal. Chem*. **2008**, *27*, 533–542.
79. Pan, L.; Pawliszyn, J. Derivatization/Solid-Phase Microextraction: New Approach to Polar Analytes. *Anal. Chem.* **1997**, *69*, 196–205.

80. Martínez-Uruñuela, A.; González-Sáiz, J.M.; Pizarro, C. Multiple solid-phase microextraction in a non-equilibrium situation Application in quantitative analysis of chlorophenols and chloroanisoles related to cork taint in wine. *J. Chromatogr. A* **2005**, *1089*, 31–38.
81. Bianchi, F.; Careri, M.; Musci, M.; Mangia, A. Fish and food safety: Determination of formaldehyde in 12 fish species by SPME extraction and GC–MS analysis. *Food Chem.* **2007**, *100*, 1049–1053.
82. 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.
83. Ellis, J.; Shah, M.; Kubachka, K.M.; Caruso, J.A. Determination of organophosphorus fire retardants and plasticizers in wastewater samples using MAE-SPME with GC-ICPMS and GC-TOFMS detection. *J. Environ. Monit.* **2007**, *9*, 1329–1336.
84. Devos, C.; Vliegen, M.; Willaert, B.; David, F.; Moens, L.; Sandra, P. Automated headspace-solid-phase micro extraction–retention time locked-isotope dilution gas chromatography–mass spectrometry for the analysis of organotin compounds in water and sediment samples. *J. Chromatogr. A* **2005**, *1079*, 408–414.
85. Mateo-Vivaracho, L.; Ferreira, V.; Cacho, J. Automated analysis of 2-methyl-3-furanthiol and 3-mercaptohexyl acetate at ng L−1 level by headspace solid-phase microextracion with on-fibre derivatisation and gas chromatography–negative chemical ionization mass spectrometric determination. *J. Chromatogr. A* **2006**, *1121*, 1–9.
86. Zhu, W.; Koziel, J.A.; Cai, L.; Özsoy, D.H.; Leeuwen, J.H. Quantification of Carbonyl Compounds Generated from Ozone-Based Food Colorants Decomposition Using On-Fiber Derivatization-SPME-GC-MS. *Chromatography* **2015**, *2*, 1−18.
87. Peter, A.; Köster, O.; Schildknecht, A.; Gunten, U. Occurrence of dissolved and particle-bound taste and odor compounds in Swiss lake waters. *Water Res.* **2009**, *43*, 2191–2200.
88. Mousavi, M.; Noroozian, E.; Jalali-Heravi, M.; Mollahosseini, A. Optimization of solid-phase microextraction of volatile phenols in water by a polyaniline-coated Pt-fiber using experimental design. *Anal. Chim. Acta* **2007**, *581*, 71–77.
89. Ji, J.; Deng, C.; Shen, W.; Zhang, X. Field analysis of benzene, toluene, ethylbenzene and xylene in water by portable gas chromatography–microflame ionization detector combined with headspace solid-phase microextraction. *Talanta* **2006**, *69*, 894–899.
90. Unceta, N.; Sampedro, M.C.; Bakar, N.K.A.; Gómez-Caballero, A.; Goicolea, M.A.; Barrio, R.J. Multi-residue analysis of pharmaceutical compounds in wastewaters by dual solid-phase microextraction coupled to liquid chromatography electrospray ionization ion trap mass spectrometry. *J. Chromatogr. A* **2010**, *1217*, 3392–3399.
91. Li, X.; Lin, L.; Zou, S.; Lan, C.; Luan, T. Determination of bisphenol A in landfill leachate by solid phase microextraction with headspace derivatization and gas chromatography-mass spectrophotometry. *Chin. J. Anal. Chem.* **2006**, *34*, 325–328.
92. Mitani, K.; Fujioka, M.; Kataoka, H. Fully automated analysis of estrogens in environmental waters by in-tube solid-phase microextraction coupled with liquid chromatography–tandem mass spectrometry. *J. Chromatogr. A* **2005**, *1081*, 218–224.
93. Gaca, J.; Wejnerowska, G. Determination of epichlorohydrin in water and sewage samples. *Talanta* **2006**, *70*, 1044–1050.

94. Larreta, J.; Usobiaga, A.; Etxebarria, N.; Arana, G.; Zuloaga, O. Optimisation of the on-fibre derivatisation of volatile fatty acids in the simultaneous determination together with phenols and indoles in cow slurries. *Anal. Bioanal. Chem.* **2007**, *389*, 1603−1609.
95. Alzaga, R.; Salgado-Petinal, C.; Jover, E.; Bayona, J.M. Development of a procedure for the determination of perfluorocarboxylic acids in sediments by pressurised fluid extraction, headspace solid-phase microextraction followed by gas chromatographic–mass spectrometric determination. *J. Chromatogr. A* **2006**, *1083*, 1–6.
96. Carvalho, P.N.; Pinto, L.F.; Clara, M.; Basto, P.; Teresa, M.; Vasconcelos, S.D. Headspace solid-phase micro-extraction and gas chromatography-ion trap tandem mass spectrometry method for butyltin analysis in sediments: Optimization and validation. *Microchem. J.* **2007**, *87*, 147–153.
97. Quintana, J.B.; Rodriguez, I. Strategies for the microextraction of polar organic contaminants in water samples. *Anal. Bioanal. Chem*. **2006**, *384*, 1447–1461.
98. Gałuszka, A.; Migaszewski, Z.; Namieśnik, J. The 12 principles of green analytical chemistry and the SIGNIFICANCE mnemonic of green analytical practices. *TrAC Trends Anal. Chem.* **2013**, *50*, 78–84.
99. Wu, J.; Xie, W.; Pawliszyn, J. Automated in tube solid-phase microextraction coupled with HPLC–ES–MS for the determination of catechins and caffeine in tea. *Analyst* **2000**, *125*, 2216–2222.
100. Górecki, T.; Yu, X.; Pawliszyn, J. Theory of analyte extraction by selected porous polymer SPME fibres. *Analyst* **1999**, *124*, 643−649.
101. Cai, J.; Liu, B.; Su, Q. Comparison of simultaneous distillation extraction and solid-phase microextraction for the determination of volatile flavor components. *J. Chromatogr. A* **2001**, *930*, 1–7.
102. Kleeberg, K.K.; Liu, Y.; Jans, M.; Schlegelmilch, M.; Streese, J.; Stegrnann, R. Development of a simple and sensitive method for the characterization of odorous waste gas emissions by means of solid-phase microextraction (SPME) and GC MS/olfactometry. *Waste Manage*. **2005**, *25*, 872–879.
103. Huang, K.P.; Wang, G.R.; Huang, B.Y.; Liu, C.Y. Preparation and application of ionic liquid-coated fused-silica capillary fibers for solid-phase microextraction. *Anal. Chim. Acta* **2009**, *645*, 42–47.
104. He, Y.; Pohl, J.; Engel R.; Rothman L.; Thomas, M. Preparation of ionic liquid based solid-phase microextraction fiber and its application to forensic determination of methamphetamine and amphetamine in human urine. *J. Chromatogr. A* **2009**, *1216*, 4824–4830.
105. Mullett, W.M.; Martin, P.; Pawliszyn, J. In-Tube Molecularly Imprinted Polymer Solid-Phase Microextraction for the Selective Determination of Propranolol. *Anal. Chem*. **2001**, *73*, 2383–2389.
106. Hofacker, S.; Mechtel, M.; Mager, M.; Kraus, H. Sol–gel: A new tool for coatings chemistry. *Prog. Org. Coat*. **2002**, *45*, 159–164.
107. Mullett, W.M.; Levsen, K.; Lubda, D.; Pawliszyn, J. Bio-compatible in-tube solid-phase microextraction capillary for the direct extraction and high-performance liquid chromatographic determination of drugs in human serum. *J. Chromatogr. A* **2002**, *963*, 325–334.
108. Chong, S.; Wang, D.; Hayes, J.; Wilhite, B.; Malik, A. Sol-gel coating technology for the preparation of solid-phase microextraction fibers of enhanced thermal stability. *Anal. Chem*. **1997**, *69*, 3889–3898.
109. Young, S.K. Sol-Gel Science for Ceramic Materials. *Mater. Matt.* **2006**, *1*, 8.

110. Hu, B.; He, M.; Chen, B. Novel Materials in Solid-Phase Microextraction and Related Sample Preparation Approaches. In *Miniaturization in Sample Preparation*; Pereira, F.P., Ed.; De Gruyter Open Ltd: Warsaw, Poland; Berlin, Germany, 2014; pp. 88–190.
111. Djozan, D.; Assadi, Y.; Haddadi, S.H. Anodized Aluminum Wire as a Solid-Phase Microextraction Fiber. *Anal. Chem.* **2001**, *73*, 4054–4058.
112. Li, Q.; Ding, Y.; Yuan, D. Electrosorption-enhanced solid-phase microextraction of trace anions using a platinum plate coated with single-walled carbon nanotubes. *Talanta* **2011**, *85*, 1148–1153.
113. Li, M.K.; Lei, N.; Gong, C.; Yu, Y.; Lam, K.; Lam, M.H.; Yu, H.; Lam, P.K. An organically modified silicate molecularly imprinted solid-phase microextraction device for the determination of polybrominated diphenyl ethers. *Anal. Chim. Acta* **2009**, *633*, 197–203.
114. Ma, X.; Li, Q.; Yuan, D. Determination of endocrine-disrupting compounds in water by carbon nanotubes solid-phase microextraction fiber coupled online with high performance liquid chromatography. *Talanta* **2011**, *85*, 2212–2217.
115. Maghsoudi, S.; Noroozian, E. HP-SPME of Volatile Polycyclic Aromatic Hydrocarbons from Water Using Multiwalled Carbon Nanotubes Coated on a Steel Fiber through Electrophoretic Deposition. *Chromatographia* **2012**, *75*, 913–921.
116. Zewe, J.W.; Steach, J.K.; Olesik, S.V. Electrospun fibers for solid-phase microextraction. *Anal. Chem*. **2010**, *82*, 5341–5348.
117. Lin, B.; Li, T.; Zhao, Y.; Huang, F.-K.; Guo, L.; Feng, Y.-Q. Preparation of a TiO2 nanoparticle-deposited capillary column by liquid phase deposition and its application in phosphopeptide analysis. *J. Chromatogr. A* **2008**, *1192*, 95–102.
118. Alizadeh, R.; Najafi, N.M.; Kharrazi, S. A new solid phase micro extraction for simultaneous head space extraction of ultra traces of polar and non-polar compounds. *Anal. Chim. Acta* **2011**, *689*, 117–121.
119. Ji, J.; Liu, H.; Chen, J.; Zeng, J.; Huang, J.; Gao, L.; Wang, Y.; Chen, X. ZnO nanorod coating for solid phase microextraction and its applications for the analysis of aldehydes in instant noodle samples. *J. Chromatogr. A* **2012**, *1246*, 22–27.
120. Farhadi, K.; Matin, A.A.; Amanzadeh, H.; Biparva, P.; Tajik, H.; Farshid, A.A.; Pirkharrati, H. A novel dispersive micro solid phase extraction using zein nanoparticles as the sorbent combined with headspace solid phase micro-extraction to determine chlorophenols in water and honey samples by GC–ECD. *Talanta* **2014**, *128*, 493–499.
121. Anbia, M.; Khazaei, M. Ordered nanoporous carbon-based SPME and determination by GC. *Chromatographia* **2011**, *73*, 379–384.
122. Rahimi, A.; Hashemi, P.; Badiei, A.; Arab, P.; Ghiasvand, A.R. CMK-3 nanoporous carbon as a new fiber coating for solid-phase microextraction coupled to gas chromatography–mass spectrometry. *Anal. Chim. Acta* **2011**, *695*, 58–62.
123. Toledo, B.R.; Hantao, L.W.; Ho, T.D.; Augusto, F.; Anderson, J.L. A chemometric approach toward the detection and quantification of coffee adulteration by solid-phase microextraction using polymericionic liquid sorbent coatings. *J. Chomatogr. A* **2014**, *1346*, 1–7.
124. Ho, T.T.; Chen, C.Y.; Li, Z.G.; Yang, T.C.C.; Lee, M.R. Determination of chlorophenols in landfill leachate using headspace sampling with ionic liquid-coated solid-phase microextraction fibers combined with gas chromatography–mass spectrometry. *Anal. Chim. Acta* **2012**, *712*, 72–77.

125. Yang, Y.; Chen, J.; Shi, J.P. Determination of diethylstilbestrol in milk using carbon nanotube-reinforced hollow fiber solid-phase microextraction combined with high-performance liquid chromatography. *Talanta* **2012**, *97*, 222–228.
126. Sarafraz-Yazdi, A.; Abbasian, M.; Amiri, A. Determination of furan in food samples using two solid phase microextraction fibers based on sol–gel technique with gas chromatography–flame ionization detector. *Food Chem.* **2012**, *131*, 698–704.
127. Attari, S.G.; Bahrami, A.; Shahna, F.G.; Heidari, M. Solid-phase microextraction fiber development for sampling and analysis of volatile organohalogen compounds in air. *J. Environ. Health Sci. Eng*. **2014**, *12*, 123–130.
128. Shearrow, A.M.; Harris, G.A.; Fang, L.; Sekhar, P.K.; Nguyen, L.T.; Turner, E.B.; Bhansali, S.; Malik, A. Ionic liquid-mediated Sol-gel coatings for capillary microextraction. *J. Chomatogr. A* **2009**, *1216*, 5449–5458.
129. Shearrow, A.M.; Bhansali, S.; Malik, A. Ionic liquid-mediated bis(3-methyldimethoxysilyl)propyl. polypropylene oxide-based polar Sol-gel coatings for capillary microextraction. *J. Chromatogr. A* **2009**, *1216*, 6349–6355.
130. Zhou, X.; Shao, X.; Shu, J.J.; Liu, M.M.; Liu, H.L.; Feng, X.H.; Liu, F. Thermally stable ionic liquid-based Sol-gel coating for ultrasonic extraction–solid-phase microextraction–gas chromatography determination of phthalate esters in agricultural plastic films. *Talanta* **2012**, *89*, 129–135.
131. Liu, M.; Zhou, X.; Chen, Y.; Liu, H.; Feng, X.; Qiu, G.; Liu, F.; Zeng, Z. Innovative chemically bonded ionic liquids-based Sol-gel coatings as highly porous, stable and selective stationary phases for solid phase microextraction. *Anal. Chim. Acta* **2010**, *683*, 96–106.
132. Fan, Y.; Feng, Y.Q.; Shi, Z.G.; Wang, J.B. Ordered mesoporous silica coated capillary for in-tube solid phase microextraction coupled to high performance liquid chromatography. *Anal. Chim. Acta* **2005**, *543*, 1–8.
133. Zhu, F.; Liang, Y.; Xia, L.; Rong, M.; Su, C.; Lai, R.; Li, R.; Ouyang, G. Preparation and characterization of vinyl-functionalized mesoporous organosilica-coated solid-phase microextraction fiber. *J. Chromatogr. A* **2012**, *1247*, 42–48.
134. Moreira, M.A.; André, L.C.; Cardeal, Z.L. Analysis of plasticiser migration to meat roasted in plastic bags by SPME–GC/MS. *Food Chem*. **2015**, *178*, 195−200.
135. Es-Haghi, A.; Hosseini, S.M.; Khoshhesab, Z.M. Development and application of a new solid-phase microextraction fiber by Solgel technology on titanium wire. *Anal. Chim. Acta* **2012**, *742*, 74–79.
136. Wang, Y.L.; Gao, Y.L.; Wang, P.P.; Shang, H.; Pan, S.Y.; Li, X.J. Sol-gel molecularly imprinted polymer for selective solid phase microextraction of organophosphorous pesticides. *Talanta* **2013**, *115*, 920–927.
137. Mu, L.; Hu, X.; Wen, J.; Zhou, Q. Robust aptamer Sol-gel solid phase microextraction of very polar adenosine from human plasma. *J. Chromatogr. A* **2013**, *1279*, 7–12.
138. Liu, X.; Ji, Y.; Zhang, Y.; Zhang, H.; Liu, M. Oxidized multiwalled carbon nanotubes as a novel solid-phase microextraction fiber for determination of phenols in aqueous samples. *J. Chromatogr. A* **2007**, *1165*, 10–17.

139. Bagheri, H.; Ayazi, Z.; Sistani, H. Chemically bonded carbon nanotubes on modified gold substrate as novel unbreakable solid phase microextraction fiber. *Microchim. Acta* **2011**, *174*, 295–301.
140. Queiroz, M.E.C.; Oliveira, E.B.; Breton, F.; Pawliszyn, J. Immunoaffinity in-tube solid phase microextraction coupled with liquid chromatography–mass spectrometry for analysis of fluoxetine in serum samples. *J. Chromatogr. A* **2007**, *1174*, 72–77.
141. Hu, X.; Pan, J.; Hu, Y.; Huo, Y.; Li, G. Preparation and evaluation of solid-phase microextraction fiber based on molecularly imprinted polymers for trace analysis of tetracyclines in complicated samples. *J. Chromatogr. A* **2008**, *1188*, 97–107.
142. Djozan, D.; Farajzadeh, M.A.; Sorouraddin, S.M.; Baheri, T. Determination of methamphetamine, amphetamine and ecstasy by inside-needle adsorption trap based on molecularly imprinted polymer followed by GC-FID determination. *Microchim. Acta* **2012**, *179*, 209–217.
143. Amini, R.; Rouhollahi, A.; Adibi, M.; Mehdinia, A. A novel reusable ionic liquid chemically bonded fused-silica fiber for headspace solid-phase microextraction/gas chromatography-flame ionization detection of methyl tert-butyl ether in a gasoline sample. *J. Chromatogr. A* **2011**, *1218*, 130–136.
144. Pang, L.; Liu, J.F. Development of a solid-phase microextraction fiber by chemical binding of polymeric ionic liquid on a silica coated stainless steel wire. *J. Chromatogr. A* **2012**, *1230*, 8–14.
145. Tamer, U.; Ertas, N.; Udum, Y.A.; Sahin, Y.; Pekmez, K.; Yıldız, A. Electrochemically controlled solid-phase microextraction (EC-SPME) based on overoxidized sulfonated polypyrrole. *Talanta* **2005**, *67*, 245–251.
146. Banitaba, M.H.; Mohammadi, A.A.; Davarani, S.S.H.; Mehdinia, A. Preparation and evaluation of a novel solid-phase microextraction fiber based on poly(3,4-ethylenedioxythiophene) for the analysis of OCPs in water. *Anal. Methods* **2011**, *3*, 2061–2067.
147. Bagheri, H.; Babanezhad, A.M.E. An electropolymerized aniline-based fiber coating for solid phase microextraction of phenols from water. *Anal. Chim. Acta* **2005**, *532*, 89–95.
148. Chen, L.; Chen, W.; Ma, C.; Du, D.; Chen, X. Electropolymerized multiwalled carbon nanotubes/polypyrrole fiber for solid-phase microextraction and its applications in the determination of pyrethroids. *Talanta* **2011**, *84*, 104–108.
149. Mehdinia, A.; Khani, H.; Mozaffari, S. Fibers coated with a graphene-polyaniline nanocomposite for the headspace solid-phase microextraction of organochlorine pesticides from seawater samples. *Microchim. Acta* **2014**, *181*, 89–95.
150. Zhao, F.; Wang, M.; Ma, Y.; Zeng, B. Electrochemical preparation of polyaniline–ionic liquid based solid phase microextraction fiber and its application in the determination of benzene derivatives. *J. Chromatogr. A* **2011**, *1218*, 387–391.
151. Gao, Z.; Li, W.; Liu, B.; Liang, F.; He, H.; Yang, S.; Sun, C. Nanostructured polyaniline-ionic liquid composite film coated steel wire for headspace solid-phase microextraction of organochlorine pesticides in water. *J. Chromatogr. A* **2011**, *1218*, 6285–6291.
152. Mehdinia, A.; Mousavi, M.F.; Shamsipur, M. Nano-structured lead dioxide as a novel stationary phase for solid-phase microextraction. *J. Chromatogr. A* **2006**, *1134*, 24–31.
153. Budziak, D.; Martendal, E.; Carasek, E. Application of an NiTi alloy coated with ZrO2 solid-phase microextraction fiber for determination of haloanisoles in red wine samples. *Microchim. Acta* **2009**, *164*, 197–202.

154. Liu, H.; Wang, D.; Ji, L.; Li, J.; Liu, S.; Liu, X.; Jiang, S. A novel TiO2 nanotube array/Ti wire incorporated solid-phase microextraction fiber with high strength, efficiency and selectivity. *J. Chromatogr. A* **2010**, *1217*, 1898–1903.
155. Cao, D.; Lü, J.; Liu, J.; Jiang, G. In situ fabrication of nanostructured titania coating on the surface of titaniumwire: A new approach for preparation of solid-phase microextraction fiber. *Anal. Chim. Acta* **2008**, *611*, 56–61.
156. Bagheri, H.; Aghakhani, A.; Baghernejad, M.; Akbarinejad, A. Novel polyamide-based nanofibers prepared by electrospinning technique for headspace solid-phase microextraction of phenol and chlorophenols from environmental samples. *Anal. Chim. Acta* **2012**, *716*, 34–39.
157. Newsome, T.E.; Zewe, J.W.; Olesik, S.V. Electrospun nanofibrous solid-phase microextraction coatings for preconcentration of pharmaceuticals prior to liquid chromatographic separations. *J. Chromatogr. A* **2012**, *1262*, 1−7.
158. Yu, Q.W.; Ma, Q.; Feng, Y. Temperature-response polymer coating for in-tube solid-phase microextraction coupled to highperformance. *Talanta* **2011**, *84*, 1019–1025.
159. International Organization for Standardization. *Water Quality–Determination of Selected Plant Treatment Agents and Biocide Products–Method Using Solid-Phase Microextraction (SPME) Followed by Gas Chromatography-Mass Spectrometry (GC-MS)*; International Organization for Standardization: Genf, Switzerland, ISO 27108:2010.
160. Deutsches Institut für Normung. *German Standard Methods for the Examination of Water, Waste Water and Sludge–Jointly Determinable Substances (group F)–Part 34: Determination of Selected Plant Treatment Agents, Biocides and Break-Down Products; Method Using Gas Chromatography (GC-MS) after Solid-Phase Micro Extraction (SPME) (F 34)*; Deutsches Institut für Normung: Berlin, Germany, DIN 38407-34:2006-05.
161. Deutsches Institut für Normung. *German Standard Methods for the Examination of Water, Waste Water and Sludge–Jointly Determinable Substances (group F)–Part 41: Determination of Selected Easily Volatile Organic Compounds in Water–Method Using Gas Chromatography (GC-MS) after Headspace Solid-Phase Micro Extraction (HS-SPME) (F 41)*; Deutsches Institut für Normung: Berlin, Germany, DIN 38407-41:2011-06.
162. International Organization for Standardization. *Water Quality–Determination of Volatile Organic Compounds in Water–Method Using Headspace Solid-Phase Micro-Extraction (HS-SPME) Followed by Gas Chromatography-Mass Spectrometry (GC-MS)*; International Organization for Standardization: Genf, Switzerland, ISO/DIS 17943:2014-07.
163. Austrian Standards Institute. *Determination of Volatile Compounds in Cellulose-based Materials by Solid Phase Micro Extraction (SPME)*; Austrian Standards Insitute: Vienna, Austria, OENORM A 1117: 2004-05-01.
164. ASTM International. *Standard Test Method for Determination of Parent and Alkyl Polycyclic Aromatics in Sediment Pore Water Using Solid-Phase Microextraction and Gas Chromatography/ Mass Spectrometry in Selected Ion Monitoring Mode*; ASTM International: West Conshohocken, PA, USA, ASTM D 7363a:2013.
165. Bagheri, H.; Babanezhad, E.; Khalilian, F. A novel sol–gel-based amino-functionalized fiber for headspace solid-phase microextraction of phenol and chlorophenols from environmental samples. *Anal. Chim. Acta* **2008**, *616*, 49−55.

166. Zeng, J.; Yu, B.; Chen, W.; Lin, Z.; Zhang, L.; Lin, Z.; Chen, X.; Wang, X. Application of ceramic/carbon composite as a novel coating for solid-phase Microextraction. *J. Chromatogr. A* **2008**, *1188*, 26−33.
167. Januszkiewicz, J.; Sabik, H.; Azarnia, S.; Lee, B. Optimization of headspace solid-phase microextraction for the analysis of specific flavors in enzyme modified and natural Cheddar cheese using factorial design and response surface methodology. *J. Chromatogr. A* **2008**, *1195*, 16−24.
168. Ravelo-Perez, L.M.; Hernandez-Borges, J.; Borges-Miquel, T.M.; Rodriguez Delgado, M.A. Multiple pesticide analysis in wine by MEKC combined with solid-phase microextraction and sample stacking. *Electrophoresis* **2007**, *28*, 4072–4081.
169. De Jager, L.S.; Perfetti, G.A.; Diachenko, G.W. Analysis of tetramethylene disulfotetramine in foods using solid-phase microextraction–gas chromatography–mass spectrometry. *J. Chromatogr. A* **2008**, *1192*, 36−40.
170. Saison, D.; De Schutter, D.P.; Delvaux, F.; Delvaux, F.R. Optimisation of a complete method for the analysis of volatiles involved in the flavour stability of beer by solid-phase microextraction in combination with gas chromatography and mass spectrometry. *J. Chromatogr. A* **2008**, *1190*, 342–349.
171. Iglesias, J.; Medina, I. Solid-phase microextraction method for the determination of volatile compounds associated to oxidation of fish muscle. *J. Chromatogr. A* **2008**, *1192*, 9−16.
172. Plutowska, B.; Wardencki, W. Determination of volatile fatty acid ethyl esters in raw spirits using solid phase microextraction and gas chromatography. *Anal. Chim. Acta* **2008**, *613*, 64−73.
173. Peldszus, S. Organic Acids. In *Chromatographic Analysis of the Environment*, 3rd ed.; Nollet, L.M.L, Ed.; CRC Press: Boca Raton, FL, USA, 2006; Volume 93, pp. 453–512.
174. Chee, K.K.; Wong, M.K.; Lee, H.K. SPME for the Determination of Organochlorine Pesticides. In *Applications of Solid Phase Microextraction*; Pawliszyn, J., Ed.; The Royal Society of Chemistry: Cambridge, UK, 1999; pp. 212–226.
175. Bocchini, P.; Pinelli, F.; Pozzi, R.; Ghetti, F.; Galletti, G.C. Quantitative determination of dimethyl fumarate in silica gel by solid-phase microextraction/gas chromatography/mass spectrometry and ultrasound-assisted extraction/gas chromatography/mass spectrometry. *Environ. Monit. Assess*. **2015**, *187*, 320.
176. Ezquerro, S.; Pons, B.; Tena, M.T. Direct quantitation of volatile organic compounds in packaging materials by headspace solid-phase microextraction-gas chromatography-mass spectrometry. *J. Chromatogr. A* **2003**, *985*, 247–257.
177. Wu, C.-M.; Wang, Z. Volatile Compounds in Fresh and Processed Shiitake Mushrooms (*Lentinus edodes* Sing.). *Food Sci. Technol. Res.* **2000**, *6*, 166–170.
178. Djozan, D.; Jouyban, A.; Norouzi, J. Ultrasonic assisted SPME coupled with GC and GC-MS using pencil lead as a fiber for monitoring the organic volatile impurities of ceftazidime. *J. Chromatogr. Sci.* **2008**, *46*, 680–685.
179. McGowin, A.E. Polycyclic Aromatic Hydrocarbons. In *Chromatographic Analysis of the Environment*, 3rd ed.; Nollet, L.M.L, Ed.; CRC Press: Boca Raton, FL, USA, 2006; Volume 93, pp. 555–616.

180. Luukkonen, V. Determination of chlorophenols from water by solid phase microextraction—Ion mobility spectrometry (SPME-IMS). Master's thesis, Lappeenranta University of Technology, Lappeenranta, Finland, 29 November 2012.
181. Larroque, V.; Desauziers, V.; Mocho, P. Development of a solid phase microextraction (SPME) method for the sampling of VOC traces in indoor air. *J. Environ. Monit.* **2006**, *8*, 106–111.
182. Qin, Z.; Bragg, L.; Ouyang, G.; Pawliszyn, J. Comparison of thin-film microextraction and stir bar sorptive extraction for the analysis of polycyclic aromatic hydrocarbons in aqueous samples with controlled agitation conditions. *J. Chromatogr. A* **2008**, *89*, 1196–1197.
183. Flores, M.; Hernández, D. Optimization of Multiple Headspace Solid-Phase Microextraction for the Quantification of Volatile Compounds in Dry Fermented Sausages. *J. Agric. Food Chem*. **2007**, *55*, 8688–8695.
184. Paschke, A.; Vrana, B.; Popp, P.; Schürmann, G. Comparative application of solid-phase microextraction fibre assemblies and semi-permeable membrane devices as passive air samplers for semi-volatile chlorinated organic compounds. A case study on the landfill ''Grube Antonie'' in Bitterfeld, Germany. *Environ. Pollut*. **2006**, *144*, 414−422.
185. Ouyang, G.; Zhao, W.; Alaee, M.; Pawliszyn, J. Time-weighted average water sampling with a diffusion-based solid-phase microextraction device. *J. Chromatogr. A* **2007**, *1138*, 42−46.
186. Koziel, J.; Jia, M.; Pawliszyn, J. Air Sampling with Porous Solid-Phase Microextraction Fibers. *Anal. Chem.* **2000**, *72*, 5178–5186.
187. Chen, Y.; Koziel, Y.A.; Pawliszyn, J. Calibration for On-Site Analysis of Hydrocarbons in Aqueous and Gaseous Samples Using Solid-Phase Microextraction. *Anal. Chem*. **2003**, *75*, 6485–6493.
188. Zhao, W.; Ouyang, G.; Alaee, M.; Pawliszyn, J. On-rod standardization technique for time-weighted average water sampling with a polydimethylsiloxane rod. *J. Chromatogr. A* **2006**, *1124*, 112–120.
189. Bragg, L.; Qin, Z.; Alaee, M.; Pawliszyn, J. Field Sampling with a Polydimethylsiloxane Thin-Film. *J. Chromatogr. Sci*. **2006**, *44*, 317–323.
190. Ouyang, G.; Cai, J.; Zhang, X.; Li, H.; Pawliszyn, J. Standard-free kinetic calibration for rapid on-site analysis by solid-phase microextraction. *J. Sep. Sci*. **2008**, *31*, 1167–1172.
191. Khaled, A.; Pawliszyn, J. Time-weighted average sampling of volatile and semi-volatile airborne organic compounds by the solid-phase Microextraction device. *J. Chromatogr. A* **2000**, *892*, 455–467.
192. Chen, Y.; O'Reilly, J.; Wang, Y.; Pawliszyn, J. Standards in the extraction phase, a new approach to calibration of Microextraction processes. *Analyst* **2004**, *129*, 702–703.
193. Zhao, W.; Ouyang, G.; Pawliszyn, J. and application of in-fibre internal standardization solid-phase microextraction. *Analyst* **2007**, *132*, 256–261.
194. Weurman, S.; van Lunteren, G. Application of gas chromatography to the study of food odours. In *Aroma- and Flavour-Producing Substances in Foods*; Solms, J., Neukom, S., Eds.; Forster: Zurich, Switzerland, 1967; pp. 21–34.
195. Rijkens, F.; Boelens, M.H. The future of aroma research. In *Aroma Research*; Proceedings of the International Symposium on Aroma Research, Central Institute for Nutrition and Food Research TNO, Zeist, Netherlands, 26–29 May 1975; Maarse, H., Groenen, P.J., Eds.; Pudoc: Wageningen, The Netherlands, 1975; pp. 203–222.

196. Pawliszyn, J. Sample Preparation: Quo Vadis? *Anal. Chem.* **2003**, *75*, 2543–2558.
197. Pawliszyn, J. *Handbook of Solid Phase MICROEXTRACTION*; University of Waterloo: Waterloo, Canada, 2007.
198. Ferreira, S.L.C.; Dos Santos, W.N.L.; Quintella, C.M.; Neto, B.B.; Bosque-Sendra, J.M. Doehlert matrix: A chemometric tool for analytical chemistry—Review. *Talanta* **2004**, *63*, 1061–1067.
199. Risticevic, S.; Carasek, E.; Pawliszyn, J. Headspace solid-phase microextraction–gas chromatographic–time-of-flight mass spectrometric methodology for geographical origin verification of coffee. *Anal. Chim. Acta* **2008**, *617*, 72–84.
200. Chen, Y.; Shirey, R.E.; Sidisky, L.M. Determination of Diacetyl in Butter and Air Samples by SPME Coupled with GC–MS. *Chromatographia* **2010**, *72*, 999–1004.
201. Mallia, S.; Fernández-Garcia, E.; Bosset, J.O. Comparison of purge and trap and solid phase microextraction techniques for studying the volatile aroma compounds of three European PDO hard cheeses. *Int. Dairy J.* **2005**, *15*, 741–758.
202. Majcher, M.A.; Kaczmarek, A.; Klensporf-Pawlik, D.; Pikul, J.; Jeleń, H.H. SPME-MS-Based Electronic Nose as a Tool for Determination of Authenticity of PDO Cheese, Oscypek. *Food Anal. Methods* **2015**, doi: 10.1007/s12161-015-0114-x.
203. Ocak, E.; Javidipour, I.; Tuncturk, Y. Volatile compounds of Van Herby cheeses produced with raw and pasteurized milks from different species. *J. Food Sci. Technol.* **2014**, doi: 10.1007/s13197-014-1458-8.
204. Tunick, M.H.; Iandola, S.K.; Hekken, D.L. Comparison of SPME Methods for Determining Volatile Compounds in Milk, Cheese, and Whey Powder. *Foods* **2013**, *2*, 534-543.
205. Xie, J.; Sun, B.; Zheng, F.; Wang, S. Volatile flavor constituents in roasted pork of Mini-pig. *Food Chem.* **2008**, *109*, 506–514.
206. Yu, A.N.; Sun, B.G.; Tian, D.T.; Qu, W.Y. Analysis of volatile compounds in traditional smoke-cured bacon (CSCB) with different fiber coatings using SPME. *Food Chem.* **2008**, *110*, 233–238.
207. Argyri, A.A.; Mallouchos, A.; Panagou, E.Z.; Nychas, G.J.E. The dynamics of the HS/SPME–GC/MS as a tool to assess the spoilage of minced beef stored under different packaging and temperature conditions. *Int. J. Food Microbiol.* **2015**, *193*, 51–58.
208. Benet, I.; Guàrdia, M.D.; Ibañez, C.; Solà, J.; Arnau, J.; Roura, E. Analysis of SPME or SBSE extracted volatile compounds from cooked cured pork ham differing in intramuscular fat profiles. *Food Sci. Technol.* **2015**, *60*, 393–399.
209. Corral, S.; Salvador, A.; Flores, M. Salt reduction in slow fermented sausages affects the generation of aroma active compounds. *Meat Sci.* **2013**, *93*, 776–785.
210. Gardini, F.; Tabanelli, G.; Lanciotti, R.; Montanari, C.; Luppi, M.; Coloretti, F.; Chiavari, C.; Grazia, L. Biogenic amine content and aromatic profile of Salama da sugo, a typical cooked fermented sausage produced in Emilia Romagna Region (Italy). *Food Control* **2013**, *32*, 638–643.
211. Ma, Q.L.; Hamid, N.; Bekhit, A.E.D.; Robertson, J.; Law, T.F. Optimization of headspace solid phase microextraction (HS-SPME) for gas chromatography mass spectrometry (GC–MS) analysis of aroma compounds in cooked beef using response surface methodology. *Microchem. J.* **2013**, *111*, 16–24.

212. Câmara, J.S.; Marques, J.C.; Perestrelo, R.M.; Rodrigues, F.; Oliveira, L.; Andrade, P.; Caldeira, M. Comparative study of the whisky aroma profile based on headspace solid phase microextraction using different fibre coatings. *J. Chromatogr. A* **2007**, *1150*, 198–207.
213. Capobiango, M.; Mastello, R.B.; Chin, S.T.; Oliveira, E.S.; Cardeal, Z.L.; Marriott, P.J. Identification of aroma-active volatiles in banana Terra spirit usingmultidimensional gas chromatography with simultaneous massspectrometry and olfactometry detection. *J. Chromatogr. A* **2015**, *1388*, 227–235.
214. Du, L.; He, T.; Li, W.; Wang, R.; Xiao, D. Analysis of volatile compounds in Chinese Laobaigan liquor using headspace solid-phase microextraction coupled with GC-MS. *Anal. Methods* **2015**, *7*, 1906–1913.
215. Giraudel, J.L.; Setkova, L.; Pawliszyn, J.; Montury, M. Rapid headspace solid-phase microextraction–gas chromatographic–time-of-flight mass spectrometric method for qualitative profiling of ice wine volatile fraction III. Relative characterization of Canadian and Czech ice wines using self-organizing maps. *J. Chromatogr. A* **2007**, *1147*, 241–253.
216. Setkova, L.; Risticevic, S.; Pawliszyn, J. Rapid headspace solid-phase microextraction-gas chromatographic–time-of-flight mass spectrometric method for qualitative profiling of ice wine volatile fraction II: Classification of Canadian and Czech ice wines using statistical evaluation of the data. *J. Chromatogr. A* **2007**, *1147*, 224–240.
217. Jurado, J.M.; Ballesteros, O.; Alcázar, A.; Pablos, F.; Martín, M.J.; Vilchez, J.L.; Navalón, A. Differentiation of certified brands of origins of Spanish white wines by HS-SPME-GC and chemometrics. *Anal. Bioanal. Chem.* **2008**, *390*, 961–970.
218. Xiao, Z.; Zhou, X.; Niu, Y.; Yu, D.; Zhu, J.; Zhu, G. Optimization and application of headspace-solid-phasemicro-extraction coupled with gas chromatography–massspectrometry for the determination of volatile compounds in cherrywines. *J. Chromatogr. B* **2015**, *978–979*, 122–130.
219. Wang, X.; Xie, K.; Zhuang, H.; Ye, R.; Fang, Z.; Feng, T. Volatile flavor compounds, total polyphenolic contents and antioxidant activities of a China gingko wine. *Food Chem.* **2015**, *182*, 41–46.
220. Kim, B.H.; Park, S.K. Volatile aroma and sensory analysis of black raspberry wines fermented by different yeast strains. *J. Inst. Brew.* **2015**, *121*, 87–94.
221. Liu, M.; Zeng, Z.; Xiong, B. Preparation of novel solid-phase microextraction fibers by sol–gel technology for headspace solid-phase microextraction-gas chromatographic analysis of aroma compounds in beer. *J. Chromatogr. A* **2005**, *1065*, 287–299.
222. Braga, C.G.; Prado, A.; Pinto, J.S.; Alencar, S.M. Volatile profile of yellow passion fruit juice by static headspace and solid phase microextraction techniques. *Cienc. Rural* **2015**, *45*, 356–363.
223. Caven-Quantrill, D.J.; Buglass, A.J. Comparison of micro-scale simultaneous distillation–extraction and stir bar sorptive extraction for the determination of volatile organic constituents of grape juice. *J. Chromatogr. A* **2006**, *1117*, 121–131.
224. Mirhosseini, H.; Salmah, Y.; Nazimah, S.A.H.; Tan, C.P. Solid-phase microextraction for headspace analysis of key volatile compounds in orange beverage emulsion. *Food Chem*. **2007**, *105*, 1659–1670.

225. Várvölgyi, E.; Gere, A.; Szöllösi, D.; Sipos, L.; Kovács, Z.; Kókai, Z.; Csóka, M.; Mednyánszky, Z.; Fekete, A.; Korány, K. Application of Sensory Assessment, Electronic Tongue and GC–MS to Characterize Coffee Samples. *Arab. J. Sci. Eng*. **2015**, *40*, 125–133.
226. Barié, N.; Bücking, M.; Stahl, U.; Rapp, M. Detection of coffee flavour ageing by solid-phase microextraction/surface acoustic wave sensor array technique (SPME/SAW). *Food Chem.* **2015**, *176*, 212–218.
227. Evangelista, S.R.; Pedrozo, M.G.; Miguel, C.P.; Cordeiro, C.S.; Silva, C.F.; Pinheiro, A.C.M.; Schwan, R.F. Inoculation of starter cultures in a semi-dry coffee (*Coffea arabica*) fermentation process. *Food Microbiol*. **2014**, *44*, 87−95.
228. Guillot, S.; Peytavi, L.; Bureau, S.; Boulanger, R.; Lepoutre, J.P.; Crouzet, J.; Schorr-Galindo, S. Aroma characterization of various apricot varieties using headspacesolid phase microextraction combined with gas chromatography–mass spectrometry and gas chromatography–olfactometry. *Food Chem.* **2006**, *96*, 147–155.
229. Solis-Solis, H.M.; Calderón-Santoyo, M.; Schorr-Galindo, S.; Luna-Solano, G.; Ragazzo-Sánchez, J.A. Characterization of aroma potential of apricot varieties using different extraction techniques. *Food Chem.* **2007**, *105*, 829–837.
230. Gokbulut, I.; Karabulut, I. SPME–GC–MS detection of volatile compounds in apricot varieties. *Food Chem.* **2012**, *132*, 1098–1102.
231. Ong, B.T.; Nazimah, S.A.H.; Tan, C.P.; Mirhosseini, H.; Osman, A.; Hashim, D.M.; Rusul, G. Analysis of volatile compounds in five jackfruit (Artocarpus heterophyllus L.) cultivars using solid-phase microextraction (SPME) and gas chromatography-time-of-flight mass spectrometry (GC-TOFMS). *J. Food Compos. Anal.* **2008**, *21*, 416–422.
232. Kralj, M.B.; Jug, T.; Komel, E.; Fajt, N.; Jarni, K.; Živković, J.; Mujić, I. Aromatic compound in different peach cultivars and effect of preservatives on the final aroma of cooked fruits. *Hem. Ind.* **2014**, *68*, 767–779.
233. Spínola, V.; Perestrelo, R.; Câmara, J.S.; Castilho, P.C. Establishment of Monstera deliciosa fruit volatile metabolomic profile at different ripening stages using solid-phase microextraction combined with gas chromatography–mass spectrometry. *Food Res. Int.* **2015**, *67*, 409–417.
234. Steingass, C.B.; Carle, R.; Schmarr, H.G. Ripening-dependent metabolic changes in the volatiles of pineapple (Ananas comosus (L.) Merr.) fruit: I. Characterization of pineapple aroma compounds by comprehensive two-dimensional gas chromatography-mass spectrometry. *Anal. Bioanal. Chem*. **2015**, 407, 2591−2608.
235. Vavoura, M.V.; Badeka, A.V.; Kontakos, S.; Kontominas, M.G. Characterization of Four Popular Sweet Cherry Cultivars Grown in Greece by Volatile Compound and Physicochemical Data Analysis and Sensory Evaluation. *Molecules* **2015**, *20*, 1922−1940.
236. Wang, D.; Cai, J.; Zhu, B.Q.; Wu, G.F.; Duan, C.Q.; Chen, G.; Shi, Y. Study of free and glycosidically bound volatile compounds in air-dried raisins from three seedless grape varieties using HS–SPME with GC–MS. *Food Chem.* **2015**, *177*, 346–353.
237. Yang, C.; Wang, Y.; Wu, B.; Fang, J.; Li, S. Volatile compounds evolution of three table grapes with different flavor during and after maturation. *Food Chem.* **2011**, *128*, 823–830.

238. Thissen, U., Coulier, L.; Overkamp, K.M., Jetten, J.; Werff, B.J.C.; Ven, T.; Werf, M.J. A proper metabolomics strategy supports efficient food quality improvement: A case study on tomato sensory properties. *Food Qual. Pref.* **2011**, *22*, 499–506.
239. Bianchi, F.; Mangia, A.; Mattarozzi, M.; Musci, M. Characterization of the volatile profile of thistle honey using headspace solid-phase microextraction and gas chromatography–mass spectrometry. *Food Chem.* **2011**, *129*, 1030–1036.
240. Lušić, D.; Koprivnjak, O.; Ćurić, D.; Sabatini, A.G.; Conte, L.S. Volatile Profile of Croatian Lime Tree (*Tilia* sp.), Fir Honeydew (*Abies alba*) and Sage (*Salvia officinalis*) Honey. *Food Technol. Biotechnol.* **2007**, *45*, 156–165.
241. Moniruzzaman, M.; Rodríguez, I.; Ramil, M.; Cela, R.; Sulaiman, S.A.; Gan, S.H. Assessment of gas chromatography time-of-flight accurate mass spectrometry for identification of volatile and semi-volatile compounds in honey. *Talanta* **2014**, *129*, 505–515.
242. Akil, E.; Castelo-Branco, V.N.; Costa, A.M.M.; Vendramini, A.L.A.; Calado, V.; Torres, A.G. Oxidative Stability and Changes in Chemical Composition of Extra Virgin Olive Oils After Short‐Term Deep‐Frying of French Fries. *J. Am. Oil Chem. Soc.* **2015**, *92*, 409–421.
243. Cecchi, T.; Alfei, B. Volatile profiles of Italian monovarietal extra virgin olive oils via HS-SPME–GC–MS: Newly identified compounds, flavors molecular markers, and terpenic profile. *Food Chem.* **2013**, *141*, 2025–2035.
244. Romero, I.; García-González, D.L.; Aparicio-Ruiz, R.; Morales, M.T. Validation of SPME–GCMS method for the analysis of virgin olive oil volatiles responsible for sensory defects. *Talanta* **2015**, *134*, 394–401.
245. Chumpolsri, W.; Wijii, N.; Boontakham, P.; Nimmanpipug P.; Sookwong, P.; Luangkamin, S.; Wongpornchai, S. Variation of Terpenoid Flavor Odorants in Bran of Some Black and White Rice Varieties Analyzed by GC×GC-MS. *J. Food Nutr. Res.* **2015**, *3*, 114−120.
246. Griglione, A.; Liberto, E.; Cordero, C.; Bressanello, D.; Cagliero, C.; Rubiolo, P.; Bicchi, C.; Sgorbini, B. High-quality Italian rice cultivars: Chemical indices of ageing and aroma quality. *Food Chem.* **2015**, *172*, 305–313.
247. Ho, C.W.; Aida, W.M.W.; Maskat, M.Y.; Osman, H. Optimization of headspace solid phase microextraction (HS-SPME) for gas chromatography mass spectrometry (GC-MS) analysis of aroma compound in palm sugar (Arenga pinnata). *J. Food Compos. Anal.* **2006**, *19*, 822–830.
248. Sanahuja,, A.B.; Santonja, M.R.; Teruel, N.G.; Carratalá, M.L.M.; Selva, M.C.G. Classification of Almond Cultivars Using Oil Volatile Compound Determination by HS-SPME–GC–MS. *J. Am. Oil Chem. Soc.* **2011**, *88*, 329–336.
249. D'Auria, M.; Mauriello, G.; Racioppi, R.; Rana, G.L. Use of SPME–GC–MS in the Study of Time Evolution of the Constituents of Saffron Aroma: Modifications of the Composition During Storage. *J. Chromatogr. Sci.* **2006**, *44*, 18−21.
250. Kim, N.Y.; Park, M.H.; Jang, E.Y.; Lee, J.H. Volatile Distribution in Garlic (Allium sativum L.) by Solid Phase Microextraction (SPME) with Different Processing Conditions. *Food Sci. Biotechnol*. **2011**, *20*, 775−782.
251. Fratini, G.; Lois, S.; Pazos, M.; Parisi, G.; Fratini, I.M.G.; Lois, S.; Pazos, M.; Parisi, G.; Medina, I. Volatile profile of Atlantic shellfish species by HS-SPME GC/MS. *Food Res. Int.* **2012**, *48*, 856–865.

252. Xiao, Q.; Yu, C.; Xing, J.; Hu, B. Comparison of headspace and direct single-drop microextraction and headspace solid-phase microextraction for the measurement of volatile sulfur compounds in beer and beverage by gas chromatography with flame photometric detection. *J. Chromatogr. A* **2006**, *1125*, 133–137.
253. da Silva, G.C.; da Silva, A.A.S.; da Silva, L.S.N.; Godoy, R.L.O.; Nogueira, L.C.; Quitério, S.L.; Raices, R.S.L. Method development by GC–ECD and HS-SPME–GC–MS for beer volatile Analysis. *Food Chem.* **2015**, *167*, 71–77.
254. Franco-Luesma, E.; Ferreira, V. Quantitative analysis of free and bonded forms of volatile sulfurcompouds in wine. Basic methodologies and evidences showing theexistence of reversible cation-complexed forms. *J. Chromatogr. A* **2014**, *1359*, 8–15.
255. Fan, W.; Tsai, I.M.; Qian, M.C. Analysis of 2-aminoacetophenone by direct-immersion solid-phase microextraction and gas chromatography–mass spectrometry and its sensory impact in Chardonnay and Pinot gris wines. *Food Chem.* **2007**, *105*, 1144–1150.
256. Gocmen, D.; Elston, A.; Williams, T.; Parish, M.; Rouseff, R.L. Identification of medicinal off-flavours generated by Alicyclobacillus species in orange juice using GC-olfactometry and GC-MS. *Lett. Appl. Microbiol*. **2005**, *40*, 172–177.
257. Bagheri, H.; Aghakhani, A.; Es-haghi, A. Sol-Gel-based SPME and GC–MS for Trace Determination of Geosmin in Water and Apple Juice Samples. *Chromatographia* **2007**, *66*, 779–783.
258. Iamanaka, B.T.; Teixeira, A.A.; Teixeira, A.R.R.; Vicente, E.; Frisvad, J.C.; Taniwaki, M.H.; Bragagnolo, N. Potential of volatile compounds produced by fungi to influence sensory quality of coffee beverage. *Food Res. Int*. **2014**, *64*, 166–170.
259. Jeleń, H.H.; Mildner-Szkudlarz, S.; Jasińska, I.; Wąsowicz, E. A Headspace–SPME–MS Method for Monitoring Rapeseed Oil Autoxidation. *J. Am. Oil Chem. Soc.* **2007**, *84*, 509–517.
260. Petersen, K.D.; Kleeberg, K.K.; Jahreis, G.; Fritsche, J. Assessment of the oxidative stability of conventional and high-oleic sunflower oil by means of solid-phase microextraction-gas chromatography. *Int. J. Food Sci.* **2012**, *63*, 160–169.
261. Petersen, K.D.; Kleeberg, K.K.; Jahreis, G.; Busch-Stockfisch, M.; Fritsche, J. Comparison of analytical and sensory lipid oxidation parameters in conventional and high-oleic rapeseed oil. *Eur. J. Lipid Sci. Technol.* **2012**, *114*, 1193–1203.
262. Petersen, K.D.; Jahreis, G.; Busch-Stockfisch, M.; Fritsche, J. Chemical and sensory assessment of deep-frying media alternatives for the processing of French fries. *Eur. J. Lipid Sci. Technol.* **2013**, *115*, 935−945.
263. Beltrán, A.; Ramos, M.; Grané, N.; Martín, M.L.; Garrigós, M.C. Monitoring the oxidation of almond oils by HS-SPME–GC–MS and ATR-FTIR: Application of volatile compounds determination to cultivar authenticity. *Food Chem*. **2011**, *126*, 603–609.
264. Panseri, S.; Soncin, S.; Chiesa, L.M.; Biondi, P.A. A headspace solid-phase microextraction gas-chromatographic mass-spectrometric method (HS-SPME–GC/MS) to quantify hexanal in butter during storage as marker of lipid oxidation. *Food Chem.* **2011**, *127*, 886–889.
265. Achouri, A.; Boye, J.I.; Zamani, Y. Identification of volatile compounds in soymilk using solid-phase microextraction-gas chromatography. *Food Chem.* **2006**, *99*, 759–766.

266. Silcock, P.; Alothman, M.; Zardin, E.; Heenan, S.; Siefarth, C.; Bremer, P.J.; Beauchamp, J. Microbially induced changes in the volatile constituents of fresh chilled pasteurised milk during storage. *Food Pack. Shelf Life* **2014**, *2*, 81–90.
267. Wold, J.P.; Skaret, J.; Dalsgaard, T.K. Assessment of the action spectrum for photooxidation in full fat bovine milk. *Food Chem.* **2015**, *179*, 68–75.
268. Mikš-Krajnik, M.; Yoon, Y.J.; Yuk, H.G. Detection of Volatile Organic Compounds as Markers of Chicken Breast Spoilage Using HS-SPME-GC/MS-FASST. *Food Sci. Biotechnol*. **2014**, *24*, 361−372.
269. Duflos, G.; Moine, F.; Coin, V.M.; Malle, P. Determination of Volatile Compounds in Whiting (*Merlangius merlangus*) Using Headspace–Solid-Phase Microextraction–Gas Chromatography–Mass Spectrometry. *J. Chromatogr. Sci.* **2005**, *43*, 304–312.
270. Robertson, R.F.; Jauncey, K.; Beveridge, M.C.M.; Lawton, L.A. Depuration rates and the sensory threshold concentration of geosmin responsible for earthy-musty taint in rainbow trout, Onchorhynchus mykiss. *Aquaculture* **2005**, *245*, 89–99.
271. Vinaixa, M.; Vergara, A.; Duran, C.; Llobet, E.; Badia, C.; Brezmes, J.; Vilanova, J.; Correig, X. Fast detection of rancidity in potato crisps using e-noses based on mass spectrometry or gas sensors. *Sens. Actuat. B* **2005**, *106*, 67–75.
272. Gallardo-Chacón, J.J.; Karbowiak, T. Sorption of 4-ethylphenol and 4-ethylguaiacol by suberin from cork. *Food Chem*. **2015**, *181*, 222–226.
273. Pizarro, C.; Pérez-del-Notario, N.; González-Sáiz, J.M. Multiple headspace solid-phase microextraction for eliminating matrix effect in the simultaneous determination of haloanisoles and volatile phenols in wines. *J. Chromatogr. A* **2007**, *1166*, 1–8.
274. Gómez-Ariza, J.L.; García-Barrera, T.; Lorenzo, F.; Beltrán, R. Use of multiple headspace solid-phase microextraction and pervaporation for the determination of off-flavours in wine. *J. Chromatogr. A* **2006**, *1112*, 133–140.
275. Tait, E.; Perry, J.D.; Stanforth, S.P.; Dean, J.R. Bacteria detection based on the evolution of enzyme-generated volatile organic compounds: Determination of Listeria monocytogenes in milk samples. *Anal. Chim. Acta* **2014**, *848*, 80–87.
276. Bianchi, F.; Careri, M.; Mangia, A.; Mattarozzi, M.; Musci, M. Experimental design for the optimization of the extraction conditions of polycyclic aromatic hydrocarbons in milk with a novel diethoxydiphenylsilane solid-phase microextraction fiber. *J. Chromatogr. A* **2008**, *1196–1197*.
277. Zhang, Y.; Huang, X.; Yuan, D. Determination of benzimidazole anthelmintics in milk and honey by monolithic fiber-based solid-phase microextraction combined with high-performance liquid chromatography–diode array detection. *Anal. Bioanal. Chem.* **2015**, *407*, 557–567.
278. Kamalabadi, M.; Ghaemi, E.; Mohammadi, A.; Alizadeh, N. Determination of furfural and hydroxymethylfurfural from baby formula using headspace solid phase microextraction based on nanostructured polypyrrole fiber coupled with ion mobility spectrometry. *Food Chem.* **2015**, *181*, 72–77.
279. Sagratini, G.; Mañes, J.; Giardiná, D.; Damiani, P.; Picó, Y. Analysis of carbamate and phenylurea pesticide residues in fruit juices by solid-phase microextraction and liquid chromatography–mass spectrometry. *J. Chromatogr. A* **2007**, *1147*, 135–143.

280. Lim, H.H.; Shin, H.S. Simple Determination of 4-Methylimidazole in Soft Drinks by Headspace SPME GC–MS. *Chromatographia* **2013**, 76, 97–101.
281. Zuin, V.G.; Schellin, M.; Montero, L.; Yariwake, J.H.; Augusto, F.; Popp, P. Comparison of stir bar sorptive extraction and membrane-assisted solvent extraction as enrichment techniques for the determination of pesticide and benzoa.pyrene residues in Brazilian sugarcane juice. *J. Chromatogr. A* **2006**, *1114*, 180–187.
282. Wen, Y.; Wang, Y.; Feng, Y.Q. A simple and rapid method for simultaneous determination of benzoic and sorbic acids in food using in-tube solid-phase microextraction coupled with high-performance liquid chromatography. *Anal. Bioanal. Chem.* **2007**, *388*, 1779–1787.
283. 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.
284. Guillot, S.; Kelly, M.T.; Fenet, H.; Larroque, M. Evaluation of solid-phase microextraction as an alternative to the official method for the analysis of organic micro-pollutants in drinking water. *J. Chromatogr. A* **2006**, *1101*, 46–52.
285. Cai, L.; Gong, S.; Chen, M.; Wu, C. Vinyl crown ether as a novel radical crosslinked sol–gel SPME fiber for determination of organophosphorus pesticides in food samples. *Anal. Chim. Acta* **2006**, *559*, 89–96.
286. Poinot, P.; Qin, F.; Lemoine, M.; Yvon, V.; Ledauphin, J.; Gaillard, J.L. Study of current analytical strategies for the dual investigation of polycyclic aromatic hydrocarbons and benzene, toluene, ethylbenzene and xylene in apples. *J. Food Compos. Anal.* **2014**, *35*, 83–93.
287. 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.
288. Siripatrawan, U.; Harte, B.R. Solid phase microextraction/gas chromatography/mass spectrometry integrated with chemometrics for detection of *Salmonella typhimurium* contamination in a packaged fresh vegetable. *Anal. Chim. Acta* **2007**, *581*, 63–70.
289. Lei, F.F.; Huang, J.Y.; Zhang, X.N., Liu, X.J.; Li, X.J. Determination of Polycyclic Aromatic Hydrocarbons in Vegetables by Headspace SPME-GC. *Chromatographia* **2011**, *74*, 99–107.
290. Sapahin, H.A.; Makahleh, A.; Saad, B. Determination of organophosphorus pesticide residues in vegetables using solid phase micro-extraction coupled with gas chromatography–flame photometric detector. *Arab. J. Chem.* **2015**, doi: 10.1016/j.arabjc.2014.12.001
291. Dong, C.; Zeng, Z.; Lia, X. Determination of organochlorine pesticides and their metabolites in radish after headspace solid-phase microextraction using calix4.arene fiber. *Talanta* **2005**, 66, 721–727.
292. Arisseto, A.P.; Vicente, E.; Ueno, M.S.; Toledo, M.C.F. Occurrence of furan in commercial samples of roasted coffee in Brazil. *Food Addit. Contam. A* **2012**, *29*, 1832−1839.
293. Liu, M.; Peng, Q.; Chen, Y.; Tang, Q.; Feng, Q. A rapid space-resolved solid-phase microextraction method as a powerful tool to determine contaminants in wine based on their volatility. *Food Chem*. **2015**, *176*, 12–16.

294. Martins, J.; Esteves, C.; Limpo-Faria, A.; Barros, P.; Ribeiro, N; Simões, T.; Correia, M.; Delerue-Matos, C. Analysis of six fungicides and one acaricide in still and fortified wines using solid-phase microextraction-gas chromatography/tandem mass spectrometry. *Food Chem.* **2012**, *132*, 630–636.
295. Pérez-Palacios, T.; Petisca, C.; Henriques, R.; Ferreira, I.M.P.L.V.O. Impact of cooking and handling conditions on furanic compounds in breaded fish products. *Food Chem. Toxicol.* **2013**, *55*, 222–228.
296. Jaffrès, E.; Lalanne, V.; Macé, S.; Cornet, J.; Cardinal, M.; Sérot, T.; Dousset, X.; Joffraud, J.J. Sensory characteristics of spoilage and volatile compounds associated with bacteria isolated from cooked and peeled tropical shrimps using SPME–GC–MS analysis. *Int. J. Food Microbiol.* **2011**, *147*, 195–202.
297. Bhattacharjee, P.; Panigrahi, S.; Lin, D.; Logue, C.M.; Sherwood, J.L.; Doetkott, C.; Marchello, M. A comparative qualitative study of the profile of volatile organic compounds associated with Salmonella contamination of packaged aged and fresh beef by HS-SPME/GC-MS. *J. Food Sci. Technol.* **2011**, *48*, 1–13.
298. Martin, D.; Ruiz, J. Analysis of polycyclic aromatic hydrocarbons in solid matrixes by solid-phase microextraction coupled to a direct extraction device. *Talanta* **2007**, *71*, 751–757.
299. Page, B.D.; Lacroix, G. Application of solid-phase microextraction to the headspace gas chromatographic analysis of halogenated volatiles in selected foods. *J. Chromatogr. A* **1993**, *648*, 199–211.
300. Shahidi, F.; Rubin, L.; D'Souza, L.A. Meat flavor volatiles: A review of the composition, techniques of analysis, and sensory evaluation. *CRC Crit. Rev. Food Sci. Nutr.* **1986**, *24*, 141–243.
301. Sostaric, T.; Boyce, M.C.; Spickett, E.E. Analysis of the volatile components in vanilla extracts and flavorings by solid-phase microextraction and gas chromatography. *J. Agric. Food Chem.* **2000**, *48*, 5802–5807.
302. Botondi, R.; DeSantis, D.; Bellincontro, A.; Vizovitis, K.; Mencarelli, F. Influence of ethylene inhibition by 1-methyl-cyclopropene on apricot quality, volatile production, and glycosidase activity of lowand high-aroma varieties of apricots. *J. Agric. Food Chem.* **2003**, *51*, 1189–1200.
303. Greger, V.; Schieberle, P. Characterization of the key aroma compounds in apricots (Prunus armeniaca) by application of the molecular sensory science concept. *J. Agric. Food Chem.* **2007**, *55*, 5221–5228.
304. Jeleń, H.H. Solid-Phase Microextraction in the Analysis of Food Taints and Off-Flavors. *J. Chromatogr. Sci.* **2006**, *44*, 399–415.
305. Melchert, H.U.; Pabel, E. Reliable identification and quantification of trichothecenes and other mycotoxins by electron impact and chemical ionization-gas chromatography–mass spectrometry, using an ion-trap system in the multiple mass spectrometry mode: Candidate reference method for complex matrices. *J. Chromatogr. A* **2004**, *1056*, 195–199.
306. Chan, D.; MacDonald, S.J.; Boughtflower, V.; Brereton, P. Simultaneous determination of aflatoxins and ochratoxin A in food using a fully automated immunoaffinity column clean-up and liquid chromatography–fluorescence detection. *J. Chromatogr. A* **2004**, *1059*, 13–16.
307. Tafuri, A.; Ferracane, R.; Ritieni, A. Ochratoxin A in Italian marketed cocoa products. *Food Chem.* **2004**, *88*, 487–494.

308. Vale, P.; Sampayo, M.A. Esters of okadaic acid and dinophysistoxin-2 in Portuguese bivalves related to human poisonings. *Toxicon* **1999**, *37*, 1109–1121.
309. Hui, C.A.; Rudnick, D.; Williams, E. Mercury burdens in Chinese mitten crabs (Eriocheir sinensis) in three tributaries of southern San Francisco Bay, California, USA. *Environ. Pollut.* **2005**, *133*, 481–487.
310. Vupputuri, S.; Longnecker, M.P.; Daniels, J.L.; Guo, X.; Sandler, D.P. Blood mercury level and blood pressure among US women: Results from the National Health and Nutrition Examination Survey 1999–2000. *Environ. Res.* **2005**, *97*, 195–200.
311. Storelli, M.M.; Storelli, A.; Giacominelli-Stuffler, R.; Marcotrigiano, G.O. Mercury speciation in the muscle of two commercially important fish, hake (Merluccius merluccius) and striped mullet (Mullus barbatus) from the Mediterranean sea: estimated weekly intake. *Food Chem.* **2005**, *89*, 295–300.
312. Meador, J.P.; Ernest, D.W.; Kagley, A.N. A comparison of the non-essential elements cadmium, mercury, and lead found in fish and sediment from Alaska and California. *Sci. Total Environ.* **2005**, *339*, 189–205.
313. Cubadda, F.; Raggi, A. Determination of cadmium, lead, iron, nickel and chromium in selected food matrices by plasma spectrometric techniques. *Microchem. J.* **2005**, *79*, 91–96.
314. Zhao, F.J.; Adams, M.L.; Dumont, C.; McGrath, S.P.; Chaudri, A.M.; Nicholson, F.A.; Chambers, B.J.; Sinclair, A.H. Factors affecting the concentrations of lead in British wheat and barley grain. *Environ. Pollut.* **2004**, *131*,461–468.
315. Sotelo, C.G.; Pineiro, C.; Perez-Martin, R.I. Denaturation of fish proteins during frozen storage: role of formaldehyde. *Lebensm. Unters. For.* **1995**, *200*, 14–23.
316. Badii, F.; Howell, N.K. Changes in the texture and structure of cod and haddock fillets during frozen storage. *Food Hydrocol.* **2002**, *16*, 313–319.
317. Bianchi, F.; Careri, M.; Corradini, C.; Musci, M.; Mangia, A. Innovative Method for Ultratrace Determination of Formaldehyde in Frozen Fish: SPME Extraction and GC-ITMS/MS Analysis. *Curr. Anal. Chem.* **2005**, *1*, 129–134.
318. Carro, A.M.; González, P.; Fajar, N.M.; Lorenzo, R.A.; Cela, R. Solid-phase micro-extraction procedure for the determination of 1,3-dichloro-2-propanol in water by on-fibre derivatisation with bis(trimethylsilyl) trifluoroacetamide. *Anal. Bioanal. Chem.* **2009**, *394*, 893–901.
319. Tumbiolo, S.; Gal, J.-F.; Maria, P.-C.; Zerbinati, O. SPME sampling of BTEX before GC/MS analysis: examples of outdoor and indoor air quality measurements in public and private sites. *Ann. Chim*. **2005**, *95*, 757–766.
320. Koziel, J.A.; Cai, L.; Wright, D.W.; Hoff, S.J. Solid-Phase Microextraction as a Novel Air Sampling Technology for Improved, GC–Olfactometry-Based Assessment of Livestock Odors. *J. Chromatogr. Sci.* **2006**, *44*, 451–457.
321. Kim, K.H.; Kim, D. A combination of Tedlar bag sampling and solid-phase microextraction for the analysis of trimethylamine in air: Relationship between concentration level and sample size. *Microchem. J.* **2009**, *91*, 16–20.
322. Ras, M.R.; Marcé, R.M.; Borrull, F. Solid-phase microextraction—Gas chromatography to determine volatile organic sulfur compounds in the air at sewage treatment plants. *Talanta* **2008**, *77*, 774–778.

323. Tassi, F.; Capecchiacci, F.; Buccianti, A.; Vaselli, O. Sampling and analytical procedures for the determination of VOCs released into air from natural and anthropogenic sources: A comparison between SPME (Solid Phase Micro Extraction) and ST (Solid Trap) methods. *Appl. Chem.* **2012**, *27*, 115–123.
324. Conde, F.J.; Afonso, A.M.; González, V.; Ayala, J.H. Optimization of an analytical methodology for the determination of alkyl- and methoxy-phenolic compounds by HS-SPME in biomass smoke. *Anal. Bioanal. Chem.* **2006**, *385*, 1162–1171.
325. Krüger, R.L.; Dallago, R.M.; do Nascimento Filho, I.; Di Luccio, M. Study of odor compounds in gaseous effluents generated during production of poultry feather and viscera meal using headspace solid phase microextraction. *Environ. Monit. Assess.* **2009**, *158*, 355-363.
326. Regueiro, J.; Garcia-Jares, C.; Llompart, M.; Lamas, J.P.; Cela, R. Development of a method based on sorbent trapping followed by solid-phase microextraction for the determination of synthetic musks in indoor air. *J. Chromatogr. A* **2009**, *1216*, 2805–2815.
327. Isetun, S.; Nilsson, U. Dynamic field sampling of airborne organophosphate triesters using solidphase microextraction under equilibrium and non-equilibrium conditions. *Analyst* **2005**, *130*, 94–98.
328. Miller, D.N.; Woodbury, B.L. A solid-phase microextraction chamber method for analysis of manure volatiles. *J. Environ. Qual.* **2006**, *35*, 2383–2394.
329. Yassaa, N.; Custer, T.; Song, W.; Pech, F.; Kesselmeier, J.; Williams, J. Quantitative and enantioselective analysis of monoterpenes from plant chambers and in ambient air using SPME. *Atmos. Meas. Tech.* **2010**, *3*, 1615–1627.
330. Menezes, H.C.; Cardeal, Z.L. Determination of polycyclic aromatic hydrocarbons from ambient air particulate matter using a cold fiber solid phase microextraction gas chromatography–mass spectrometry method. *J. Chromatogr. A* **2011**, *1218*, 3300–3305.
331. Hippelein, M. Analysing selected VVOCs in indoor air with solid phase microextraction (SPME): A case study. *Chemosphere* **2006**, *65*, 271–277.
332. Mocho, P.; Nicolle, J.; Desauziers, V. Modelling of adsorption kinetics and calibration curves of gaseous volatile organic compounds with adsorptive solid-phase microextraction fibre: Toluene and acetone for indoor air applications. *Anal. Bioanal. Chem.* **2008**, *392*, 97–104.
333 Cai, L.; Koziel, J.A.; Lo, Y.C.; Hoff, S.J. Characterization of volatile organic compounds and odorants associated with swine barn particulate matter using solid-phase microextraction and gas chromatography–mass spectrometry–olfactometry. *J. Chromatogr. A* **2006**, *1102*, 60–72.
334. Ding, Z.; Peng, S.; Xia, W.; Zheng, W.; Chen, X.; Yin, L. Analysis of Five Earthy-Musty Odorants in Environmental Water by HS-SPME/GC-MS. *Int. J. Anal. Chem*. **2014**, 1–11.
335. Ma, K.; Zhang, J.N.; Zhao, M.; He, Y.J. Accurate analysis of trace earthy-musty odorants in water by headspace solid phase microextraction gas chromatography-mass spectrometry. *J. Sep. Sci.* **2012**, *35*, 1494–1501.
336. Sung, Y.H.; Li, T.Y.; Huang, S.D. Analysis of earthy and musty odors in water samples by solid-phase microextraction coupled with gas chromatography/ion trap mass spectrometry. *Talanta* **2005**, *65*, 518–524.

337. Díaz, A.; Ventura, F.; Galceran, M.T. Analysis of odorous trichlorobromophenols in water by in-sample derivatization/solid-phase microextraction GC/MS. *Anal. Bioanal. Chem.* **2006**, *386*, 293–298.
338. Lu, X.; Fan, C.; Shang, J.; Deng, J.; Yin, H. Headspace solid-phase microextraction for the determination of volatile sulfur compounds in odorous hyper-eutrophic freshwater lakes using gas chromatography with flame photometric detection. *Microchem. J.* **2012**,*104*, 26–32.
339. Polo, M.; Garcia-Jares, C.; Llompart, M.; Cela, R. Optimization of a sensitive method for the determination of nitro musk fragrances in waters by solid-phase microextraction and gas chromatography with micro electron capture detection using factorial experimental design. *Anal. Bioanal. Chem*. **2007**, *388*, 1789–1798.
340. Cervera, M.I.; Beltran, J.; Lopez, F.J.; Hernandez, F. Determination of volatile organic compounds in water by head space-solid-phase microextraction gas chromatography coupled to tandem mass spectrometry with triple quadrupole analyzer. *Anal. Chim. Acta* **2011**, *704*, 87–97.
341. Badoil, L.; Benanou, D. Characterization of volatile and semivolatile compounds in waste landfill leachates using stir bar sorptive extraction–GC/MS. *Anal. Bioanal. Chem*. **2009**, *393*, 1043–1054.
342. Kos, G.; Ariya, P.A. Determination of a wide range of volatile and semivolatile organic compounds in snow by use of solid-phase micro-extraction (SPME). *Anal. Bioanal. Chem.* **2006**, *385*, 57–66.
343. Casas, V.; Llompart, M.; Garcia-Jares, C.; Cela, R.; Dagnac, T. Effects of sample pretreatment and storrage conditions in the determination of pyrethroids in water samples by solid-phase microextraction and gas chromatography-mass spectrometry. *Anal. Bioanal. Chem.* **2007**, *387*, 1841–1849.
344. Vázquez, P.P.; Mughari, A.R.; Galera, M.M. Application of solid-phase microextraction for determination of pyrethroids in groundwater using liquid chromatography with post-column photochemically induced fluorimetry derivatization and fluorescence detection. *J. Chromatogr. A* **2008**, *1188*, 61–68.
345. López Monzón, A.; Vega Moreno, D.; Torres Padron, M.E.; Sosa Ferrera, Z.; Santana Rodriguez, J.J. Solid-phase microextraction of benzimidazole fungicides in environmental liquid samples and HPLC-fluorescence determination. *Anal. Bioanal. Chem.* **2007**, *387*, 1957–1963.
346. Dong, C.; Zeng, Z.; Yang, M. Determination of organochlorine pesticides and their derivations in water after HS-SPME using polymethylphenylvinylsiloxane-coated fiber by GC-ECD. *Water Res.* **2005**, *39*, 4204–4210.
347. Raposo, J.L., Jr.; Ré-Poppi, N. Determination of organochlorine pesticides in ground water samples using solid-phase microextraction by gas chromatography-electron capture detection. *Talanta* **2007**, *72*, 1833–1841.
348. Padrón, M.E.T.; Ferrera, Z.S.; Rodríguez, J.J.S. Optimisation of solid-phase microextraction coupled to HPLC-UV for the determination of organochlorine pesticides and their metabolites in environmental liquid samples. *Anal. Bioanal. Chem.* **2006**, *386*, 332–340.
349. Brondi, S.H.G.; Rodrigues da Silva, J.C.; Lanças, F.M. Development and validation of a methodology for the determination of pesticides in water by SPME–LC/DAD. *J. Liquid Chromatogr. Rel. Technol.* **2005**, *28*, 2909–2919.

350. Filho, A.M.; Neves dos Santos, F.; Pereira, P.A.P. Development, validation and application of a method based on DI-SPME and GC–MS for determination of pesticides of different chemical groups in surface and groundwater samples. *Microchem. J.* **2010**, *96*, 139–145.
351. Bagheri, H.; Ayazi, Z.; Babanezhad, E. A sol-gel-based amino functionalized fiber for immersed solid-phase microextraction of organophosphorus pesticides from environmental samples. *Microchem. J.* **2010**, *94*, 1–6.
352. GonÇalves, C.M.; Esteves da Silva, J.C.G.; Alpendurada, M.F. Evaluation of the Pesticide Contamination of Groundwater Sampled over Two Years from a Vulnerable Zone in Portugal. *J. Agric. Food Chem.* **2007**, *55*, 6227–6235.
353. Coelho, E.; Ferreira, C.; Almeida, C.M.M. Analysis of Polynuclear Aromatic Hydrocarbons by SPME-GC-FID in Environmental and Tap Waters. *J. Braz. Chem. Soc.* **2008**, *19*, 1084–1097.
354. Rianawati, E.; Balasubramanian, R. Optimization and validation of solid phase micro-extraction (SPME) method for analysis of polycyclic aromatic hydrocarbons in rainwater and stormwater. *Phys. Chem. Earth* **2009**, *34*, 857–865.
355. Wei, M.C.; Jen, J.F. Determination of polycyclic aromatic hydrocarbons in aqueous samples by microwave assisted headspace solid-phase microextraction and gas chromatography/flame ionization detection. *Talanta* **2007**, *72*, 1269–1274.
356. Zuazagoitia, D.; Millán, E.; Garcia, R. A Screening Method for Polycyclic Aromatic Hydrocarbons Determination in Water by Headspace SPME with GC-FID. *Chromatographia* **2007**, *66*, 773–777.
357. Luan, T.; Fang, S.; Zhong, Y.; Lin, L.; Chan, S.M.N.; Lan, C.; Tam, N.F.Y. Determination of hydroxy metabolites of polycyclic aromatic hydrocarbons by fully automated solid-phase microextraction derivatization and gas chromatography–mass spectrometry. *J. Chromatogr. A* **2007**, *1173*, 37–43.
358. Jaber, F.; Schummer, C.; Chami, J.A.; Mirabel, P.; Millet, M. Solid-phase microextraction and gas chromatography–mass spectrometry for analysis of phenols and nitrophenols in rainwater, as their t-butyldimethylsilyl derivatives. *Anal. Bioanal. Chem.* **2007**, *387*, 2527–2535.
359. Ho, H.P.; Lee, R.J.; Lee, M.R. Purge-assisted headspace solid-phase microextraction combined with gas chromatography–mass spectrometry for determination of chlorophenols in aqueous samples. *J. Chromatogr. A* **2008**, 1213, 245–248.
360. Beceiro-González, E.; Guimaraes, A.; Alpendurada, M.F. Optimisation of a headspace-solid-phase micro-extraction method for simultaneous determination of organometallic compounds of mercury, lead and tin in water by gas chromatography–tandem mass spectrometry. *J. Chromatogr. A* **2009**, *1216*, 5563–5569.
361. López-Grimau, V.; Guadayol, J.M.; Griera, J.A.; Gutiérrez, M.C. Determination of non halogenated solvents in industrial wastewater using solid phase microextraction (SPME) and GC-MS. *Lat. Am. Appl. Res.* **2006**, *36*, 45–55.
362. Hudson, E.D.; Okuda, K.; Ariya, P.A. Determination of acetone in seawater using derivatization solid-phase microextraction. *Anal. Bioanal. Chem.* **2007**, *388*, 1275–1282.
363. Lee, M.R.; Chang, C.M.; Jianpeng, D. Determination of benzene, toluene, ethylbenzene, xylenes in water at sub-ng l_1 levels by solid-phase microextraction coupled to cryo-trap gas chromatography–mass spectrometry. *Chemosphere* **2007**, *69*, 1381–1387.

364. Lim, H.H.; Shin, H.S. Simple Determination of Acrolein in Surface and Drinking Water by Headspace SPME GC–MS. *Chromatographia* **2012**, *75*, 943–948.
365. Yang L.; Luan, T.; Lan, C. Solid-phase microextraction with on-fiber silylation for simultaneous determinations of endocrine disrupting chemicals and steroid hormones by gas chromatography–mass spectrometry. *J. Chromatogr. A* **2006**, *1104*, 23–32.
366. Hernández, F.; Portolés, T.; Pitarch, E.; López, F.J. Target and Nontarget Screening of Organic Micropollutants in Water by Solid-Phase Microextraction Combined with Gas Chromatography/High-Resolution Time-of-Flight Mass Spectrometry. *Anal. Chem.* **2007**, *79*, 9494–9504.
367. Derouiche, A; Driss, M.R.; Morizur, J.P.; Taphanel, M.H. Simultaneous analysis of polychlorinated biphenyls and organochlorine pesticides in water by headspace solid-phase microextraction with gas chromatography–tandem mass spectrometry. *J. Chromatogr. A* **2007**, *1138*, 231–243.
368. Jochmann, M.A.; Yuan, Y.; Schmidt, T.C. Determination of volatile organic hydrocarbons in water samples by solid-phase dynamic extraction. *Anal. Bioanal. Chem.* **2007**, *387*, 2163–2174.
369. Shutao, W.; Yan, W.; Hong, Y.; Jie, Y. Preparation of a Carbon-Coated SPME Fiber and Application to the Analysis of BTEX and Halocarbons in Water. *Chromatographia* **2006**, *63*, 365–371.
370. Bagheri, H.; Aghakhani, A. Novel nanofiber coatings prepared by electrospinning technique for headspace solid-phase microextraction of chlorobenzenes from environmental samples. *Anal. Methods* **2011**, *3*, 1284–1289.
371. Avila, M.A.S.; Breiter, R.; Mott, H. Development of a simple, accurate SPME-based method for assay of VOCs in column breakthrough experiments. *Chemosphere* **2007**, *66*, 18–29.
372. Wang, J.X.; Jiang, D.Q.; Gu, Z.Y.; Yan, Y.P. Multiwalled carbon nanotubes coated fibers for solid-phase microextraction of polybrominated diphenyl ethers in water and milk samples before gas chromatography with electron-capture detection. *J. Chromatogr. A* **2006**, *1137*, 8–14.
373. Laor, Y.; Koziel, J.A.; Cai, L.; Ravid, U. Chemical-Sensory Characterization of Dairy Manure Odor Using Headspace Solid-Phase Microextraction and Multidimensional Gas Chromatography Mass Spectrometry-Olfactometry. *J. Air Waste Manage. Assoc.* **2008**, *58*, 1187–1197.
374. Kim, H.; McConnell, L.L.; Millner, P. Comparison of odorous volatile compounds from fourteen different commercial composts using solid-phase microextraction. *Trans. ASAE* **2005**, *48*, 315–320.
375. Higashikawa, F.S.; Cayuela, M.L.; Roig, A.; Silva, C.A.; Sanchez-Monedero, M.A. Matrix effect on the performance of headspace solid phase microextraction method for the analysis of target volatile organic compounds (VOCs) in environmental samples. *Chemosphere* **2013**, *93*, 2311–2318.
376. Larreta, J.; Vallejo, A.; Bilbao, U.; Alonso, A.; Arana, G.; Zuloaga, O. Experimental design to optimise the analysis of organic volatile compounds in cow slurry by headspace solid-phase microextraction–gas chromatography–mass spectrometry. *J. Chromatogr. A* **2006**, *1136*, 1–9.
377. Banar, M.; Özkan, A.; Vardar, C. Characterization of an urban landfill soil by using physicochemical analysis and solid phase microextraction (SPME)—GC/MS. *Environ. Monit. Assess.* **2007**, *127*, 337–351.

378. Cela, R.; Dagnac, T. Simultaneous determination of traces of pyrethroids, organochlorines and other main plant protection agents in agricultural soils by headspace solid-phase microextraction–gas chromatography. *J. Chromatogr. Sci.* **2008**, *1188*, 154–163.
379. Bondarenko, S.; Spurlock, F.; Gan, J. Analysis of Pyrethroids in sediment pore water by solid-phase microextraction. *Environ. Toxicol. Chem.* **2007**, *26*, 2587–2593.
380. Witt, G.; Liehr, G.A.; Borck, D.; Mayer, P. Matrix solid-phase microextraction for measuring freely dissolved concentrations and chemical activities of PAHs in sediment cores from the western Baltic Sea. *Chemosphere* **2009**, *74*, 522–529.
381. Rocha, M.J.; Ferreira, P.C.; Reis, P.A.; Cruzeiro, C.; Rocha, E. Determination of Polycyclic Aromatic Hydrocarbons in Coastal Sediments from the Porto Region (Portugal) by Microwave-Assisted Extraction, Followed by SPME and GC–MS. *J. Chromatogr. Sci.* **2011**, *49*, 695–701.
382. Hawthorne, S.B.; Grabanski, C.B.; Miller, D.J.; Kreitinger, J.P. Solid-phase microextraction measurement of parent and alkyl polycyclic aromatic hydrocarbons in milliliter sediment pore water samples and determination of K_{DOC} values. *Environ. Sci. Technol.* **2005**, *39*, 2795−2803.
383. Shen, G.; Huang, J.; Yu, G. Measurement of the free concentrations of alkyl phenols and bisphenol A to determine their biodegradation kinetics by activated sludge. *Chin. Sci. Bull.* **2007**, *52*, 2766–2770.
384. Zhou, J.; Yang, F.; Cha, D.; Zeng, Z.; Xu, Y. Headspace solid-phase microextraction with novel sol–gel permethylated-ß-cyclodextrin/hydroxyl-termination silicone oil fiber for determination of polybrominated diphenyl ethers by gas chromatography–mass spectrometry in soil. *Talanta* **2007**, *73*, 870–877.
385. Campillo, N.; Peñalver, R.; Hernández-Córdoba, M. Solid-phase microextraction combined with gas chromatography and atomic emission detection for the determination of cyclopentadienylmanganese tricarbonyl and (methylcyclopentadienyl)manganese tricarbonyl in soils and seawaters. *J. Chromatogr. A* **2007**, *1173*, 139–145.
386. Drescher, S.R.; Brown, S.D. Solid phase microextraction-gas chromatographic-mass spectrometric determination of nitrous oxide evolution to measure denitrification in estuarine soils and sediments. *J. Chromatogr. A* **2006**, *1133*, 300−304.
387. Bicchi, C.; Cordero, C.; Liberto, E.; Rubiolo, P.; Sgorbini, B. Automated headspace solid-phase dynamic extraction to analyse the volatile fraction of food matrices. *J. Chromatogr. A* **2004**, *1024*, 217–226.
388. Grosch, W. Evaluation of the Key Odorants of Foods by Dilution Experiments, Aroma Models and Omission. *Chem. Senses* **2001**, *26*, 533−545.
389. Schieberle, P. New Developments in Methods for Analysis of Volatile Flavor Compounds and their Precursors. In *Characterization of Food: Emerging Methods*; Goankar, A.G., Ed.; Elsevier Science B.V.: Amsterdam, The Netherlands, 1995; pp. 403−433.