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Chapter 3

SOLID PHASE MICROEXTRACTION: STATE OF THE ART, OPPORTUNITIES AND APPLICATIONS

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ABSTRACT

Solid phase microextraction is one of the most popular green techniques used for sample preparations in analytical chemistry. It is a simple, rapid, sensitive, and solvent-free technique. Since SPME was first introduced in the early 1990s, there has been an intensification of research in order to elaborate new methodical solutions in many research facilities around the world, which could increase the use of this technique. More robust fiber assemblies and coatings with higher extraction efficiencies, selectivity and stability have been commercialized. Moreover, automation and on-line coupling to analytical instruments have been achieved in many applications. Furthermore, devices using tubes, needles or tips for extraction instead of a fiber have been designed. It also needs to be

mentioned that improved calibration procedures have been developed to overcome existing limitations regarding quantitation. The numerous advantages of SPME means that it is almost universal, because it allows for the analysis of different samples in multiple physical states – liquid, gas and solid – often with very complex matrices, and it provides the determination of analytes at trace and ultra-trace levels. All those features make SPME a hot topic in the development of analytical chemistry and one of the most chosen techniques for sample preparation and analyte enrichment.

Keywords: solid phase microextraction, calibration of SPME, fiber, SPME techniques

1. SOLID PHASE MICROEXTRACTION: INTRODUCTION

Without any doubt, the present analytical and separation methods can resolve practically all kinds of samples also characterized by the complex composition of the matrix, from gases to biological macromolecules, with detection limits down to the femtogram range. Generally, suitable procedures include many steps, including sampling (a collection of the samples), sample preparation (analyte separation from the matrix, concentration, fractionation and derivatization if necessary), and the determination of target compounds consisting of qualitative, quantitative and data analysis (Vas & Vékey, 2004). Despite the fact that modern analytical chemistry offers many techniques as well as instruments for the determination of target analytes in different kinds of matrices, there are still some goals to achieve (Płotka-Wasylka et al., 2016), which arise from the assumptions of Green Analytical Chemistry (GAC) (Gałuszka et al., 2013). These goals include:

- Reduction/elimination of chemical substances consumption such as solvents, reagents, additives and others;
- Minimalization of energy consumption;
- Proper management of analytical waste;
- Operator's safety ensured

There are different ways to make sample preparations "green" (Tobiszewski, 2016; Płotka-Wasylka et al., 2015). One of them is the elimination or reduction of the solvents and reagents used in the analysis. Otherwise, solvent recovery and reuse are recommended. Moreover, green media, such superheated water, ionic liquids (ILs) or supercritical fluids are preferable, rather than petrol-based solvents. In addition, there are requirements to the scale of analytical operations which should be reduced, and so instruments should be miniaturized. Aspects such as the integration of operations and the automation (or robotization) of a sample preparation are also important. Furthermore, the application of factors enhancing the effectiveness of sample preparation (including high temperature and/or pressure, microwave and UV radiation, and ultrasound energy) also impact on the "green" characteristics of the whole procedure. These recommendations are largely met by using the solid phase microextraction (SPME) technique.

Solid phase microextraction is a simple, rapid, sensitive and solvent-free technique for the extraction of analytes from solid, gaseous and liquid samples. Without a doubt, SPME takes a leading position among microextraction methods, and the application of this technique in sample preparation has been increasing continuously over the last decade. Due to the fact that SPME is a technique which combines several processes including sampling, extraction, pre-concentration and sample introduction into an analytical instrument in one single step, it has gained popularity in many fields of application, especially in routine laboratories and industrial applications (Merkle et al., 2015). Moreover, SPME can be coupled without any problem with such identification techniques as gas chromatography (GC) and high performance liquid chromatography (HPLC). Automatised fiber injection systems hyphenated with GC and gas chromatography-mass spectrometry (GC-MS) are the most popular instruments combined with SPME in use (Merkle et al., 2015). These systems have been successfully applied to a wide range of compounds, especially for the extraction of volatile and semivolatile organic compounds from samples characterized by complex matrices. However,

SPME was also developed for direct coupling to HPLC and liquid chromatography-mass spectrometry (LC-MS), and applied to weakly volatile or thermally labile compounds (Kataoka et al., 2000).

In this chapter, general principles of SPME are discussed. Moreover, it provides a comprehensive overview on recent trends of SPME method development including new devices and new techniques, as well as essential parameters in SPME processes. In addition, the latest development of fiber coating and the application of nanotechnology in SPME technology are also described. This chapter also reports applications of SPME published over the last few decades.

1.1. History

SPME was designed in 1989 by Pawliszyn and his coworkers from the University of Waterloo in Canada as an attempt to redress limitations inherent in SPE and LLE. SPME was invented to "address the need for a fast, solvent-free, and field compatible sample preparation method". This technique was patented and introduced into analytical practice in 1990 and since then, there has been an intensification of research in order to elaborate new methodical solutions in many research facilities around the world, which could increase the use of this technique (Souza Silva et al., 2013).

In the original work of SPME, uncoated or coated with liquid or solid polymer fused silica optical fibers were dipped into the aqueous sample to extract the analytes which were then desorbed into the GC injector. This solution needs to open the injector during the insertion and later movement of the fiber; however, this results in the loss of head pressure at the column (Liu & Ouyang, 2017). Afterwards, the combination of coated fiber into a microsyringe tremendously accelerates the SPME development that results in the first devices of SPME. In another type of SPME sample, a piece of microtube with coating inside, which can be installed inside a needle or can be the "needle" of a syringe, is applied (Liu & Ouyang, 2017). In this solution, heating or cooling the air in the upper part of the tube can push

gas or liquid samples into and out of the microtube, which results in the accelerating of mass analytes transport from the sample to the coating. This aids in the realization of the active sampling.

Several other solutions need to be mentioned, including the sorbent material exterior of the magnetic stirring bars, the coating interior of vessels, and even the pieces of poly(dimethyl)siloxane tubes and thin film (Liu & Ouyang, 2017).

Due to the weaknesses of commercial fibers, including low thermal stability, short expiry date and small selectivity, many research facilities have focused on improving the fibers proposed for SPME based on the use of new classes of materials. Those new materials may include:

- ILs and polymeric ILs (PILs);
- molecularly-imprinted polymers (MIPs);
- immunosorbents (ISs);
- metal complex imprinted polymers;
- conductive polymers;
- metal nanoparticles (NPs);
- carbon materials;
- mesoporous and nanoporous silicates, and aniline-silica;
- materials obtained via the sol-gel process; and,
- nanocomposites

Nowadays, fibers coated with these materials are successfully employed to isolate and to enrich a wide range of analytes present in complex matrices.

1.2. SPME Principles

Generally, the microextraction process is considered complete when the analyte concentration has reached distribution equilibrium between the sample matrix and the fiber coating.

In this case, if only two phases are considered (for example, the sample matrix and the fiber coating), the equilibrium conditions can be described by equation (1), according to the law of mass conservation (Pawliszyn, 2000):

$$C_0 \cdot V_s = C_s^{\infty} \cdot V_s + C_f^{\infty} \cdot V_f \quad (1)$$

where C_0 is the *initial concentration of the analyte in the sample;* V_s, V_f, the volume of the sample and fiber coating, respectively; C_s^{∞}, and C_f^{∞} are equlibrium concentrations of the sample and the fiber coating, respectively.

Taking into account the distribution coefficient K_{fs} of the analyte between the fiber coating and sample matrix, which is defined as (2):

$$K_{fs} = \frac{C_f^{\infty}}{C_s^{\infty}} \quad (2)$$

the following equation (3) can be derived:

$$C_f^{\infty} = C_0 \cdot \frac{K_{fs} \cdot V_s}{K_{fs} \cdot V_s + V_s} \quad (3)$$

Thus, the number of analyte moles (*n)* extracted by the coating can be calculated from equation (4):

$$n = C_f^{\infty} \cdot V_f = C_0 \cdot \frac{K_{fs} \cdot V_s \cdot V_f}{K_{fs} \cdot V_f + V_s} \quad (4)$$

which indicates that the analyte amount extracted onto the coating (n) is linearly proportional to the analyte concentration in the sample (C_0), which is the analytical basis for quantification using SPME.

In the case when the sample volume is very large, e.g., $V_s \gg K_{fs} \cdot V_f$, equation (4) can be simplified as follows:

$$n = K_{fs} \cdot V_f \cdot C_0 \quad (5)$$

which indicates the usefulness of the SPME technique when the sample volume is unknown. This means that when the fiber coating is exposed directly to the flowing blood, ambient air or water, the amount of extracted analyte will correspond directly to its concentration in the sample matrix without depending on the sample volume (Liu & Ouyang, 2017; Pawliszyn, 2000).

The amount of analyte extracted onto the fiber coating is at a maximum when the equilibrium is reached, thus achieving the highest sensitivity. In the case when sensitivity is not a major concern of analysis, shortening the extraction time is desirable. Moreover, due to the displacement effect at high concentrations, the equilibrium extraction approach is not practical for solid porous coatings. In this case, the extraction is stopped and the fiber is analyzed before the equilibrium is reached. The kinetics of analytes absorption onto a liquid fiber coating can be described as:

$$n = (1 - e^{-\alpha \cdot t})\, C_0 \cdot \frac{K_{fs} \cdot V_s \cdot V_f}{K_{fs} \cdot V_f + V_s} \tag{6}$$

where t is the extraction time, and a is a time constant which represents how fast an equilibrium can be reached. In the case when the extraction time is long, equation (6) becomes equation (4), characterizing equilibrium extraction. On the other hand, if the extraction equilibrium is not reached, equation (6) indicates that there is still a linear relationship between the amount of analyte extracted onto the fiber (n) and the analyte concentration (C_0) in the sample matrix, provided that the extraction time, the agitation, and the extraction temperature remain constant.

Considering three phases: the fiber coating, the gas phase or headspace, and a homogeneous matrix such as air or pure water, during the extraction process, the analyte will migrate among the three phases until the equilibrium is reached.

The analyte amount extracted by the liquid polymeric coating is related to the overall equilibrium of the three-phase system. Therefore, the total

mass of the analyte should remain constant during the whole process, and so:

$$C_0 \cdot V_s = C_f^{\infty} \cdot V_f + C_h^{\infty} \cdot V_h + C_s^{\infty} \cdot V_s \quad (7)$$

where C_0 is the initial analyte concentration; V_s, V_f, and V_h are volumes of the sample, the fiber coating and the headspace, respectively; and C_s^{∞}, C_f^{∞}, and C_h^{∞} are equlibrium concentrations of the sample, the fiber coating and the headspace, respectively.

Defining the distribution coefficient K_{th} of the analyte between the fiber coating and the headspace as follows:

$$K_{th} = \frac{C_f^{\infty}}{C_h^{\infty}} \quad (8)$$

and the distribution coefficient K_{hs} of the analyte between the headspace and the sample matrix as follows:

$$K_{hs} = \frac{C_h^{\infty}}{C_s^{\infty}} \quad (9)$$

the amount of the analyte extracted by the fiber coating can be turned into:

$$n = \frac{K_{fh} \cdot K_{hs} \cdot V_f \cdot C_0 \cdot V_s}{K_{fh} \cdot K_{hs} \cdot V_f + \cdot K_{hs} \cdot V_h + V_s} \quad (10)$$

taking into account that

$$K_{fs} = K_{th} \cdot K_{hs} \quad (11)$$

Thus, equation (10) can be simplified as follows:

$$n = \frac{K_{fs} \cdot V_f \cdot C_0 \cdot V_s}{K_{fs} \cdot V_f + \cdot K_{hs} \cdot V_h + V_s} \quad (12)$$

Equation (12) indicates that the presence of headspace does not influence the amount of the extracted analytes. As long as the volumes of the sample, headspace and the fiber coating are constant, it does not matter whether the coating is placed in the headspace or into the sample.

2. SPME PROCESS AND PARAMETERS INFLUENCING EXTRACTION EFFICIENCY

Without a doubt, an understanding of SPME theory provides insight and direction when developing methods, and it identifies parameters for rigorous control and optimization. The number of experiments that need to be performed can be minimized in the case of effectively using the theory, which has been developed to understand the principal processes involved in SPME by applying the fundamentals of mass transfer and thermodynamics (Pawliszyn, 2000; Pawliszyn, 2012). In this section, the basic knowledge on the different available extraction and desorption techniques for SPME applications is provided. Moreover, other parameters that impact the proper extraction process are discussed. Furthermore, calibration procedures that have been developed to overcome existing limitations regarding quantitation are described.

2.1. Extraction Techniques

The extraction mode is an important parameter which should be considered and optimized in the experimental design of SPME for a particular analyte under investigation. The extraction process of fiber SPME can be performed in three basic modes: as direct or immersion extraction (DI), in headspace configuration (HS) and in a membrane-protected approach (Figure 1). The efficiency of each mode of extraction is dependent on the sample matrix composition as well as the nature and volatility of the analytes. For aqueous sample matrices, volatile and non-polar compounds are extracted faster than semi-volatiles and polar

volatiles (Merkle et al., 2015). In addition, increasing the sample temperature and agitation efficacy may decrease the extraction time (Merkle et al., 2015).

In DI SPME, the fiber coating is directly immersed in the sample and allows analytes to partition between the matrix and the coating. There is a need for agitation in the case of a liquid sample to reduce the extraction time, while in the case of volatile compounds in gaseous samples, the natural occurring air flow is often sufficient to reach the equilibrium (Merkle et al., 2015). In DI-SPME, the amount extracted by the coating is directly proportional to the sample concentration and completely independent of the sample volume. This implication is very important, since it denotes the capability of SPME to achieve quantitative results when directly exposed to flowing fluids that, from the environmental point of view, apply to on-site sampling in rivers or lakes, for example, or air analysis (Souza-Silva et al., 2015).

In HS extraction, the fiber is exposed to the vapor phase of the aqueous matrix during extraction (Liu & Ouyang, 2017). Despite the fact that only volatile analytes are extracted, the method is advantageous for samples with high molecular weight interferences. HS-SPME is the preferred method for the extraction of analytes from samples characterized by complex matrix composition, since no direct contact with a sample protects the fiber coating from being damaged by high molecular mass and other nonvolatile interferences present in the sample matrix (Andraščíková & Hrouzková, 2015). However, HS-SPME is not suitable for all cases. The major limitations include low rates of extraction for poorly volatile or polar analytes (Andraščíková & Hrouzková, 2015). The extraction kinetics are governed by Henry's law (Merkle et al., 2015). If Henry's constant of a given substance is high, then the concentration of the compounds in the headspace is high, too. Under these conditions, rapid extraction from the headspace takes place.

In the static headspace extraction process, diffusion occurs between the fiber and the sample without any interference, while the dynamic headspace extraction process involves air movement devices like air sampling pumps that serve to move the headspace air (Razote et al., 2002).

To pick up and pre-concentrate the headspace gas, the headspace air is transferred into another chamber where the SPME filament or another extraction trap is present (Merkle et al., 2015).

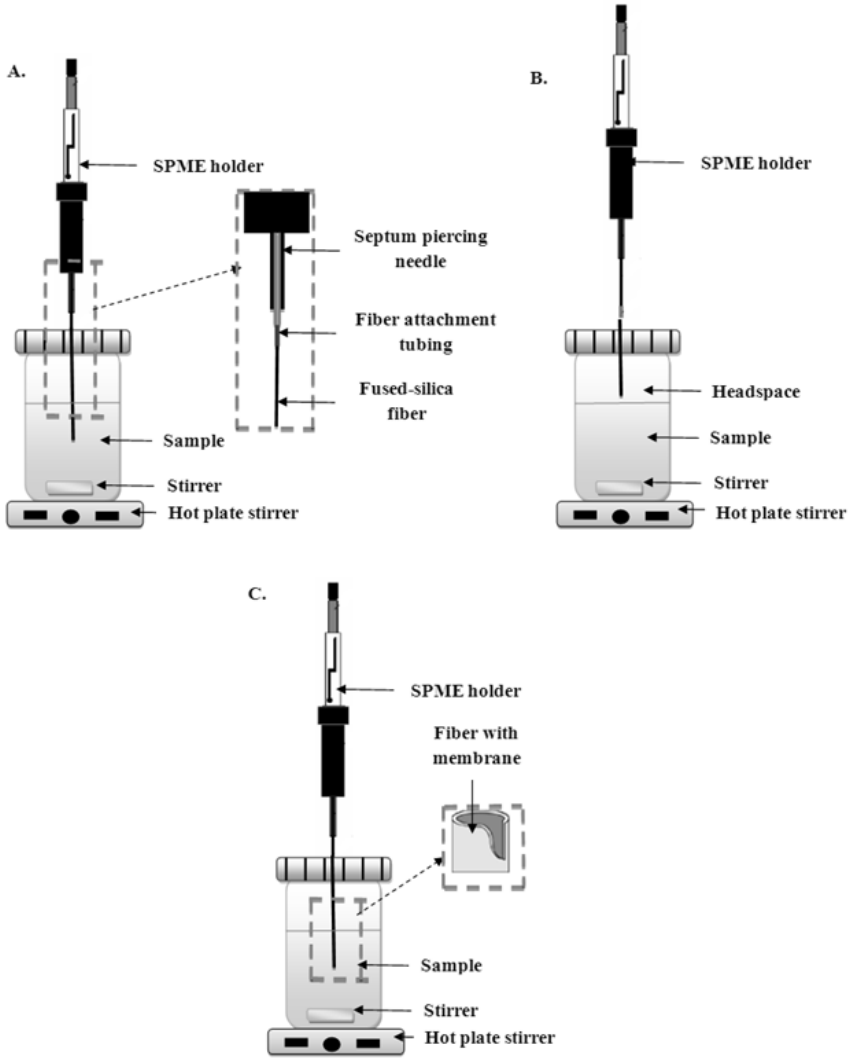

Figure 1. Schematic representation of different SPME mode: A. Direct immersion; B. Head space; C. Membrane-protected SPME.

An advantage of static headspace sampling over the dynamic headspace extraction process is that the first mode does not require careful

calibration processes and expensive air sampling pumps (Parreira et al., 2002). Moreover, static headspace sampling is characterized by sensitivity, selectivity, simplicity and ease of automation (Jung & Ebeler, 2003).

Several advantages of HS-SPME over DI-SPME exist including: shorter equilibrium time, due to the higher diffusion coefficients in gaseous state; higher concentration of the analytes in the headspace prior to extraction; and a variation of sample matrix properties without any effect on the fiber (Tan & Abdulra'uf, 2012).

For samples containing both high molecular weight interfering compounds (e.g., humic acids or proteins) and non-volatile target analytes, the application of DI or HS-SPME may be challenging. In such cases, use of restricted-access materials or membrane-protected SPME results in better reproducibility and accuracy (Pawliszyn, 2000). In membrane-protected SPME (Figure 1c), the extraction is conducted using a membrane which is selectively permeable for analytes of interest (Merkle et al., 2015). This mode of SPME is slow in comparison with other extraction techniques, but effectively extracts compounds with low volatility (Balasubramanian & Panigrahi, 2011).

In order to achieve good reproducibility, resulting from a compromise between sensitivity and extraction time, all extraction procedures require an optimization of performing parameter. Parameters that need to be optimized are: extraction technique, extraction time, temperature, agitation conditions, depth of the SPME fiber inside the vial, condition of fiber coating, geometry of the fiber, headspace and sample volume vial shape, and pH conditions (Merkle et al., 2015).

2.2. Desorption Techniques

After the extraction process, analytes of interest are introduced into an appropriate instrument for detection. This process (called "desorption") can be performed in two ways: in a static or dynamic mode. The first mode

proceeds by dipping the fiber into the mobile phase or solvent for a specific period of time, while in the dynamic mode the analytes are desorbed into a flowing mobile phase (Balasubramanian & Panigrahi, 2011). It is important to choose such desorption solutions that allow for the complete removal of analytes from the fiber; this eliminates carry over, but does not degrade the target analytes or damage the sorbent material of the fiber (Costas-Rodriguez & Pena-Pereira, 2014).

In the case when GC is a final detection technique, the SPME fiber is introduced to the GC inlet and heated to a temperature that increases analyte volatility sufficiently enough for their release (thermal desorption). The critical parameters affecting effective thermal desorption are the carrier gas flow rate and the injector temperature. It is important to know that thermal stability of the fiber coating determines the upper desorption temperature limit. This is due to the fact that high desorption temperatures impact the rapid transfer of the analytes of interest from the injector to the chromatographic column; however, this may reduce the stability of the sorbent and lead to the bleeding of the polymeric material (Costas-Rodriguez & Pena-Pereira, 2014; Pawliszyn, 2002).

In the case when HPLC is a final detection technique, desorption is performed by solvent extraction in the desorption chamber (liquid desorption). Liquid desorption is a process conducted by applying a small volume of appropriate solvents to transfer the analytes to the analytical instrumentation (Merkle et al., 2015). For thermally labile compounds liquid desorption has the advantage of not requiring elevated temperatures compared to thermal desorption (Merkle et al., 2015; Costas-Rodriguez & Pena-Pereira, 2014). A commercially available device that enables desorption of all analytes directly into the LC injector exists (Balasubramanian & Panigrahi, 2011), but individually designed desorption interfaces have also been reported (Saito & Jinno, 2003). Another type of desorption is the laser technique, and it is applied in the case of SPME in combination with matrix-assisted laser desorption/ionization mass spectrometry (Merkle et al., 2015).

2.3. Salting Out

The addition of small amounts of salts, usually sodium chloride or sodium sulphate, affects the extraction efficiency, as it raises the ionic strength of the solution (Spietelun et al., 2013). The efficiency of the extraction is improved due to the fact that the solubility of analytes decreases, their partition coefficients increase, and thus the amount of analyte sorbed on the fiber increases (Merkle et al., 2015). However, it needs to be noted that this effect depends on the particular analyte and salt concentration in the sample. In addition, it should be realized that the addition of a salt may substantially increase the risk of a sample contamination. Moreover, in the case of DI-SPME, the fiber should be thoroughly rinsed, as under these conditions it becomes much more prone to mechanical damage (Spietelun et al., 2013).

2.4. Types of Fiber Coatings and Its Thickness

There are four major criteria that are commonly applied in choosing the proper fiber coating. These are molecular weight/size of an analyte, the analyte concentration level, the polarity and the complexity of the sample matrix.

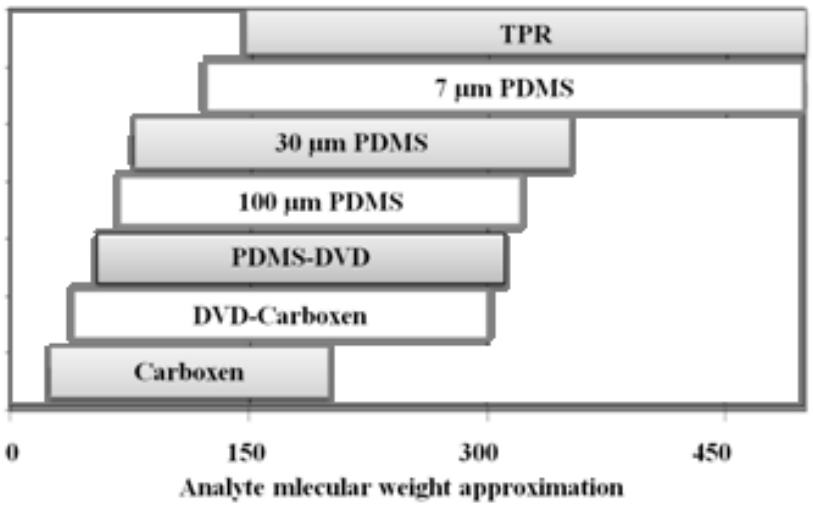

Figure 2. Suitable types of fiber applied for target analytes of differ molecular weight.

The analyte molecular weight determines how rapidly it can move in and out of the fiber phase coating and through the sample. And so, a smaller analyte will move faster and is not as well retained, whereas the larger analytes migrate through the coating and sample more slowly and take a much longer time to reach equilibrium. The coating thickness plays a major role in determining the equilibrium time and the desorption efficiency of the analyte from the fiber coating (Figure 2) (Shirey, 2014).

The choice of commercially available fiber coatings is rather limited. Moreover, the available extraction fibers do not always meet expectations and have a number of shortcomings, e.g., their selectivity is low, they are thermally unstable and mechanically rather weak, and they do not meet expectations for high recovery of polar analytes from samples with a polar matrix composition (Spietelun et al., 2013). Generally, the choice of SPME fiber coatings is limited to divinylbenzene (DVB), Carboxen (CAR), polyacrylate (PA), poly(dimethylsiloxane) (PDMS), and poly(ethylene glycol) (PEG; Carbowax, CW), available in various thicknesses and combinations such as PDMS/DVB, PDMS/CAR, or CW/DVB. The basic principle in choosing the fiber coating is that polar and nonpolar sorbents

reveal a greater affinity for polar and nonpolar analytes, respectively (Spietelun et al., 2013). Thus, in accordance with this principle, extraction coatings such as PA are applied for extracting polar analytes, e.g., phenols and some pesticides and herbicides, while even more polar coatings, such as PDMS/CAR, PDMS/DVB, and CW/DVB, are used for sampling highly polar compounds such as amines, alcohols, and ethers. Adequately, the nonpolar PDMS is used mainly for sampling nonpolar compounds, e.g., BTEX or PAHs (Spietelun et al., 2013). PDMS/CAR coatings, with their poly- (diethylene glycol) cross-links, have a larger surface area-tovolume ratio, ensuring a better extraction efficiency of BTEX analytes. Specific information on types of fiber coating are presented in Section 3.

It is obvious that the efficiency of extraction also depends on the sorbent volume, which in the case of SPME is equivalent to the thickness of the fiber coating. The quantity of analyte adsorbed on the extraction fiber is proportional to the thickness of the sorbent coating. Generally, a thicker coating will retain larger amounts of analyte than a thin one, however, the time to reach equilibrium in the former case is correspondingly longer. Thin coatings are usually applied for extracting high-molecular-weight molecules and nonpolar compounds, while thick SPME fiber coatings ensure good recoveries of volatile analytes since they can be transferred to the injector of the measuring instrument without loss (Spietelun et al., 2013; Shirey, 2014).

2.5. Extraction Time and Temperature

Other fundamental parameters that impact the extraction efficiency are the temperature and time of extraction. Although the increase in temperature allows the efficiency to improve the rates of mass transport between the phases, its utilization is rather restricted due to the fact that its increase also impacts the worse partition coefficient (Spietelun et al., 2013). Therefore, temperature manipulation is mainly used in the case of headspace extraction, as an increase in temperature accelerates the transport of analytes from the solution or solid to the headspace. However,

due to the fact that increasing temperature impacts the partition coefficient, it is important to select an optimum extraction temperature considering the following aspects: the matrix composition of the medium under investigation, the volatility of the target analytes (e.g., increasing temperature increases the vapor pressure, thus permitting the extraction of medium- and low-volatility compounds), and the type of sorbent in the SPME fiber coating.

Several parameters impact the time of extraction including sample temperature, partition coefficient of the analyte, and stirring. Generally, to achieve the maximum sorption of the analyte, it is necessary to reach equilibrium. Because the times needed to reach equilibrium are usually long, they may be shortened by intensive stirring, which is the main factor in the direct extraction mode, when increasing the temperature is not practical due to the aforementioned factors (Spietelun et al., 2013).

However, in practice, reaching equilibrium is rarely applied due to the fact that the equilibration times are still too long. Thus, the extraction process is mainly carried out in a nonequilibrium mode, where the optimum time of extraction is defined on the basis of sorption diagram-plots of the amounts of extracted analytes vs their adsorption time (Spietelun et al., 2013). In this approach, however, stirring must be kept under very strict control and calibration usually requires the utilization of internal standards.

2.6. Quantitation

In contrast to traditional sample preparation methods including solid-phase extraction (SPE), liquid–liquid extraction (LLE), and Soxhlet, SPME is a non-exhaustive extraction technique in which only a small portion of analyte is removed from the sample matrix, which allows for the monitoring of partitioning equilibria, chemical changes, and speciation in the investigated system (Ouyang & Pawliszyn, 2008) since sampling causes minimal perturbation to the system. Thus, the application of SPME gives more accurate information about the system or process under

investigation compared to exhaustive techniques. Moreover, SPME provides signal magnitudes that are proportional to the free concentration of an analyte of interest, defining the fraction of the analyte that is bioavailable (Ouyang & Pawliszyn, 2008). This feature allows for the measurement of binding constants in samples characterized by complex matrices, providing additional information about the investigated system (Ouyang & Pawliszyn, 2008; Zhang et al., 2007).

Due to the fact that SPME is a non-exhaustive extraction technique, the careful calibration for quantitative analysis is necessary. The development of SPME calibration methods is based on an understanding of fundamental principles governing the mass transfer of analytes in multiphase systems such as thermodynamics and mass-transfer. Besides traditional calibration methods such as internal standard, external standard and standard addition, other methods are applied including exhaustive extraction, equilibrium extraction and diffusion-based calibration to calibrate the SPME.

2.6.1. Calibration Methods

Well-known, traditional calibration methods including internal standard, external standard (calibration curve) and standard addition methods can be applied for the quantification of the SPME technique; however, these methods are more suitable for laboratory analysis. Each of these methods presents different advantages and drawbacks which are presented in Table 1. Applying traditional calibration methods for the quantification of the SPME technique, two approaches – equilibrium and pre-equilibrium – can be employed. In equilibrium calibration, a partitioning equilibrium between the sample matrix and extraction phase is reached. Here, convection conditions do not affect the amount of extracted analytes (Ouyang & Pawliszyn, 2008). In a second approach, the amount of extracted analytes is related to the time of extraction, in the case when the convection/agitation is constant. Quantification can then be performed based on timed accumulation of analytes in the coating. Although, using equilibrium calibration for quantitation purposes is more sensitive and does not depend on the time, in cases when the equilibrium extraction is too

long, the pre-equilibrium extraction is recommended (Ouyang & Pawliszyn, 2008; Merkle et al., 2015).

The external standard (calibration curve) is one of the most popular methods of SPME calibration. This is mainly due to the fact that this method does not require extensive sample preparation. From the other side, the sampling procedure and chromatographic conditions must remain constant for both the standard solutions and the sample, and if there are matrix effects, a blank sample matrix is necessary. Moreover, a standard gaseous mixture or a standard gas generating system is required for gaseous samples. Although this method of calibration is mainly used in laboratory analysis, on-site sampling is also possible. Due to the fact that the convection conditions make it difficult to keep the same for both on-site and laboratory circumstances, the equilibrium extraction approach is preferable. Therefore, the method is more suitable for the on-site sampling of gaseous samples compared with on-site water sampling because the equilibrium time is short for volatile compounds. Nevertheless, the loss of the extracted analytes during the transportation of the sampler should be avoided (Ouyang & Pawliszyn, 2008).

In comparison to external standard calibration, the standard addition method requires extensive sample preparation. Therefore, the application of this method for a large number of samples can be extremely tedious and time-consuming. Due to the fact that the sample matrix effects can be compensated, the standard addition method is appropriate. Thus, the standard addition calibration method should be the primary consideration in the case of most heterogeneous samples. Applying the standard additions for heterogeneous or solid samples, the mechanism of mass-transfer can be different for the standards added as well as for the native analytes, and thus the pre-equilibrium approach is not suitable (Merkle et al., 2015; Ouyang & Pawliszyn, 2008).

Another traditional calibration method used in SPME is the internal standard, which can be applied to compensate for the matrix effect, losses of analytes during sample preparation and irreproducibility in parameters. However, sometimes it is a problem to find the suitable internal standards for complex samples. This can be resolved by using the isotope-labelled

standards, however, the compounds are not available for all analytes and are expensive (Merkle et al., 2015; Ouyang & Pawliszyn, 2008).

One of the newest SPME calibration methods is named equilibrium extraction and is a widely used quantification method, especially for on-site sampling. In this calibration approach, the amount of the extracted analyte is independent of the sample volume but corresponds directly to its concentration in the sample. Therefore, in practice, the collection of a defined sample prior to its analysis is not needed, since the fiber can be exposed directly to the flowing ambient air, water, blood, production stream, etc. In the case of eliminating a sampling step, the whole analytical process can be accelerated, and errors associated with analyte losses through the decomposition or adsorption on the sampling container walls will be prevented (Ouyang & Pawliszyn, 2008). In that case, the concentration of the target analytes can be determined. In the case when the sample volume is very large, the concentration of the examined analytes can be determined by the amount of the analytes on the fiber under extraction equilibrium, by knowing the distribution coefficients of the analytes between the coating material and the sample matrix which can be directly determined by experimentation. Determining fiber coating distribution coefficients and applying dynamic systems is more accurate compared to static systems, and analyte losses in the system (due to the fiber uptake, sorption on the walls, etc.) can be compensated (Poerschmann et al., 2000). The SPME equilibrium extraction method is commonly used for on-site air or water sampling.

The next method – namely, the exhaustive calibration method – is not often used in SPME because it is typically only suitable for small sample volumes and very large distribution coefficients. In this approach, utilizing special devices or methods is necessary. Exhaustive extraction calibration can be done by using an internally cooled fiber device (Zhang & Pawliszyn, 1995), in which the distribution coefficient is significantly increased by simultaneously heating the sample matrix and cooling the fiber material with CO2. Another application of exhaustive extraction is multiple SPME (Ouyang & Pawliszyn, 2008). Here, the sample is repeatedly extracted with the fiber, and the total analyte amount can be

extrapolated from only a few extractions, even if the analyte in the sample matrix is not extracted exhaustively. The advantage of this method is that the matrix effects can be avoid by determining the total analyte amount in the sample. However, the usefulness of this method is limited.

A later method, the diffusion coefficient approach is essential to describe the kinetic process of SPME. Recently, several diffusion-based calibration methods were developed for the quantification of SPME from Fick's first law of diffusion, the interface model, the cross-flow model and the kinetic processes of absorption/adsorption and desorption. These methods are mainly used for on-site sampling, including grab sampling and long-term monitoring.

Fick's first law is applicable to calibration when diffusion paths are well-defined and the main applications are air and water sampling because the diffusion coefficients of the analytes should be known and the parameters in air or water are easy to either find in the literature or calculate with empirical equations (Khaled & Pawliszyn, 2000).

In the case of poorly defined diffusion paths, for instance, the SPME fiber is directly exposed in the matrix for sampling, and the interface model and cross-flow model can be used for calibration. Both models are limited to the linear sampling regime and the convection of air/water should keep constant. Moreover, the flow velocity of air/water should be controlled or determined when using these models for calibration (Khaled & Pawliszyn, 2000).

Kinetic calibration was based on a diffusion-controlled mass transfer model in 1997 (Ai, 1997). The basic principle of this dynamic model is that there is a linearly proportional relationship between the adsorbed analyte and its initial concentration in the sample matrix. This model gave rise to two calibration methods of SPME, namely, the kinetic calibration with standard or in-fiber standardization technique (Chen et al., 2004) and the standard-free kinetic calibration (Ouyang et al., 2008). The first is a pre-equilibrium method and can be used for the entire sampling period. The in-fiber standardization technique makes it possible to apply a simple PDMS-rod or PDMS-membrane as a passive sampler to obtain the time-weighted average concentrations of examined analytes in a sampling

environment (Ouyang et al., 2007). The concept of calibrants in the extraction phase can be used for *in vivo* studies (Zhang et al., 2007). Kinetic calibration with standards in the extraction phase can be directly calibrated with only two samplings. This method of SPME calibration can be applied to grab samplings as well as long-term monitoring (Ouyang & Pawliszyn, 2008). However, this method may not work properly in some fast sampling situations because of the loss of the standard during sampling.

A standard-free kinetic calibration method was developed for fast on-site and *in vivo* analysis (Ouyang et al., 2008). In comparison to 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 the achievement of equilibrium in the system (Ouyang et al., 2008).

Table 2.1. Information on different types of SPME calibration methods

Calibration method	Characterization	Advantages	Drawbacks	Ref.
External standard (calibration curve)	Involves the preparation of several standard solutions in sample matrix to obtain the relationship between the peak responses and the target standard concentrations. The samples are analyzed with the same extraction conditions subsequently. The concentrations of the target analyte in the samples can be calculated with the equation of the calibration curve.	No extensive sample preparation.	Need for availability of blank sample matrices. Need for stable sampling procedure and chromatographic conditions.	(Wu & Wang, 2000; Ezquerro et al., 2003; Bagheri et al., 2008; Januszkiewicz et al., 2008)
Standard addition	Involves adding known quantities of the target analyte(s) to the sample matrix, which initially contains an unknown concentration of the analyte, and this mixture is then analyzed. A plot of the responses for the range of target analyte concentrations is then developed, and the extrapolation of the plot of the response to zero defines the original concentration in the un-spiked sample. The concentration of the target analyte in the sample can be easily calculated with the analyte extracted in the sample and the slope of the plot.	Appropriate for the sample compositions unknown and complex because the sample matrix effects can be compensated.	Extensive sample preparation and analysis	(Zhou et al., 2008; De Jager et al., 2008; Saison et al., 2008)
Internal standard	Involves the addition of a compound to the calibration solutions and samples. The compound is different from the analytes, but is well resolved in the separation, and it should mimic the equilibrium of the analytes and that the process is not taken to equilibrium for both the internal standard and analytes. Here, a calibration plot is developed by determining the ratio of the peak area of the analyte to the internal standard for calibration solutions that contain different concentrations of the analyte with a fixed concentration of the internal standard. This ratio is subsequently used to calibrate the sample.	Correction of sample matrix effects. Compenzation of matrix effects and losses of analytes during sample preparation and irreproducibility in parameters (injection in GC/LC)	Limited availability of suitable internal standards. High cost and limited availability of isotope-labelled standards.	(Ravelo-Perez et al., 2007; Iglesias & Medina, 2008; Plutowska, & Wardencki, 2008)

Calibration method	Characterization	Advantages	Drawbacks	Ref.
Equilibrium extraction	A small amount of extraction phase (SPME fiber coating or other sorbent or polymer in appropriate format) is exposed to a sample matrix until an equilibrium is reached.	Calculation of analyte concentration by amount of extracted analytes is possible. Independence of amount of extracted analytes of sample volume in the case of very large samples.	Need for knowledge about distribution Coefficients of the analytes between the fiber material and the sample matrix.	(Qin et al., 2008; Larroque et al., 2006; Laak et al., 2008)
Exhausive method	The analyte in the sample matrix is totally extracted onto the fiber material and the concentration of the target analyte can be easily calculated with the amount of analyte extracted by the fiber coating and the volume of the sample.	Calculation of analyte concentration by amount of extracted analytes and volume is possible.	Suitable only for small sample volumes and large distribution coefficients or need for special devices	Zhang & Pawliszyn, 1995, Carasek et al., 2007)
Diffusion-based	*Fick's first law of diffusion* 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.	Appropriate for time-weighted average sampling. Independency of sampling rate of face velocity.	Sorbent should be zero sink for target Analytes. Very low sample rate for water sampling.	(Khaled & Pawliszyn, 2000; Chen et al., 2006)
	Interface model This model enables one to calibrate the extracted analyte mass as a function of the molecular diffusion coefficient, the analyte concentration, the sampling time, the air velocity, the air temperature and the fiber geometry. *Cross-flow model* An empirical correlation to this model was used to predict the mass transfer coefficient.	High sampling rate and short sampling time, minimized the competitive effect for solid coating. Appropriate for on-site sampling where the construction of calibration curve and addition of standard are difficult.	The flow velocity of sampling matrix should be controlled or determined. Limited to the linear sampling regime	(Poinot et al., 2014; Abdulra'uf & Tan, 2015)

Table 2.1. (Continued)

Calibration method	Characterization	Advantages	Drawbacks	Ref.
	equilibrium is a time-weighted average concentration due to the fact that the desorption of the pre-loaded standard calibrated the analyte extraction and the extraction is an integrate process. In the time when the sampling reached equilibrium, the determined data are the concentrations of the analytes in the sample at the time the samplers were retrieved.	Suitability for time-weighted average sampling.	Need for determination of standard loading	(Chen et al., 2004; Ouyang et al., 2007)
	Standard-free kinetic calibration Equilibrium extraction results in the highest sensitivity in SPME because the amount of analyte extracted on to the fiber material is maximized when equilibrium is reached.	Standard loading is not needed. Calculation of concentrations of all extracted analytes in sample is possible.	Need for stable sampling conditions. Unsuitability for long-term monitoring.	(Ouyang et al., 2008)

3. FIBER COATING AND DEVICES

An SPME device consists of a holder and a fiber. The "heart" of the SPME system is the fiber covered with an appropriate sorption material (extraction phase) with specific thickness. The SPME holder looks like a microsyringe (Pawliszyn, 2011; Rutkowska et al., 2014). Fibers are installed in the microsyringe (Figure 3) for protection (e.g., during transport of the device) and ease of manipulation (e.g., during insertion of the fiber into a sample vial or an injection port) (O'Reilly et al., 2005).

The choice of commercially available fiber coatings is the first step in SPME method development and it mostly depends on the nature of the analytes (Merkle et al., 2015). The type of fiber coating used in the SPME has a huge effect on extraction yield which is highly dependent on the distribution constant between the analytes and the stationary phase (Ghaemi et al., 2014). In practice, limited range of stationary phases are commercially available for SPME, including polydimethylsiloxane (PDMS), divinylbenzene (DVB), polyacrylate (PA), Carboxen (CAR; a carbon molecular sieve), templated resin (TPR) and Carbowax (CW; polyethylene glycol) in various thickness (Dietz et al., 2006). These materials are also combined to create fibers capable of sampling compounds having a wider range of properties than if a single material was used (Heaven et al., 2012). Table 2 presents the advantages and disadvantages of selected types of fiber coatings.

In addition to commercially available sorbents, various new coating procedures have been used to expand the types of coatings in SPME devices. These can include: coating procedure lean 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 (Merkle et al., 2015; Aziz-Zanjani et al., 2014).

Physical coating processes have been developed as the first and simplest solution. They are compatible with almost all kinds of sorbents and use new types of coating such as carbon nanomaterials, ordered mesoporous materials, ionic liquids and polymeric ionic liquids on both

fused silica fibers and metal wires (Aziz-Zanjani et al., 2014; Dietz et al., 2006).

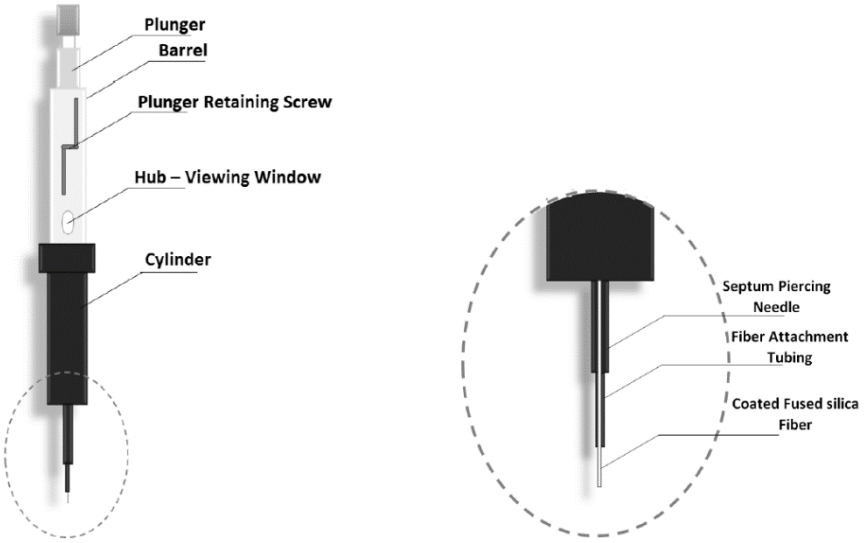

Figure 3. Commercial fiber-SPME device.

Table 2. Characteristic of selected types of fiber coatings

Type of Fiber Coatings	Characteristic	References
PDMS	Ability to withstand high temperatures (up to 300°C); High stability; Suitable for the analysis of nonpolar analytes; Suitable for exploratory analysis; High extraction efficiency of metals and alkanes; Unsuitable for the analysis of unsuitable volatile molecules; Low efficiency in relation to polar compounds; Limited reuse times; Expensive; Instability; Relatively high thickness; Difficult preparation in a routine laboratory.	(Merkle et al., 2015; Balasubramanian & Panigrahi, 2011; Tuduri et al., 2009; Lee et al., 2002; Roberts et al., 2000)
PA	Suitable for extract polar analytes; High extraction efficiency semi-volatiles compounds; Good sensitivity and dynamic range when it coupled with GC-MS; Limited reuse times; Expensive; Instability; Low operating temperature (200—270 ˚C) causes incomplete sample desorption and memory effect problems; Relatively high thickness; Difficult preparation in a routine laboratory.	(Merkle et al., 2015; Balasubramanian & Panigrahi, 2011; Boyce et al., 2002; Fu et al., 2012)

Type of Fiber Coatings	Characteristic	References
CAR	Well-suited for the extract trace level volatiles and low molecular weight compounds (because of microporous structure); Limited reuse times; Expensive; Instability; Low operating temperature (200—270 ˚C) causes incomplete sample desorption and memory effect problems; Relatively high thickness; Difficult preparation in a routine laboratory.	(Balasubramanian & Panigrahi, 2011; Fu et al., 2012)
DVB	Well-suited for the extract semi-volatiles analytes; High extraction efficiency of polar compounds like disulfides and trisulfides; Limited reuse times; Expensive; Instability; Low operating temperature (200—270 ˚C) causes incomplete sample desorption and memory effect problems; Relatively high thickness; Difficult preparation in a routine laboratory.	(Balasubramanian & Panigrahi, 2011; Cai et al., 2001)
PDMS/DVB	Used for the extraction of low molecular weight volatile and polar analytes; Lesser extraction time speeds up the analysis process; Linear dependence of the extraction of compounds as a function of time; Lower sensitivity and selectivity compared to CAR/PDMS.	(Balasubramanian & Panigrahi, 2011)
CAR/DVB	Used for the extraction of low molecular weight volatile and polar analytes.	(Garcia-Esteban et al., 2010)
CAR/PDMS	High extraction efficiencies for a wide range of analytes with different polarities and molecular weights; Recommended for extracting small particle analytes; High selectivity and sensitivity; High extraction efficiency of metals and alkanes; Displacement effect of analytes with a lower affinity to the coating.	(Garcia-Esteban et al., 2010; Kleeberg et al., 2005; Merkle et al., 2015; Pawliszyn, 2011)
DVB/CAR/PDMS	Recommended for larger particle analytes; High extraction efficiencies for a wide range of analytes with different polarities and molecular weights; Displacement effect of analytes with a lower affinity to the coating.	(Garcia-Esteban et al., 2004; Merkle et al., 2015)
CW/DVB	Lower sensitivity and selectivity compared to CAR/PDMS.	(Achouri et al., 2006)

The most common approach to physical coating procedures is sol-gel technology (Chong et al., 1997). The sol–gel process involves the building of inorganic networks by the formation of a colloidal suspension (sol) and gelation of the sol to create a network in a continuous liquid phase (gel). At the level of functional groups, generally there are three chemical reactions in succession: hydrolysis, alcohol condensation and water condensation. The use of this process makes it possible to produce homogeneous inorganic oxide materials at room temperature with desirable properties of

hardness, chemical and thermal resistance, polarity and adjusted porosity (Dietz et al., 2006; Nerín et al., 2009).

The next group of alternative procedures for fiber production is based on low cost and a simple setup of electrochemical methods, in which the variable thickness of films on unbreakable metal support can be obtained. These methods can be divided into three modes: electrodeposition, anodization and electrophoretic deposition (EPD). Electrodeposition is based on the deposition of a metallic or conductive polymer (CP) on base materials via the electrochemical reduction of metal ions or electropolymerization of CPs from electrolytes. As a result of this process, new coatings with a porous structure and high thermal stability are created (Hu et al., 2014). Anodization is a simple, low cost and rapid method for the preparation of a new porous fiber, which is characterized by high thermal stability, firmness and long durability. This process is an electrolytic passivation used to extend the thickness of the natural oxide layer on the surface of metal parts (e.g., anodized aluminum by a direct current in a solution of sulfuric acid) (Djozan et al., 2001; Hu et al., 2014). Electrophoretic deposition is a direct particle assembly method that deposits charged nanoparticles from a solution onto a substrate using an electric field. The main advantages of this approach are high chemical, mechanical and thermal stabilities of coating with a long lifespan. This solution was used to prepare single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT) coatings on platinum and steel surfaces, respectively (Câmara et al., 2007; Capobiango et al., 2015; Hu et al., 2014; Du et al., 2015).

Electrospinning is a new, inexpensive and simple method to coat the stainless steel wires with a mat of nanofibers. This is a solution to create micro/nanofibers where a high molecular weight polymer with high viscosity is drawn into nanofibers by repulsive electrostatic forces. These high surface area fibers can be used to extract non-polar and polar compounds (Merkle et al., 2015; Zewe et al., 2010).

Low cost and an environmentally-friendly process for nanomaterial thin film preparation is liquid phase deposition (LPD) method. This procedure involves the formation of oxide thin films from an aqueous

solution of a metal-fluoro complex, which is gradually hydrolyzed by adding water, boric acid (H_3BO_3) or aluminum metal. 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, and In (individually or combined) (Lin et al., 2008; Merkle et al., 2015).

4. OTHER METHODOLOGICAL SOLUTIONS IN SPME

The solid phase microextraction technique is characterized by many advantages. First of all, it is a rapid, simple and solvent-free extraction technique which provides linear results for a wide range of analytes and their concentrations. An important feature of SPME is that despite the low analytes' concentration, quantitative or semi-quantitative data are provided and losses of analytes that can occur during the sample preparation step of traditional sample procedures including extraction, concentration and clean-up steps are mostly avoidable. These advantages are the reason that SPME is almost universal, because it allows an analysis of many kinds of samples on different physical states – liquid, gas and solid – often with a very complex composition of the matrix, including trace and ultra-trace capacity levels for the determination of analytes (Płotka-Wasylka et al., 2015). However, it is not without drawbacks, including a limited number of commercially available stationary phases only roughly covering the polarity of target analytes. Especially, the extraction of polar analytes from samples with a polar matrix poses a problem (Merkle et al., 2015). Moreover, it can be operated under relatively low temperature (240–280°C), which also impacts the reduction of the application range. Another problem includes the instability and swelling in organic solvents, stripping of coatings, breakage of the fiber, bending of the needle, and the cost as well as the limited lifetime of the fiber (Nerín et al., 2009). In addition, a sample carry-over may occur and high molecular weight compounds cannot be analyzed when SPME is combined with GC. Taking into account the advantages as well as the limitations of SPME, this technique has

undergone continuous technical development over the years. Therefore, several other methodological solutions have appeared.

4.1. Fiber Solid-Phase Microextraction

Fiber SPME is the most popular mode of this technique. The main elements of fiber SPME are a fiber holder and fiber assembly, which consists of a 1 to 2cm long retractable SPME fiber and a built-in coated fiber that looks like a modified syringe (Lord & Pawliszyn, 2000; Vas & Vékey, 2004). To conduct the fiber SPME method, a vial sealed with a septum-type cap is used. After placing the sample into the vial, the SPME needle is pierced through the septum, and the fiber is extended into the vial. After contact with sample, analytes are absorbed or adsorbed by the fiber phase (depending on the nature of the coating) until an equilibrium is reached in the system. 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 (Merkle et al., 2015). After the extraction step, the fibers are transferred with the help of a syringe-like handling device to an analytical instrument for the separation and quantitation of target analytes.

4.2. In-tube Solid-Phase Microextraction

An alternative to the application of coated fibers is the internally coated needle or capillary, which is the base of the so-called in-tube techniques. In-tube SPME was primarily developed to provide an automation option for fiber SPME-HPLC. In this technique, open-tubular capillary columns for analyte retention are used. The application of the in-tube mode of SPME can overcome some problems related to the conventional fiber SPME, including low sorption capacity, fragility, and bleeding of thick-film coatings of fiber (Silva et al., 2008). In-tube systems can be applied in both the static and dynamic modes. In the static mode,

analytes are transferred by diffusion, while in the dynamic mode, the analytes are transferred actively via pumping or under gravitational flow of the sample phase through needles or tubes (Figure 4) (Płotka-Wasylka et al., 2015). Although the basic concepts of traditional and in-tube SPME methods are similar, there is a significant difference between these methods. Extraction of analytes is performed on the inner capillary column for in-tube SPME and the outer surface of fibers for fiber SPME. In in-tube SPME, it is required to prevent the plugging of the extraction capillary, and thus, the removal of the particulates from sample by filtration before extraction is necessary. This contrasts the fiber SPME method, which does not need particulates to be removed because it can be simply done by washing the fiber with water before the insertion into the desorption chamber of the SPME-HPLC interface (Płotka-Wasylka et al., 2015).

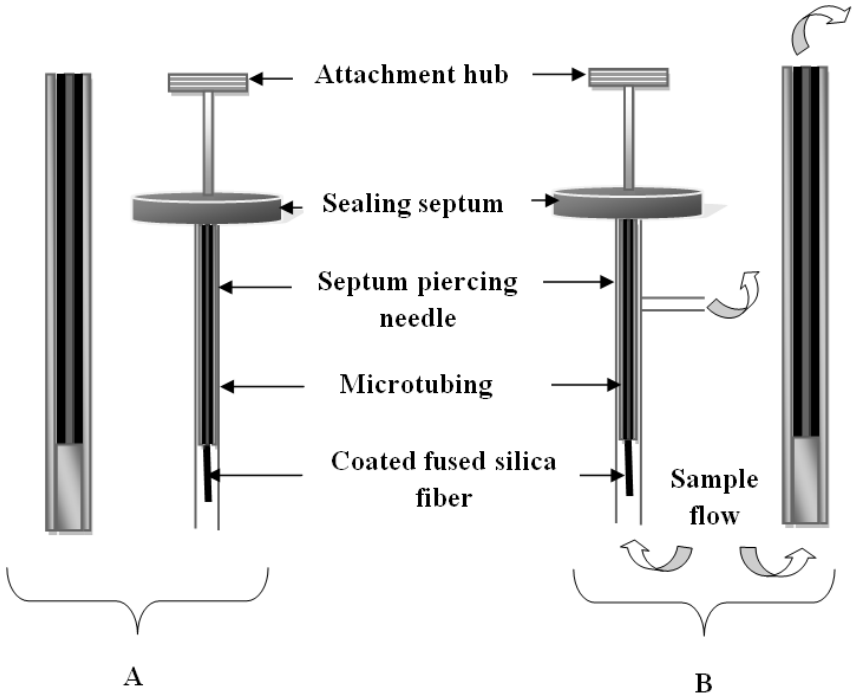

Figure 4. Schematic representation of passive (A) and dynamic (B) modes of in-tube extraction.

Taking this into account, the in-tube mode requires more complex instrumentation than traditional SPME, but by applying longer tubes and an increased amount of sorbent, it can be expected to increase in sensitivity. Another reason for the development of in-tube SPME was the lack of automation in the use of SPME coupled with HPLC. By means of automation, it is possible to perform extraction, desorption and injection at the same time (Merkle et al., 2015). This feature promotes several advantages, including shorter total analysis times as well as higher accuracy and precision. In-tube SPME is not without its drawbacks. One important limitation is the tendency of the capillary to clog up, which can be avoided by working with samples without interfering phases like particles or macromolecules (Nerín et al., 2009). Furthermore, the enrichment factor is reduced compared to fiber SPME.

In-tube techniques may be categorized into methods applying extraction coatings, which affect the internal extraction phase immobilized in the needle or in the capillary wall and the extraction fillings, which use a sorbent-packed material during the extraction phase, as demonstrated in Figure 5.

Although in-tube SPME was originally developed for HPLC applications, it can also be applied with other instrumental equipment such as capillary electrophoresis (CE) or gas chromatography (GC). Open tubular trapping is used for the online coupling of tube SPME to GC, and this solution is mainly applied to HS samples. In open tubular trapping, analyte desorption is performed with a small amount of solvent or by thermal desorption. From the other site, open tubular trapping is characterized by a complex instrumental setup as well as unfavorable sampling conditions, such as high pressure drop from long traps and limited flow rates (Nerín et al., 2009). In the literature, information can be found about the use of in-tube SPME for the determination of inorganic and organic contaminants in environmental, clinical, forensic and food analysis (Płotka-Wasylka et al., 2015).

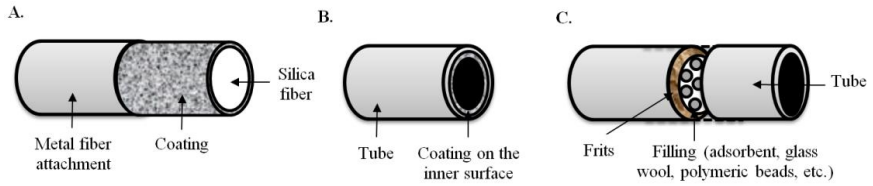

Figure 5. Schematic drawing of classical SPME fiber (A), and in tube SPME fibers with extraction coatings (B) and extraction fillings (C).

4.3. Cooled Coated Fiber Device

An internally cooled coated fiber device (CCF) or cold fiber HS-SPME device was introduced in 1995 to improve the release of analytes from the interfering phases in complex matrices (Zhang & Pawliszyn, 1995). An internally cooled SPME device allows for the heating of the sample matrix while simultaneously cooling the fiber coating. With this sampling strategy, the mass transfer is accelerated and a temperature gap is created between the internally cooled coated fiber and the hot headspace, which significantly increases the distribution coefficient (Chen & Pawliszyn, 2006). This device is especially useful for matrices with high viscosity or for volatiles with low partition coefficients (Nerín et al., 2009). It is reported that cold-fiber HS-SPME offers more sensitivity and a higher sample throughput than conventional HS-SPME (Carasek et al., 2007). From the other site, CCF is characterized by the loss of selectivity since the fiber capacity through this cooled coated fiber increased; not only are the analytes exhaustively extracted onto the coating, but the interference is as well (Merkle et al., 2015). In 2006, a CCF device was miniaturized to allow its direct introduction into a gas chromatography injector, while maintaining a reasonable septum lifetime. The automation of the internally cooled coated fiber device provided the feasibility of high throughput for the analysis of the analytes in complex matrices that required simultaneous heating of the sample matrices and cooling of the fiber coating (Zhang &

Pawliszyn, 1995). This technology is successfully employed to extract analytes from various environmental matrices (Chen & Pawliszyn, 2006; Ghiasvand et al., 2006; Zhang & Pawliszyn, 1995) and food samples (Carasek & Pawliszyn, 2006).

4.4. Non-Fiber SPME Techniques

Among the non-fiber SPME techniques, there are two techniques to distinguish. The stir bar sorptive extraction (SBSE) and thin-film microextraction (TFME).

4.4.1. Stir Bar Sorptive Microextraction (SBSE)

SBSE is a new, non-exhaustive sample-preparation technique with a greater extraction capacity than conventional the SPME method, because it has a larger surface area than SPME fibers (Tan & Abdulra'uf, 2012). This technique uses a 10 to 40mm long magnetic stir bar coated with 50 – 300µL of PDMS, which is stirred in or set up above a liquid sample for a selected period of extraction time (Figure 6). The extraction time is kinetically verified and determined by the amount of sample, stirring rate, temperature and stir bar size, and must be optimized for a given usage (Kataoka, 2010). After the extraction process, the stir bar is removed with a tweezer and a fraction of the concentrated extract can be transferred to a GC or LC system (Kataoka, 2010; Padrón et al., 2014).

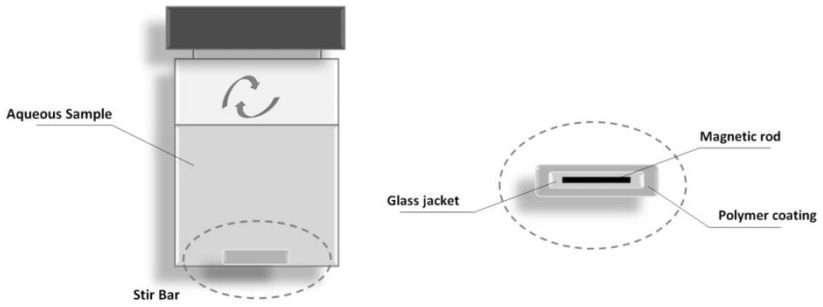

Figure 6. Scheme of stir - bar sorptive microextraction.

In the case of a SBSE-GC coupling, thermal desorption of the analytes is induced by placing the bar into the GC injection port or by inserting it in a small vial, and the desorption can be performed by adding a few microliters of an appropriate liquid solvent. Contrary to the SBSE-LC method, the mobile phase can be added directly to the stir bar (Merkle et al., 2015). However, this technique has several disadvantages such as: a small number of commercially available coatings, the inability to achieve full automation of the SBSE process and reconstitution in a solvent before chromatographic analysis, where it is possible to contaminate and lose analytes (O'Reilly et al., 2005; Tan & Abdulra'uf, 2012). In recent years, the SBSE technique has successfully been applied for the extraction of volatile and semivolatile organic compounds in the environment, food and biomedicines samples (Table 3).

4.4.2. Thin-Film Microextraction

Thin-film microextraction (TFME) links most of the advantages of the SPME method, and as a consequence, it increases the sensitivity in a shorter amount of time and less thickness of the extraction phase is obtained (Mirnaghi et al., 2013). In TFME, a flat film with a high surface area-to-volume ratio is used as the extraction phase (Merkle et al., 2015). In the TFME method, various sampling formats can be used. The most commonly sampled formats used are: directly placing the membrane on/in the sample matrix (Qin et al., 2010; Sisalli et al., 2006; Wei et al., 2011) and coating the flat film on the surface of the vial that contains the sample (Golding et al., 2007 ; Wilcockson & Gobas, 2001). The extraction material for thin films should be chosen and prepared for a multiplicity of sample-matrix applications. As for the extraction phase in the TFME technique, PDMS [B44-45] and mixed-phase thin films (e.g., PDMS/b-cyclodextrin, Hu, et al., 2005) were used. In a 96-blade systems, coatings were also developed. Thin-films can be prepared using dipping, spreading, spraying, spinning and electronspinning methods (Jiang & Pawliszyn, 2012). In the dipping technique, a piece of glass, stainless steel or other substrate is immersed in the coating preparation

solution several times until the design thickness of the film is obtained. After this, the support substrate can be removed or used together with the thin film during the sampling (Jiang & Pawliszyn, 2012; Jomekian et al., 2011; Mirnaghi et al., 2011). The simplest and most commonly method used for wet film preparation is the spreading technique. The flat film is prepared by manually or automatically spreading the solution with a film applicator. This technique was used to prepare both single phase PDMS and mixed phase PDMS/b-cyclodextrin thin films (Hu et al., 2005; Jiang & Pawliszyn, 2012; Wei et al., 2011). High stability and reproducibility characterize the traditional spraying method for coating preparation. This approach was used, for example, for preparing a C18-PAN 96-blade format thin film (Jiang & Pawliszyn, 2012). In the last few decades, the spin coating method has also been used. The spinning process is based on the depositing of a small puddle of coating solution onto the center of a substrate and then spinning the substrate at a high speed of about 1000 rev/min (Guerra et al., 2008; Jiang & Pawliszyn, 2012). One of the newest solutions for the coating preparation method is the electrospinning method which, like the electrospray technique, involves the spraying of the polymer solution between two electrodes with a high voltage to form a nanofiber, which is uniformly deposited on a flat substrate to prepare the thin-film extraction phase (Bagheri et al., 2011; Hota et al., 2008; Jiang & Pawliszyn, 2012). TFME can be applied to samples of different matrices and can be coupled to both liquid and gas chromatographic systems (Table 3) (Jiang & Pawliszyn, 2012; Merkle et al., 2015; Mirnaghi et al., 2013).

4.5. In-Needle SPME Methods

In-needle SPME methods use a needle instead of a tube for extraction and can be classified as a solid-phase dynamic extraction (SPDE), microextraction by packed syringe (MEPS) and fiber-packed needle microextraction (FNME).

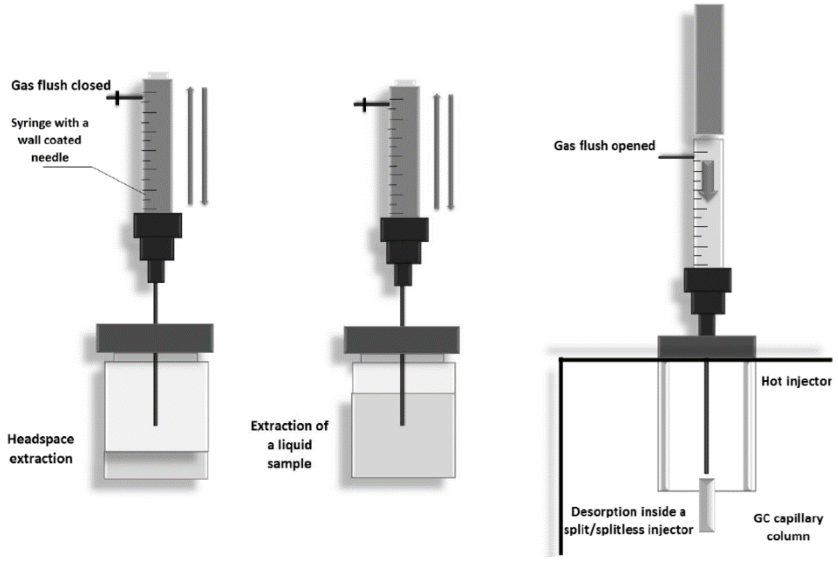

Figure 7. Schematic representation of SPDE principles.

4.5.1. Solid-Phase Dynamic Extraction

SPDE uses a syringe with a stainless steel needle with an inner wall coated by a thin film of PDMS and 10% activated carbon. The needle is inserted automatically or manually into the sample and the plunger is moved up and down repeatedly while the analytes from a liquid or headspeace sample are concentrated onto a thin film. Recovery of the analytes takes place by heat desorption directly into the injection port of the GC. Principles of SPDE are presented in Figure 7. The SPDE technique is characterized by many advantages, e.g., short extraction time, good repeatability, high mechanical stability of the SPDE device and a larger coating volume compared to the SPME method, which causes an increase in the concentration capacity (Lipinski, 2001; Merkle et al., 2015).

4.5.2. Microextraction by Packed Syringe

A relatively new method is known as microextraction by a packed syringe technique, which is an automated and miniaturized version of the SPE technique. A small amount of the SPE sorbent is inserted into a

syringe or pipette-tip as a plug, which is secured at both ends. Sorbent materials include: silica (C2, C8, C18), benzenesulfonic acid cation exchanger, polymer (polystyrene particles), MIP material and an organic monolithic sorbent. The sample is withdrawn through the syringe, and the analytes adsorb into the SPE material. The sorbent is then washed and the analytes are eluted and injected into the chromatograph. The main advantage of the MEPS solution is that only a small amount of sorbent, sample and organic solvents for elution of the analytes are used. In addition, the MEPS technique can be used with GC, LC, or MS without any modification of the instrument (Blomberg, 2009; Hyotylainen & Riekkola, 2008; Merkle et al., 2015).

4.5.3. Fiber-Packed Needle Microextraction

Fiber-packed needle microextraction is an optional method using fiber instead of particle materials inside the needle (Merkle et al., 2015). An extraction medium in the FNME device serves as a short capillary (which hs made of fused-silica, polyetheretherketone (PEEK) or polytetrafluoroethylene (PTFE)), in which several hundred filaments of synthetic polymers are packed (Figure 8) (Jinno et al., 2007). FNME can be used in liquid-phase separation methods and as the separation medium in GC (Saito et al., 2009).

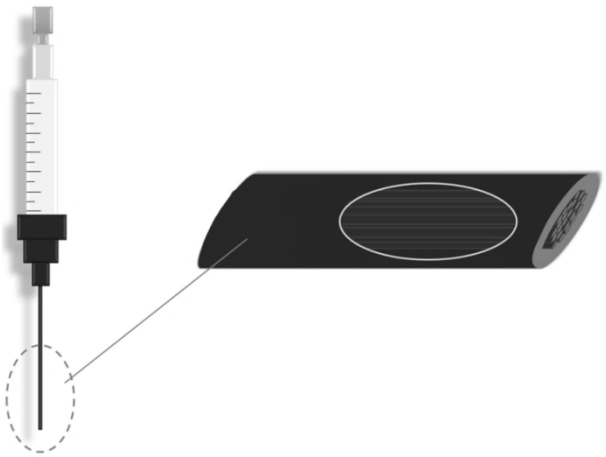

Figure 8. The structure of fiber-packed needle extraction device.

Apart from miniaturization and the possibility of directly coupling the extraction process with microscale analytical separation methods, the FNME solution offers a reduction of pressure drop and undesirable blockage caused by insoluble and/or particulate materials in real sample matrices (Jinno et al., 2007).

4.6. In-Tip SPME

One of the newest approaches for sample preparation is the in-tip SPME technique. In this method, solid packing material is placed into pipette tips and the extraction process, which is generally done offline, takes place on the packed bed (Figure 9). The most commonly used sorbents are silica and methacrylate monoliths because they can be prepared with a number of different selectivities and they are stable over a wide pH range. The biggest advantages of in-tip SPME technology is the possibility of total automation of the process and the possibility of parallel handling of several samples. An alternative approach to the in-tip SPME solution is to use fiber instead of particle materials (Kataoka, 2010; Merkle et al., 2015).

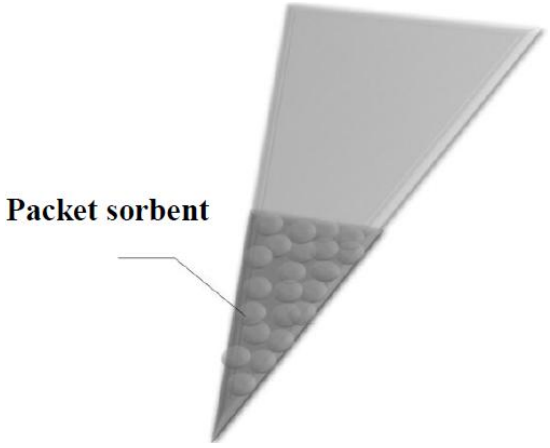

Figure 9. Schematic representation of in-tip SPME.

4.7. SPME Arrow System

A relateivly new SPME method is the SPME Arrow system. Lowering the numerical value of the limit of detection is often achieved by increasing the sorbent volume in SPME. However, the combination of large volumes of SPME sorbents and GC analysis can be problematic due to difficulties in the desorption of the analytes' stages. To solve these problems, the SPME Arrow system was created. This device consists of a steel rod coated with more sorbent material than the fiber used in traditional SPME (Helin et al., 2015). However, it is still possible to combine it with the desorption method in a standard GC liner because of the SPME Arrow system dimensions and the sharp, closed tip (Figure 10). Compared to conventional SPME fiber, the SPME Arrow had better robustness and sensitivity, and it could be used to extract large amounts of analytes from complex matrices.

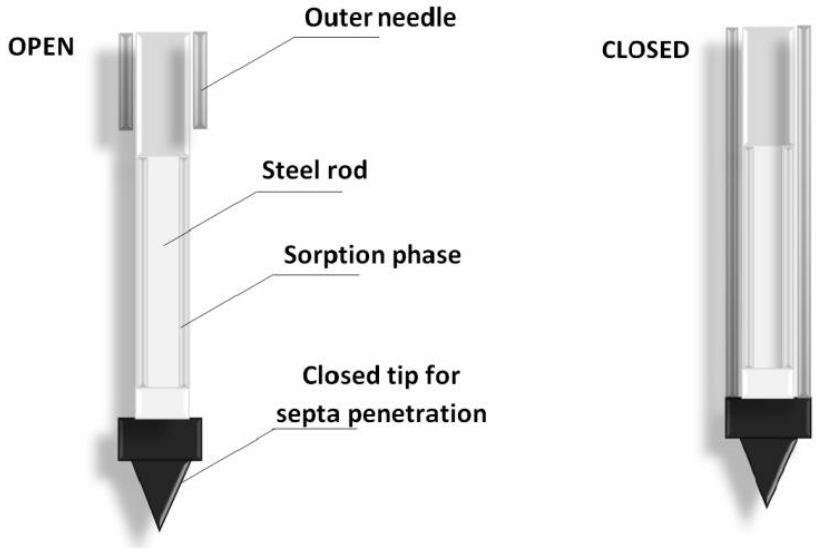

Figure 10. The SPME Arrow system with sorbent exposed and with sorbent covered by a steel tube.

Table 3. Information on application of SPME and other techniques based on SPME principles

Technique	Analyte	Sample	Sorbent/ Coating	Analytical Method	Linear Range	Recovery	Lod	References
In-tip SPME	Metoprolol; pindolol; [$^2H_7$]-ropivacaine (IS)	Human plasma	Monolithic methacrylate polymer	LC-MS-MS	5–5.000 nmol L^{-1}	-	-	Abdel-Rehim et al., 2008
	Cyclophosphamide; iphosphamide (IS)	Mouse blood	Monolithic methacrylate polymer	LC-MS-MS	10–5.000 nmol L^{-1}	-	-	Altun et al., 2010
	Methamphetamine; amphetamine	Human urine	C_{18} -bonded monolithic silica gel	GC-MS	0.25–200 ng /0.5 mL	82.9%; 82.2%	0.04 ng/0.5 m; 0.05 ng/0.5 mL	Kumazawa et al., 2007
	Methamphetamine; amphetamine	Human whole blood	C_{18} -bonded monolithic silica gel	GC-MS	0.5–100 ng 0.1 mL^{-1}	87.6%; 81.7%,	0.15 and 0.11 ng/0.1 mL,	Hasegawa et al., 2009
SBSE	Barbiturates	Human urine	24 µl PDMS	TD/CGC/ MS	5 -500 mg L^{-1}	-	1-10 ng/l	Tienpont et al., 2003
	Phenolic xenoestrogens (PXs)	Human urine	24 µl PDMS	GC-MS	g mL^{-1}	>95%	-	Kawaguchi et al., 2005
	Caffeine	Biological fluids	Alkyl-diol-silica (ADS)	HPLC-UV	0.5–100 µg mL^{-1}	-	25 ng/mL	Saito et al., 2000

Table 3. (Continued)

Technique	Analyte	Sample	Sorbent/ Coating	Analytical Method	Linear Range	Recovery	Lod	References
Microextraction by packed syringe	Mepivacaine; lidocaine; prilocaine; ropivacaine; [$^2H_7$]-ropivacaine (IS)	Human plasma	Silica C_2	GC-MS	5–2.000 nmol L^{-1}	60%; 90 %.	-	Abdel-Rehim, 2004
	Cyclophosphamide; [$^2H_3$]-lidocaine (IS)	Mouse blood	Silica C_2	LC-MS-MS	0.1–100 µg mL^{-1}	-	-	Said et al., 2008
	Methadone; [$^2H_7$]-ropivacaine (IS)	Human urine	Silica-C_2; -C_8; -C_{18};	GC-MS	2.3–3.100 µg mL^{-1}	-	-	El-Beqqali & Abdel-Rehim, 2007
Solid phase dynamic extraction	Organophosphate triesters	Indoor air	100 µm PDMS	GC-NPD	-	-	-	Isetun & Nilsson, 2005
	Pesticides	Water	100 µm PDMS	GC-ECD	-	-	0.001 - 0.1 µg L^{-1}	Lipinski. 2001
Thin-film microextraction	PAHs	Lake water	PDMS	GC-MS	0.1 to 10 ng/mL	82% -115%	25 pg/mL	Bruheim et al., 2003
	PAHs; polar phenolic compounds	Water	PDMS/-CD	GC-MS	0.10 – 1000 µg L^{-1}; 0.10 to 5000 µg L^{-1}	82.3% - 100.2%	0.01–0.2 µg L^{-1}; 0.02 to 1.5 µg L^{-1}	Hu et al., 2005

Technique	Analyte	Sample	Sorbent/ Coating	Analytical Method	Linear Range	Recovery	Lod	References
	Alkylphenols; bisphenol-A	Seawater	Hydroxylated polymethacrylate	GC-MS	0.01-15 ng L^{-1}	-	0.07 ng L^{-1}; 2.34 ng L^{-1}	Basheer et al., 2005
Fiber-packed needle microextraction	n-butylphthalate;	Wastewater	Zylon® fiber/ PEEK	LC	-	-	< 1 ng m L^{-1}	Saito et al., 2000
	Phthalates;	Wastewater	Zylon® fiber/ PEEK and PTFE	LC	-	26.2%-102.1%	0.03 ng mL^{-1}	Saito et al., 2004
SPME Arrow system	Dimethylamine; Trimethylamine	Ambient air; wastewater	PDMS/CAR 1000; PDMS/CAR WR	GC-MS	10–500µg L^{-1} ; 0.13–130 µg L^{-1}		10 µg L^{-1}; 0.13 µg L^{-1}	Helin et al.,, 2015
in-tube SPME	Ochratoxin A	Wine	PEEK/C18	HPLC-MS/MS	-	73%	0.02 µg L^{-1}	Andrade & Lancas, 2017
	Estrogens	Human urine	NH_2-MIL-53(Al)	HPLC-SPD/RF	-	75.1% – 120%	2.0 – 40 ng L^{-1}	Luo et al., 2017
	Trans-fatty acids (TFAs)	Instant coffee	Poly (OMA-co-EDMA)] monolith	HPLC - SPD	0.01-1.00 mg kg^{-1}	58.3% - 70.9%	3.0-7.1 µg kg^{-1}	Wu et al., 2017
Cooled Coated Fiber Device	PAHs	Soil; sediment	PDMS	GC-FID	-	-	-	Haddadi et al., 2009
	Flavor and perfume ingredients	Aqueous media	PDMS	GC-FID	1–3000 µg g^{-1}	>80%	0.2–1 µg g^{-1}	Chen et al., 2007
	Volatile Compounds	Tropical Fruit	DVB/CAR/PDMS, 50/30 µm; CAR/ PDMS, 75 µm;	GC-FID	-	-	-	Carasek & Pawliszyn, 2006

Table 3. (Continued)

Technique	Analyte	Sample	Sorbent/ Coating	Analytical Method	Linear Range	Recovery	Lod	References
			PDMS, 100 µm; PA, 85 µm;					
SPME	Organomercury Compounds	Water, fish tissue	100 µm PDMS	AFS	-	-	3.0 ng L^{-1}	Cai et al., 1998
HS-SPME	Organomercury Compounds; Organotin Compounds	Water samples	100 µm PDMS; 50 µm/30 µm DVB/CAR/PDMS	GC-MS	-	-	3 ng L^{-1}; 7 ng L^{-1}; 16.8 ng L^{-1}	Centineo et al., 2004

5. CONCLUSION

Without any doubt, the miniaturization of traditional sample preparation techniques such as solid-phase extraction or solvent extraction led to the development of environmentally benign analytical methods. Thus, to overcome drawbacks of SPE, a solid phase microextraction technique was introduced and it required less time and labor than multi-step procedures of SPE. The SPME technique as well as techniques based on SPME principles allow for the integration of activities (e.g., sampling, extraction and analyte enrichment to the level above the method limit of detection (LOD) and analyte isolation from the sample matrix that cannot be directly introduced into a measuring instrument. SPME and techniques based on SPME principles accelerate the sample pretreatment and reduce the environmentally deleterious effects of sample pretreatments. Presently, they offer green extraction options for the treatment of gaseous, liquid and/or solid samples. These techniques present numerous positive features such as relatively low costs of instrumentation, simplicity of operation, versatility, easy coupling to chromatographic systems and short extraction time. The application of SPME and others techniques described in this chapter are very wide and include the extraction of analytes from aqueous samples including environmental water, but they are also widely applied to samples with matrix complexity such as biological fluids, food or natural products, which are characterized by the varied, low level contents of their respective components (Table 3).

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