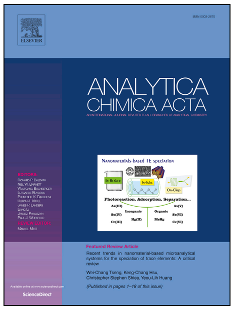

Review of Geometries and Coating Materials in Solid Phase Microextraction: Opportunities, Limitations, and Future Perspectives

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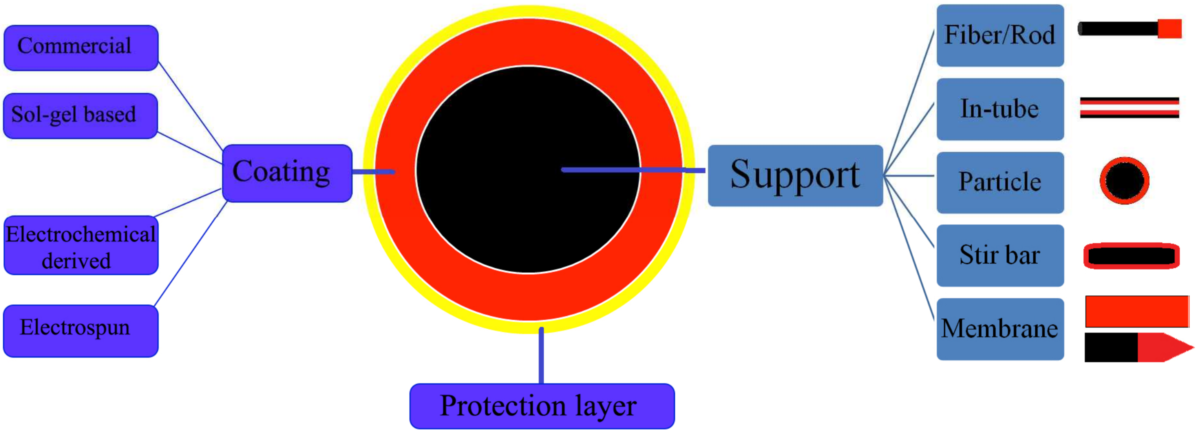
Commercial
Sol-gel based
Electrochemical derived
Electrospun
Coating
Support
Fiber/Rod
In-tube
Particle
Stir bar
Membrane
Protection layer

Review of Geometries and Coating Materials in Solid Phase Microextraction: Opportunities, Limitations, and Future Perspectives

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Abstract

The development of new support and geometries of solid phase microextraction (SPME), including metal fiber assemblies, coated-tip, and thin film microextraction (TFME) (*i.e.* self-supported, fabric and blade supported), as well as their effects on diffusion and extraction rate of the analytes were discussed in the current review. Application of main techniques widely used for preparation of a variety of coating materials of SPME, including sol-gel technique, electrochemical and electrospinning methods as well as the available commercial coatings, were presented. Advantages and limitations of each technique from several aspects, such as range of application, biocompatibility, availability in different geometrical configurations, method of preparation, incorporation of various materials to tune materials to desired properties, and thermal and physical stability, were also investigated. Future perspectives of each technique to improve the efficiency and stability of the coatings were also summarized. Some interesting coatings including ionic liquids (ILs), metal organic frameworks (MOFs) and particle loaded coating were briefly presented.

Keywords: Solid phase microextraction; Support geometries; Coating chemistry; Commercial coatings; Sol-gel method; Electrochemical and Electrospinning techniques

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1- Overview

Solid phase microextraction (SPME) is a sample preparation technique introduced in the 1990s [1, 2] as a solvent-free and miniaturized technique to be used as a green alternative to conventional techniques such as liquid-liquid extraction (LLE) and solid phase extraction (SPE). SPME is a technique that isolates and pre-concentrates the analytes of interest on the polymeric coating (known as extraction phase) from the matrix in one step, facilitating the method of sampling. SPME consists of a support, coating material [2], and protection layer (if necessary; particularly for complex matrices such as food) [3]. The first applications of SPME were conducted using the so-called fiber geometry [1], which was composed of a fused silica rod as support for the polymeric coating that is either exposed directly to the sample or via headspace extraction. Following, in-tube SPME was introduced [4] by coating extraction phases inside a tube with aims to facilitate automation, particularly to LC instrumentation, while providing higher extraction efficiency. To further facilitate improved sampling and the extraction procedure, several geometries have been developed by coating extraction phases on particles, stir bar and fabric/blade supports. Figure 1 shows the different geometries of SPME technique [2,5] including a) fiber, b) coated-tip (miniaturized fiber with coating length of 150 μm applied to single cell of Allium cepa L) [6], c) arrow (modified fiber)[7,8], d) in-tube [9,10], e) thin film [11], f) 96-blade blade configuration (thin film on a blade support) [12], g) in-tip [13,14], and h) magnetic nanoparticles (MNPs) [15]. In comparison to other SPME geometries, thin film microextraction (TFME) (*i.e.* membrane geometry) [11,16] and coated stir bar (TwisterTM) provide more sensitivity of analysis. The coated stir bar, is commercially available under the trade name of twister/stir bar sorptive extraction (SBSE) technique, coated with polydimethylsiloxane (PDMS) [17–19], introduced by Sandra and co-workers in 1999 [20], and it is not discussed in the current review. As PDMS is the only coating commercialized for SBSE, it has limited number of applications compared to the other mode SPME.

There are several reviews in which coating materials, geometries, and applications of SPME in different matrices are discussed [5,11,21–23]. In the current review, new developments of SPME in terms of geometries and coating materials are comprehensively presented from different perspectives. As a technique, SPME has significantly advanced since its first introduction in the early 1990s, including undergoing several modifications on supports and coating materials to improve the stability and sensitivity of the SPME probes. For instance, the replacement of the fused silica with a metal support has led to the increased lifetime of SPME fibers. As well, commercially available SPME fibers provide a new assembly containing a special metal alloy in the needle, plunger, and fiber core (support) that allows bending of the fiber without any breakage [24]. The new metal commercial fiber has a physical durability of over 360 cycles (compared to 30-40 cycles of the standard fiber, fused silica support), subsequently increasing the lifetime of the fiber coating to 120-200 cycles (compared to 30-40 cycles of the standard fiber) in view that the lifetime of the fiber coating is directly limited by the physical stability of the fiber assembly. Apart from the commercially available unbreakable fiber, several other attempts have been made to chemically bind the coating material to metal supports; these are discussed in detail throughout the manuscript. Development of TFME using various fabric and blade supports, as well as different coating materials, are also discussed. The recent development of the coated-tip geometry of SPME is also presented as a new perspective for analysis of small volumes of samples in complex matrices and single cells with short equilibrium time due to the radial diffusion. In addition to discussing the development of new geometries, available coating materials and new approaches to the preparation of robust fibers for direct analysis of food samples (*i.e.* overcoated fiber) are discussed. Several technologies have been developed and used for preparation of the variety of polymeric coatings in view of the goal of the analysis, including considerations of target compounds and the required instrument (*e.g.* use of thermally stable fibers for GC). For instance, the sol-gel technique was employed in the preparation of thermally stable coatings owing to the rigid structure of the crossed-lined silica network, while electrospinning was implemented to prepare nanofibers with aims to improve extraction efficiency, as the electrochemical method is usually the method of choice in cases where a thin layer of coating is required. The aforementioned techniques have their own strengths and limitations, which are discussed throughout the manuscript. In addition, ionic liquids (ILs), metal organic frameworks (MOFs) and particle-loaded coatings prepared by spray and dip coating methods that have also been gained attention as SPME coatings for several applications are also discussed.

2- SPME vs exhaustive approaches

While SPME is a microextraction technique that is considered a non-exhaustive method, unlike SPE and LLE, some geometries, including in-tube, stir bar, and TFME, might provide exhaustive extraction. In the case of exhaustive extraction, although there are similarities between TFME and SPE in terms of extracted amounts, some substantial differences remain in regards to the procedure of extraction and method of quantitation. As an open-bed extraction system, TFME applications do not require the use of a pump and any apparatus, while SPE, as a packed-bed system, requires that extraction be performed by passing the sample through the SPE cartridge, which employs a pump. In comparison to TFME, SPE analysis can be accomplished within a smaller period of time owing to its very high extraction phase to sample matrix contact surface contact area. However, in instances where a given sample contains particulate matter, blockages of the SPE cartridges are likely to occur; this is particularly true for complex matrices, and a distinctive drawback of the SPE method. Quantitation of a given compound in SPME is mainly based on an external calibration curve of the extracted amount vs. concentration, regardless of the total recovery, or whether the extraction is exhaustive or non-exhaustive (In negligible depletion cases, the slope of the calibration curve is the fiber constant, $K_{fs} \times V_f$); more details regarding calibration methods for SPME can be found in literature [25]. On the other hand, quantitation using SPE is based on the volume of the sample, as it is assumed to be exhaustive. One limitation in SPE is attributed to the breakthrough volume, where the sample volume needs to be lower than the retention capacity of the sorbents; otherwise, compounds are not quantitatively retained by the sorbents. As such, it is difficult to apply SPE for untargeted analysis to accurately quantify compounds, as there is no information regarding the breakthrough volume of the sample. Therefore, the microextraction approach is a more convenient and suitable approach for untargeted analysis. In addition, TFME, as an open-bed approach, allows for in-vivo analysis (*e.g.* analysis human saliva) [26] and on-site sampling [11,27], which presents SPME with an unique advantage compared to conventional extraction methods. More detail regarding comparisons of SPME and SPE can be found in the literature [28,29].

SPME is also able to accurately quantify the free amounts of compounds (as an effective amount/dosage) in complex matrices in cases where there is binding between analytes and the matrix under study, such as for instance protein binding in blood and plasma samples, or particles in water samples. It should be noted that free amounts of compounds can only be obtained when there is negligible depletion by the SPME probe (without disturbing the protein/analyte binding. Free and total amounts of compounds can be obtained by SPME with the use of matrix-free and matrix-matched calibrations, respectively [30–32]. On the other hand, SPE and LLE are only capable of determining the total amounts of analytes in such matrices.

3- Geometries and diffusion

In recent times, numerous authors have pointed out that SPME is not only a solventless extraction technique in nature but also a rapid, convenient sample preparation device useful for both laboratory use, and on-site or in vivo applications [33]. This is due to the fact that a wide variety of geometries of SPME have been developed to improve speed, sensitivity, and convenience of use. The development of various coating geometries arises from the requirement of two basic performance parameters, namely, extraction rate and extraction efficiency.

In SPME, analytes are transported (through diffusion, with added convection for flow systems) from the bulk to the coating surfaces, where extraction occurs. Most of these processes are mass transfer limited due to faster sorption kinetics [34]. An important performance parameter of SPME is equilibration time, which is defined as the time required to reach 95% of equilibrium, where statistically no difference in extracted amounts is observed by leaving the coating in the sample for a longer time period.

Enhancements in the extraction rate facilitate rapid equilibrium, allowing for more convenient determination of analytes, in terms of sensitivity and rapidity. For a sample under agitation and an SPME device with a thin coating (typical coating thickness is less than 100 µm), a thin boundary layer is developed around the coating [35]. If the extraction rate is determined by diffusion through the boundary layer, which is most commonly observed in applications of SPME that use a very thin coating, the initial extraction rate can be expressed by eq. 1:

$$\frac{dn}{dt} = \left(\frac{D_s A}{s}\right. \; C_s \qquad 1$$

where *n* is the mass of analyte extracted over the sampling time *t,* and *A* is the geometric surface area of the coating, which does not account for the porosity of the particles used in the coating. The thickness of the boundary layer (δ_s) is a function of factors such as the geometric configuration of the SPME device, the direction of flow, the sample agitation speed, temperature, and the diffusion coefficient (D_s) of the analytes under study. Increasing the agitation speed decreases thickness of the boundary layer which subsequently enhances the mass transfer of analytes to the polymeric coating. In addition, decreasing the diameter of the SPME device (one dimension ≤ 50 µm, support + coating), results in the increased extraction rate and mass transfer due to radial diffusion. Equation 1 demonstrates that the initial extraction rate (dn/dt) is proportional to the geometric surface area of the coating for a given analyte sample, irrespective of the chemical or physical properties of the coating. Furthermore, based on the assumption of boundary layer controlled extraction, equilibration time can be estimated from eq. 2:

$$t_{eq} \approx t_{95\%} = \frac{3\ {}_{s}K_{cs}(b-a)}{D_s} \qquad 2$$

where K_{cs} is a thermodynamic quantity describing the distribution of analytes between the coating and sample (also called K_{fs}, fiber/sample) and b-a is the coating thickness. Therefore, for a given SPME coating chemistry and analyte sample, equilibration time can be shortened by using a thinner coating and higher agitation rates.

The amount of analyte extracted at equilibrium (n^{eq}), can be described by eq. 3:

$$n^{eq} = \frac{K_{cs}V_cV_s}{K_{cs}V_c + V_s}C_s^0 \qquad 3$$

Where V_c and V_s are the volume of the coating (also V_f as fiber) and sample respectively, and C_s^0 is the analyte concentration in the sample matrix (K_{cs} V_c = fiber constant). If the sample volume is very large compared to the coating, especially for in vivo or on-site applications,[4] then $V_s >> K_{cs}$ V_c , and eq. 3 is written as:

$$n^{eq} = K_{cs}V_cC_s^0 \qquad 4$$

Equations 3 and 4 show that extraction efficiency in SPME techniques can therefore be enhanced via two different approaches, either by increasing K_{es}, or by increasing the volume of the coating, or total active surface area in the case of porous coatings.

Several strategies to improve the extraction rate without significant reduction of the extraction efficiency of SPME have been reported in the literature. Some researchers attempted to improve the extraction rate by incorporating multiple fibers with lower diameters [36] or through development of a nano/micro-porous structure of the coating [37]. Although these coatings provide better extraction efficiency, the initial extraction rate was not significantly improved due to the fact that the boundary layer controls the kinetics, as described by eq. 1. The distance between the narrow fibers or the open spaces porous structures is very small compared to the thickness of the boundary layer, which prevents them from significantly providing improved extraction rates. Recently, Mei et al. [38] prepared a novel SPME coating by joining four fibers consisted of a diameter of 500 µm each with a gap of 200 µm between each individual fiber. The overall extraction efficiency obtained for a device composed of multiple fibers of a smaller radius was higher than that of a single fiber of the equivalent area, exemplifying the importance of miniaturization of coating geometry. It should be noted that the multiple-fibers technique can only improve the extraction rate in cases where sample agitation is high enough so as to provide a boundary layer thickness of less than 100 µm. Helin et al.[7] introduced the SPME arrow, which contains a larger volume of sorbent compared to a standard SPME fiber, demonstrating its capacity to provide improved robustness and extraction efficiency.

Bruheim et al. [16] have shown that shorter equilibration times can be obtained by employing a coating substrate consisted of a thin film geometry instead of the original cylindrical geometry of the SPME fiber. Inspired by the TFME concept, a variety of thin film geometries have been developed [11,39]. While improving the extraction efficiency of the fiber needs a thick coating that results in the longer equilibrium time, TFME improves the sensitivity without sacrificing the time of analysis owing to the thin coating and the large surface area-to-volume ratio [16,40,41]. Extraction phase can be coated on the fabric support[27,39,42,43], stainless steel (so-called blade) [12,44] or even self-supported [16,43,45], and can be used for high throughput analysis (Figure 1f)[12,46]. Recently, a few other different geometric configurations, such as the hollow-fiber and nanoparticles used in SPME have been reviewed [47]. The fundamental principles applied in such techniques to increase extraction rate and efficiency are the same as described in this section.

Further, Piri-Moghadam et al. [6] introduced a miniaturized SPME fiber, also called coated-tip, for rapid extraction of the compounds from different matrices by showing the effect of the fiber radius on the uptake rate. In contrast to the above-mentioned geometries, the coated-tip format exploits a phenomenon called radial diffusion, which is observed only if the diameter of the probe is below a certain length, typically less than 50 µm. In this work, the conical shape tip (tip diameter about 20 µm, increased to 50 µm with the coating length of 500 µm) was noted to offer better stability and convenient handling, while preventing the device from bending during sampling. The short equilibration time (up to 2 minutes) of the tip-SPME devices comes from the very thin coating (<5 µm) as well as the radial diffusion of the analytes. For the tips, the transport of analytes can occur in both the linear (as expressed by the eq. 1) and radial directions; thus, providing fluxes both in the linear and the radial directions.

Our research group is currently evaluating effect of shape and size of the miniaturized SPME fiber using numerical models (Figure 2 shows some modeling results). Figure 2a shows the three different miniaturized fibers used for this study including i) SPME fiber (diameters of 5-30 µm and 1 mm length), ii) Tip-1 (top radius of 30 µm and the bottom radius was varied from 5-30 µm, 1 mm length) and iii) tip-2 (top radius of 15 µm and the bottom radius was varied from 5-15 µm, 0.5 mm length). As shown in the Figure 2b, by decreasing the SPME fiber radius from 30 µm to 5 µm, approximately 3 times improvement of the mass flux was observed. By keeping the top radius fixed and varying the bottom radius from 30 to 5 µm (Tip-1), increase of the flux was observed but not as high as the fiber. However, if only the narrowest part of the tip was coated with extraction phase, much higher flux can be obtained, for example for SPME Tip-2. In contrast to the increase of flux with decreasing the radius of the extraction device, as shown in Figure 2c, the extraction efficiency decreases about 115 % for the fiber and 25 % for the Tip-1, due to the decreased volume of the coating. For the Tip-2, the extraction efficiency is even lower due to the use of smaller length of the extraction device. It is worthwhile to mention that, it is technically challenging, from the practical point of view, to prepare and operate SPME fibers with such a narrow radius. If sensitivity is not an issue, decreasing the tip radius and using smaller length of the tip is a viable option to perform a fast sample analysis and when dealing with single cell analysis and in-vivo sampling from small organism. Table 1 shows specification of different geometries of SPME.

4- Major technologies for preparation of SPME coatings

An increasing number of materials have been prepared and used as extraction phases of SPME for a wide range of applications. However, in the current manuscript, only the most popular and widely used techniques employed for preparation of coating materials, including sol-gel technique, electrochemical, and electrospinning methods, are discussed. As a significant number of publications are related to the currently available commercial coatings, these materials are also presented. In addition, ILs and MOFs as well as interesting coatings prepared by dipping and spray coating methods were briefly mentioned.

4.1. Commercial coatings

There are several SPME fibers commercially available, including carboxen/polydimethylsiloxane (CAR/PDMS), polydimethylsiloxane/divinylbenzene (PDMS/DVB), divinylbenzene/carboxene/ polydimethylsiloxane (DVB/CAR/PDMS), polydimethylsiloxane (PDMS), polyacrylate (PA), Carbowax-polyethyleneglycol (PEG), carbowax/template resin (CW/TPR), and the SPME-overcoated fiber (using PDMS protection layer), as well as PDMS and PDMS/DVB on carbon fabric thin films that have been used for a wide range of applications owing to their different polarities and properties.

4.1.1. Advantages of commercial coatings

4.1.1.1. Inter-laboratory validation, standard and official methods

One of the main advantages of commercially available fibers is that such fibers are submitted to an inter-laboratory validations and evaluation process comprised of standard and official methods, which provide comprehensive information regarding their sensitivity, accuracy, and repeatability. Consequently, the selection of such fibers is simplified according to the available data. For instance, Rodriguez-Lafuente et al. [48] validated SPME method according to the strict standard operation procedures of an accredited commercial analytical laboratory, where the PDMS/DVB fiber was used for the determination of 25 pesticides in surface and ground water samples. An extensive study between SPME and LLE was performed from several analytical aspects, including sensitivity, accuracy, repeatability, and greenness. The goal of the aforementioned study was to demonstrate that the SPME method might be adopted as a standard protocol by commercial analytical testing laboratories. The results proved that the SPME method, which utilizes the commercial PDMS/DVB fiber, has similar accuracy to the LLE method (US EPA 8270 method), while providing several other advantages. In another study, DVB/CAR/PDMS fiber was validated for determination of VOCs in water samples [49]. Inter-laboratory validation was conducted in surface water and municipal wastewater samples for determination of 61 compounds, and included 42 participants from 16 countries (*i.e.* Austria, Brazil, Canada, Croatia, France, Germany, Great Britain, Italy, Portugal, Romania, Serbia, South Africa, Spain, Sweden, Switzerland, and United States). The obtained results showed good agreement between laboratories based on recovery rates, with repeatability less than 10 %, and reproducibility less than 35 %. The PDMS fiber was also validated for determination of organochlorine, organonitrogen, and organophosphate pesticides in water samples by 11 participating laboratories from Europe and North America [50]. Validation of the

Carbowax/DVB fiber was reported by 10 participating laboratories for determination of triazine herbicides and their metabolites in aqueous samples [51]. The described inter-laboratory validation efforts have served to demonstrate that commercial SPME fibers are reliable, accurate, and reproducible to be used for determination of target compounds in environmental samples.

The currently available US environmental protection agency (EPA), American Society for Testing and Materials (ASTM), and international standardisation organisation (ISO) standards of SPME are based on commercial fibers. For instance, the EPA method 8272 (2007), entitled “parent and alkyl polycyclic aromatics in sediment pore water by solid-phase microextraction and gas chromatography/mass spectrometry in selected ion monitoring mode”, is based on the commercial PDMS fiber [52]. This method is beneficial for the determination of dissolved PAHs in interstitial water or pore water in sediment samples.

The ASTM D 6520 (2000) is a standard practice for determination of semi-volatile organic compounds (semi-VOCs) and VOCs in water samples [53]. In this standard, a commercial SPME fiber is used for both direct and headspace water sampling coupled to GC and GC/MS determination. The aforementioned standard practice can be used for a wide range of compounds including VOCs, organochlorine and organophosphorous pesticides, PAHs, PCBs, phenols, nitrophenols, and amines. ASTM 6889 (2003) is also another standard practice for analysis of water samples for VOCs based on commercial SPME fibers [54]. Although the majority of the validation processes of SPME, in terms of inter-laboratory studies and official methods, have been conducted in water samples, standard methods of SPME are not limited to environmental samples. For instance, ASTM E 2154 (2001) is a standard practice for separation and concentration of ignitable liquid residues from fire debris [55]. In this standard, the procedure for removing small quantities of ignitable liquid residues from samples of fire debris by headspace sampling is presented. As well, ASTM D 6438 (2005) [56] is a practice for analysis of paints and coating for acetone, methyl acetate, and parachlorobenzotriflouride by headspace sampling SPME-GC based on commercial fibers. It has been evaluated for cellulose nitrate, acrylic, and urethane solvent-borne systems. It should be noted that with minor modifications, this standard method can also be used for analysis of the same analytes in water-borne coatings.

There are two ISO of SPME, including ISO 27108[57], and ISO 17943 [49]. As previously discussed, inter-laboratory validation of SPME was accomplished by 42 participants from 16 countries for determination of VOCs in water samples by the commercially available DVB-CAR-PDMS fiber. This inter-laboratory trial has resulted in the upcoming release of the new ISO 17943, currently under development. This ISO is based on DIN 38407-F34 from Germany, which presents standard methods for the examination of water, wastewater, and sludge. ISO 27108 (2013) is also related to determination of plant treatment agents and biocide products in drinking, ground, and surface water samples by SPME-GC/MS. The presence of standard and official methods based on commercial fibers makes them popular and widely accepted as promising fibers to be used for industrial applications that involve routine analysis of samples.

4.1.1.2. Different geometries of commercial coatings

Available commercial SPME fibers were already mentioned in the section 4.1. Application of a the commercially available thin sheet cross-linked PDMS membrane with 25.4 µm thickness, was first reported in 2003 by Bruheim et al. [16] for analysis of semi-volatile analytes in direct and headspace modes.

To improve the sensitivity and stability of the PDMS thin film, some modifications were applied including preparation of particle-loaded thin films. However, some modified thin films are not commercially available at the moment (PDMS/DVB self-supported and glass wool fabric support membranes), although the method of preparation is somehow similar to the commercial fibers in terms of the reagents and catalysts used, with some modifications. Riazi-Kermani et al. [42] coated CAR/PDMS and PDMS/DVB on glass wool fabric by spin coating technique, which provides several advantages including fastness, low use of volume of fluid, and uniformity of the prepared membranes, while the thickness of the coating can be easily controlled by controlling the time and speed of the rotation. DVB particles were added to the diluted PDMS at the ratios similar to those of commercial fiber coatings (property of Supelco, Bellefonte, USA) followed by addition of the curing agent, deposition on the fabric mesh and spin coating. (more details regarding membrane preparation by spin coating can be found in the literature [42]). A comparison between the prepared thin film and a traditional fiber with the same coating material showed improvements in sensitivity over an order of magnitude when TFME was used.

Jiang et al. [45] developed a self-supported PDMS/DVB thin film using the bar coating method. The effects of amount of DVB particles in the membrane (particle ratio) and the size of the membrane on the extraction efficiency of the TFME were investigated. A comparison of the PDMS and the PDMS/DVB thin films demonstrated significant enhancement of sensitivity by PDMS/DVB, up to 2 orders of magnitudes for extraction of benzene. Apart from improving the sensitivity, an improvement in the resilience of the prepared thin film when the DVB particles were added was noted to occur as compared to the pure PDMS thin film. A PDMS/DVB-carbon mesh supported TFME thin film was also developed by Grandy et al. [27] to introduce a robust membrane capable of handling high flow rates and sample agitation. It was reported that employment of the high density PDMS provided by Supelco (Bellefonte, PA, U.S.A) resulted in a decrease in the noise of the prepared PDMS/DVB membrane when used in combination with GC/MS. The developed membrane was used for on-site TFME, followed by on-site determination by a hand-portable GC/toroidial ion trap mass spectrometry (TMS) instrument [27]. An inter-laboratory study of the PDMS/DVB self-supported and PDMS/DVB-carbon mesh supported thin films was conducted to validate the TFME technique in comparison to LLE [43]. Comparison of the results of a split blind analysis showed good agreement between LLE (US EPA 8270), and TFME, while lower detection limits, up to 2 orders of magnitude, were achieved when TFME was used. It is worth mentioning that the developed membrane is now commercially available.

4.1.1.3. Biocompatibility

Biological microsampling and in-vivo applications were facilitated by bioSPME as non-invasive probes owing to the utilisation of biocompatible materials. Polymers such as polypyrrole (PPy), derivatised cellulose, polysulfones, polyacrylonitrile (PAN), polyethylene glycol and polyamides are used to prepare biocompatible materials. Some of the polymers such as PAN has low extraction efficiency and therefore, particles such as C18 and HLB (hydrophilic-lipophilic balance) can be loaded in the PAN polymer to improve the sensitivity of the SPME device (PAN is used as binder and has to completely covers the particles) [58]. Biocompatible coatings are able to extract analytes in complex biological matrices (*i.e.* blood, urine, plasma) without co-extraction of proteins and macromolecules as interferences, having no side effects on the host when in-vivo sampling is performed. The biocompatible C18 fiber, the mixed mode C18 with benzenesulfonic acid (incorporated inside the polyacrylonitrile, PAN), and the 96-tip array are commercially available today, and have been used for several applications. Cudjoe et al. [59] applied bio-SPME, as a commercial biocompatible fiber, for in-vivo brain sampling owing to the minimal perturbation and invasiveness of the technique. The biocompatible mixed-mode probes

(C18 with benzenesulfonic acid, 45 mm thickness, and 4 mm long, Supelco Inc.) were used for brain sampling as a complementary in vivo sampling method to microdialysis. Bessonneau et al. [60] used biocompatible C18 fibers (45 µm thickness and 1 cm length) for analysis of human saliva metabolome. The bioSPME provided simultaneous extraction of metabolites, covering a wide range of polarity, and can be useful for monitoring of changes in metabolic pathways. Application of SPME biocompatible C18 fibers for in-vivo SPME was also demonstrated by Bessonneau et al. [61] for monitoring of blood eicosanoids time profiles after lipopolysaccharide-induced inflammation in Sprague-Dawley rats, followed by LC/MS/MS determination. In all of the studies, no matrix effect was reported when biocompatible fibers were used as the sampling device.

4.1.1.4. Wide range of applications

Since its introduction, there have been many applications of SPME in the environmental area [5,62] (particularly towards analysis of water samples), biofluids [63], food samples [64], and metabolomics [65] studies. There are several applications of the commercial SPME coatings for analysis of water samples which was mainly discussed in the section 4.1.1.1. Application of SPME for analysis of biological samples and in-vivo sampling as a powerful tool for analysis has been discussed in several publications [63,66,67]. The first prototype of a commercial biocompatible single use in-vivo SPME fiber was evaluated in 2011 by Vuckovic et al. [68]. Single use SPME probes with three different coatings, including octadecyl silica (C18), C16 with an embedded amide group, and cyanopropyl were used for in-vivo analysis of selected drugs as model compounds. The application of a commercial fiber (*i.e.* mixed mode, C18+benzenesulfonic acid) for in vivo SPME for metabolite profiling was also reported by

Vuckovic et al. [69]. In vivo SPME can be used as an ideal probe for monitoring of metabolites characterized by a fast turnover rate, and those prone to degradation. Metabolomics is yet another application of commercial SPME fibers, aiming for analysis of low molecular weight compounds. Such data can be used to complement data obtained through proteomics, genomics, and transcriptomics, and can provide better insights into the dynamic processes of the living system. The suitability of the SPME technique as a powerful tool for metabolomics has been discussed in well-documented reviews [65,70]. Commercial SPME fibers have been widely used for metabolomics studies coupled to GC/MS [71] and LC-MS/MS [60,69,70] instrumentation.

Application of SPME fibers for food analysis poses critical challenges, as irreversible fiber fouling damage can be incurred when fibers are in direct contact with the matrix [64]. To overcome the aforementioned drawback, Souza Silva et al. [3] developed a new SPME fiber by overcoating a layer of PDMS onto the commercial PDMS/DVB fiber for determination of triazole pesticides in grape pulp. The results showed that the overcoated fiber can be reused up to 90 times for all studied compounds. A methodical evaluation and further improvement of the PDMS overcoated fiber for direct immersion sampling is also discussed by Souza Silva et al. [72]. Application of the overcoated PDMS/DVB fiber as a matrix-compatible probe for food analysis, including grape and strawberry [73], plant tissue [71], and raw blended vegetable [74], demonstrated the robustness of the newly developed fiber for direct analysis of complex matrices with no/minimum sample preparation. However, in the aforementioned applications, traditional commercial SPME fibers were purchased then overcoated in-lab, although an overcoated PDMS/DVB fiber is currently commercially available [75]. Figure 3 shows applications of the commercial fibers for in-vivo sampling (a), food analysis (b), and saliva metabolome (c).

4.1.2. Limitations of commercial coatings

The main drawback associated with the currently available commercial fibers is related to their low recommended operating temperatures (generally in the range 240-280 ºC). Although some fibers such as PDMS and carboxen/PDMS are thermally stable (*i.e.* up to 340 °C for PDMS, depending on the thickness of the coating, and 320°C for carboxen/PDMS), but the PDMS/DVB fiber is limited to 270 °C, and the maximum temperature of the PEG fiber is 250 ºC. While longer desorption times (at lower temperatures) can be used to improve the desorption of analytes, there would still be carryover of some non-volatile compounds. Non-selectivity is another issue of the commercial coating; although the mixed-mode and particle-loaded coatings have a high sensitivity for extraction of a wide range of compounds, they do not have selectivity to a specific class of compounds unlike, the molecularly imprinted polymers (MIPs).

4-2- Sol-gel technique

The sol-gel technique is an inorganic polymerization that is compatible with all molecular chemistries, facilitating inclusion of other materials to prepare nanocomposites and nanomaterials. In addition, this technique allows for the shaping of the material processed during the viscous sol stage so as to prepare the desired shape of the final product. Owing to their excellent optical quality, mechanical resistance, thermal and chemical stability, sol–gel silica derived films have been extensively used in several applications [76–85]. Figure 4 shows different steps, routes, and products of the sol-gel technology.

Application of the sol-gel technique for preparation of SPME fibers was first developed by Malik's research group [86] to prepare thermal and chemical stable coatings. Methyltrimethoxysilane (MTMOS) was selected as a precursor, and hydrolysis was performed in the presence of water in acidic condition and by addition of TFA, while employing PDMS as the polymeric coating. The coating was prepared by dipping the activated fused silica into the prepared sol. The sol-gel based PDMS fiber (coating thickness of about 10 µm) was used for extraction of a wide range of compounds including PAHs, alkanes, aniline derivatives, alcohols, and phenolic compounds in aqueous solutions, followed by GC analysis. The results showed that the prepared PDMS coating was thermally stable at a much higher temperature (*i.e.* > 320 ºC) than commercial SPME fibers, with good repeatability and efficiency. The sol-gel technique has gained increasing popularity for preparation of coating materials of SPME, with a large number of publications regarding preparation of the SPME coating by sol-gel technique showing the popularity and versatility of this technique. There are some reviews that specifically discuss the sol-gel technique in SPME [22,87]. Sol-gel materials have been used for biomedical applications [88], however their biocompatibility and matrix effect as SPME coatings have not been investigated yet.

4.2.1. Advantages of sol-gel technique

4.2.1.1. Thermal, chemical and physical stability

One of the main advantages of sol-gel derived materials is their high thermal, chemical, and physical stability, owing to the rigidity of the silica-based materials that is resulted from the high degree of cross-linking in their network. As previously discussed, the high thermal stability of the sol-gel based SPME fiber made it feasible for such fibers to be used at the high temperatures of GC injectors (*i.e.* over 300 ºC) [86]. Yu et al. [89] reported that the sol-gel derived SPME fiber is able to withstand high temperatures up to 360 ºC. MTMOS was selected as precursor, polymerization was performed in the presence of OH-TSO (silicon oil), water and TFA (catalyst), while hydroxyfullerene (fullerol) was also added to the sol solution to modify the coating. The prepared fiber was used for extraction of polychlorinated biphenyls (PCBs), PAHs, and polar aromatic amines in water samples, followed by GC-ECD and GC-FID determination. The results showed no decreases in the extraction efficiency of the studied compounds after conditioning the fiber at 280, 300, 310, 320, 330, 340, 350, and 360 ºC for 1h, owing to the nature of fullerene and silica, and the strong chemical binding and crosslinking provided by the sol-gel technique. The thermal stability and long lifetime of sol-gel derived SPME fibers have been widely reported in the literature [22,85,90–92].

Aiming to develop pH resistant sol-gel based coatings, Malik's research group reported the development of new SPME fibers using zirconia [93], titania [94] and germania [95,96] precursors as pH resistant extraction media. Transition metal oxides (*e.g.* zirconia, titania and germania) are well-known for pH stability, and have been used as an ideal alternative to silica precursors when highly pH resistant coatings are required. In all studies, the prepared coatings (*i.e.* fiber and in-tube) were exposed to extremely acidic and basic conditions for long periods, with no reported decreases in extraction efficiencies.

4.2.1.2. Different SPME geometries obtained by sol-gel technique

Due to its extraordinarily mild conditions, sol-gel technique can be used to design the shape of the material being fabricated (fiber, thin film, in-tube, and magnetic nanoparticles) during the viscous sol phase. The first application of the sol-gel technique for in-tube SPME, also called capillary microextraction (CME), was reported by Bigham et al. in 2002 [97]. Two coatings, including PDMS and PEG, were prepared and applied for determination of a wide range of polar and non-polar compounds using GC instrumentation. After extraction, compounds were transferred to the GC column through thermal desorption. A home-made interface that included a two-way press-fit fused silica was used for easy connection of the developed CME device, to the inlet end of the GC column.

Bagheri et al. [98,99] reported the development of an unbreakable in-tube SPME for on-line coupling to HPLC as an automated device for extraction of some selected PAHs in water samples. The main goal was replacing the fragile fused silica with a copper metal tube to be used as a robust and physically stable device. A solution of 3-(mercaptopropyl)trimethoxysilane, 3MPTMOS was selected for the formation of self-monolayers as an efficient way to functionalize the inner surface of the copper tube for further chemical bonding between the coating and the copper tube support. The sol-gel based in-tube device was assembled as the HPLC injection loop for on-line extraction and determination of the selected compounds. The applications of the sol-gel technique was further expanded to other metal tubes by functionalizing the inner walls of any given metal tube using diazonium salts [100].

Thin film is another geometrical configuration of SPME provided by the sol-gel technique. First reported by Kumar et al. in 2014 [39] for determination of some selected estrogens by HPLC-FLD, the technique was named fabric phase sorptive extraction (FPSE). Cellulose fabric was selected as the substrate due to its biodegradability and porosity. Poly-THF was coated on the cellulose by sol-gel technique using MTMOS as precursor [39]. The developed thin film integrates the advantages of sol-gel derived films, and a flexible and permeable fabric substrate.

Application of the sol-gel technique to prepare the thin films was also reported for determination of emerging contaminants in environmental water [101], analysis of water samples for alkyl phenols [102], determination of non-steroidal anti-inflammatory drugs in water samples [103], and analysis of sewage samples for benzotriazole UV stabilizers [104].

As discussed in the introduction, suspended particles comprise one of the configurations of the SPME technique. However, suspended-particle SPME has yet to gain significant attention due to the requirement of some tedious steps to separate the particles from the sample, as well as the existence of more convenient configurations of SPME such as fiber, thin film, and in-tube. Magnetic nanoparticles [105] simplify the method of extraction and sample collection through the use of an external magnetic field. It should be noted that this technique is also called magnetic micro-solid phase extraction (M-μ-SPE) and M-SPE [106,107]. Magnetic particles can be modified by sol-gel technique to attach the desired functional group as organic/inorganic shell to the magnetic core to modify the properties of the MNPs (*i.e.* extraction efficiency, magnetic responsivity, biocompatibility) [15,108,109]. Chen et al. [108] reported application of the C18 magnetic bead, modified using the sol-gel technique, for determination of oligonucleotides by MALDI/MS instrumentation. Several applications of sol-gel modified MNPs have been reported to date, including selective removal of bovine hemoglobin from bovine blood [15], determination of fat-soluble vitamins in fruit juice-milk beverage [110], extraction of chlorobenzenes [111], surface MIPs for the selective extraction of dimetridazole [112] and non-steroidal anti-inflammatory drugs from human hair (reinforced in the hollow fiber) [113].

4.2.1.3. Tailoring the coating by incorporating the desired compounds

One of the main advantages of sol-gel technology is its capability to incorporate the desired material into the final product. Several materials were incorporated into the polymer network by sol-gel technique to tune the properties of the coating materials including crown ether (Figure 5a) [114], carbon nanotubes (Figure 5b) [115,116], graphene [117,118], ILs (Figure 5c) [119,120], and MNPs (Figure 5d) [15].

Nanomaterials

Carbon nanotubes (CNTs) and graphene have been incorporated into the silica network to modify the properties of coatings by integrating the properties of sol-gel (*i.e.* rigidity and high thermal stability) and nanomaterials (*i.e.* high surface area). CNTs was first found in 1991 by Iijima [121], have found applications in several areas [122,123]. Preparation of sol-gel fiber by incorporation of SWCNTs was first reported in 2009 by Zhang et al for determination of polybrominated diphenyl ethers (PBDEs) in water samples by GC-ECD. [115]. To prepare sol-gel based CNT coating, SWCNT was first functionalized (-COOH) to assure the chemical binding between SWCNT and the silica network (e.g. TEOS as precursor, and TSO-OH) during the sol-gel process. To investigate the effect of CNTs on the extraction efficiency of the fiber, a comparison between the PEG sol-gel derived fiber and PEG/MWCNTs was performed by Sarafraz et al. for analysis of BTEX [91] and MTBE [92] in water samples. Although it was predicted that addition of CNTs in the polymeric coatings would significantly improve sensitivity, only about 3-fold increase in extraction efficiencies observed. The aggregation of

CNTs in sol would appear to be one of the limitations of this technique, which reduces the surface area of the CNTs.

Graphene is another allotrope of carbon in a two-dimensional format that has been experimentally produced in 2004 [124]. Incorporating graphene in the silica network by sol-gel technique as a SPME fiber was first reported by Zhang et al. [117] in 2011 for determination of PBDEs in environmental samples by GC/MS. The extraction efficiency of the developed fiber was evaluated by comparison with commercial fibers (*i.e.* 100 µm and 7 µm PDMS and PA). The results showed that the sol-gel graphene fiber is up to 7 times more efficient than commercial fibers for the selected compounds. A comparison of three SPME fibers, including pure sol-gel (55 µm), graphene (35 µm), and graphene sol-gel (50 µm), was reported [125] for extraction of 7 organophosphorous compounds from water samples. Results showed a 2-4 fold increase in the extraction efficiency of the graphene sol-gel compared to the pure sol-gel. Comparison of PEG and graphene-PEG fibers, based on the sol-gel technique, also showed a 2 fold improvement in extraction efficiency when graphene was added to the fiber [118,126] for determination of VOCs and organophosphate ester flame retardants in water samples. However, it would appear that a similar issue as that observed for CNTs regarding aggregation and a decrease in surface area also occurs in graphene sol-gel base fibers. Considering the cost of preparation of CNTs and graphene, the tediousness and the time-consuming processes involved in their functionalization, an improvement in the extraction efficiency of only 2-4 times in comparison to pure sol-gel is unlikely to generate further interest in the use of these materials for SPME coatings. Applications of nanomaterials in sample preparation are available in the literature [127–129].

Ionics liquids

The first application of ILs as an SPME coating was reported in 2005 by Liu et al. [119] as a disposable fiber for extraction of BTEX from paint samples followed by GC-FID. ILs were first used in the sol-gel technique only as co-solvents and porogens to improve porosity of the coating, in 2009 [130]. Addition of trihexyltetradecylphosphonium tetrafluoroborate (TTPT) decreased the gelation time due to the increased viscosity of the sol. Considering that the thermal decomposition temperature of TTPT is 190 ºC, it is assumed that no ILs remained in the final coating, as the sol-gel fiber was conditioned at 300 ºC. Therefore, the noted improvement in the extraction efficiency of the fiber prepared in the presence of ILs, of 3-5 times, can be attributed to the increased porosity of the coating. The bonding of ILs to the silica network through use of the sol-gel process has since then been developed [120,131,132]. The chemical bond between the allyl-functionalized ILs to the evolving sol-gel network was achieved by free-radical cross linking under UV, with benzophenone as the initiator [131]. The IL-sol-gel derived fiber showed a higher extraction efficiency, up to 3 times, than that of the pure sol-gel fiber for the studied compounds [120,132].

Selective coating

Preparation of selective coatings by sol-gel technique can be achieved by several methods, including addition of some materials (e.g. crown ethers) to the coating to increase its selectivity toward some compounds, or preparation of molecularly imprinted polymers/xerogels (MIPs). Incorporation of crown ethers in the silica network during the sol-gel process was reported in 2001 by Zeng et al. [133] for determination of selected phenolic compounds by preparation of a hydroxydibenzo-14-crown-4 (OH-DB14C4)/hydroxy-terminated silicone oil (OH-TSO) fiber. Preparation of three other sol-gel based SPME fibers [134], containing hydroxydibenzo-14-

crown-4 (OH-DB14C4), dihydroxy-substituted saturated urushiol crown ether (DHSU14C4), and 3,5-dibutyl-unsymmetry-dibenzo-14-crown-4-dihydroxy crown ether (DBUD14C4), were also reported. The obtained results showed selectivity of the hydroxy-dibenzo-14-crown-4-coated sol-gel based fiber. Applications of crown ether sol-gel derived fibers have been reported in several studies [114,135–139].

Molecularly imprinted polymers (MIPs) have been widely used for preparation of selective coatings by imprinting the target compound into the polymer network [140]. Preparation of MIPs by sol-gel technique was first reported in 2009 by Li et al. [141] for the determination of polybrominated diphenyl ethers in water samples. Phenyltrimethoxysilane and TEOS were used as precursors, ethanol as solvent, and Decabromodiphenyl ether (BDE-209) as the template molecule. A comparison between results obtained for the MIPs and control fibers showed an improvement in the extraction efficiency for the MIPs fiber, demonstrating its increased selectivity towards the imprinted molecule. In addition to BDE-209, the template molecule, the prepared fiber showed good affinity to other smaller BDE congeners [141]. Bagheri et al. [142] developed molecularly imprinted xerogel (MIX) using 3-(trimethoxysilyl)propylmethacrylate (TMSPMA) as a precursor due to the presence of a methacrylate group, which can effectively interact with the template molecule. Non-imprinted xerogel (NIX) was also prepared as the control coating. MIX and NIX were coated inside the copper tube, and used as a CME device in on-line coupling to HPLC. The obtained results showed a significant improvement in extraction efficiency when MIX was used for extraction of atrazine in comparison to NIX. Application of MIX for extraction of fentanyl from urine samples was also reported [143]. To decrease the gelation time, aniline was added to the sol solution while polyaniline was electrochemically entrapped inside the copper tube, resulting in a significant decrease in gelation time to few hours [144]. To evaluate the efficiency of the prepared MIX, three control CME devices, including

NIX, PAN and pure sol-gel, were prepared and applied towards extraction of selected compounds, with the obtained results confirming the higher affinity of the MIX to naproxen, the template compound.

4.2.2. Limitations of the sol-gel technique

Although sol-gel derived materials are robust and well-known as thermally stable materials, their extraction efficiencies have not been fully investigated in comparison to several commercial fibers for a wide range of compounds from several analytical aspects. While a significant number of publications of sol-gel based SPME coatings exist in the literature, such coatings have yet to be fully validated, unlike official methods, with the available publications mainly focused on the development of new materials through the incorporation of various materials. In addition, no inter-laboratory validation studies of these materials have been conducted. It would seem a huge gap currently exists between method development of sol-gel based coatings and industrially-oriented validation as they have not been commercialized as SPME coatings, yet.

4-3- Electrochemical technique

The electrochemical method is a well-know and convenient approach to prepare coatings with the desired thickness by controlling the voltage, electrodeposition time, and concentration of the electrolyte and monomers. The application of the electrochemical method to the preparation of an SPME fiber was reported by Djozan et al. in 2001 [145] by oxidation of the metal wire. Aluminum wire was anodized by a direct current in a solution of H_2SO_4, and was used for extraction of some selected aliphatic alcohols, BTEX, and petroleum products from gaseous samples. Application of anodized zinc wire [146], aluminum tube [147], and modified pencil lead [148] as the SPME fiber and in-tube device were also reported. Improvements to the extraction efficiency of the SPME fibers prepared by the electrochemical technique have been made by employing conductive polymers as polymeric coating. CPs are the recent generation of polymers to be employed in this function, opening the way towards a better understanding of the fundamental chemistry and physics of p-bonded macromolecules [149,150]. These interesting materials have found lots of applications in different fields, including in analytical chemistry, considering that they can be employed as extracting media. These polymers interact with analytes through hydrogen bonding and π-π stacking. Polyaniline (PANI), PPy, polythiophene (PT), polyacetylene (PA), poly(p-phenylene) (PPV), and poly(p-phenylene vinylene) (PPV) are some of the conductive polymers that have been widely used as extraction media [151]. Conductive polymers are synthesized either by chemical method via addition of oxidant, or by electrochemical method and application of voltage in the electrochemical cell. Although there are several publications regarding preparation of CPs by chemical methods [152–155], the current review only focuses on the electrochemical preparation of coatings. The first application of a conductive polymer as an SPME fiber was reported in 1999 by Gbatu [156] for extraction of arsenate ions from an aqueous solution. 3-methylthiophene (3-MT) was selected as a monomer in H_2SO_4, and a tetrabutylammonium tetrafluoroborate (TBATFB) electrolyte solution on a platinum electrode was used to prepare the poly(3-methylthiophene) SPME fiber. More detail regarding preparation of conductive polymers as coatings in SPME, using both chemical and electrochemical synthesis, can be found in the literature [151].

4.3.1. Advantages of electrochemical methods

4.3.1.1. Preparation of the desired thickness in a rapid and cost effective procedure

Rapid preparation of the coatings (*e.g.* few seconds to minutes) with the desired thickness is one of the main strength of electrochemical method as no chemical oxidant or catalyst is used, and the coating electrodeposition is performed by applying the voltage provided by the power supply [6]. Cost-effectiveness is another advantage of this coating preparation method, since only a small volume of monomer and counter ions in the mM range of concentration are needed. In addition, the technique does not require any post-treatment, including initiating the catalytic reaction at high temperature or long time of conditioning at high temperature.

4.3.1.2. Different SPME geometries by electrochemical method

As previously discussed, the first application of a conductive polymer as SPME fiber was reported in 1999 by Gbatu [156]. Following, Wu et al. in 2000 [157] reported electrochemical preparation of a PPy SPME fiber for extraction of anionic species from aquatic media without any derivatization. The metal wires (*e.g.* platinum, gold or stainless steel) were used as substrate and working electrode, while platinum wire was used as the counter electrode, with an Ag/AgCl reference electrode in the three-electrode electrochemical cell. PPy was electrochemically coated on the wires from a 0.1 M tetrabutylammonium perchlorate-acetonitrile solution containing 0.1 M pyrrole monomer, using a constant potential of 1.0 V and employing a potentiostat. The developed method was used for extraction of anionic ions such as fluoride, chloride, bromide, nitrate, phosphate, and sulfate, and was followed by ion chromatography. In other studies, PPy and poly-N-phenylpyrrole (PPPY) SPME fibers were prepared and used for extraction of VOCs and ionic analytes [158]. The role of different counter ions in the preparation of PPy SPME fibers was also investigated by Wu et al. [159,160]. PPy was electrochemically deposited on the platinum wire, with application of several counter ions, including PPY-Cl (NaCl as the electrolyte during polymerization and Cl^- as the counter ion), PPY-ClO_4 ($LiClO_4$ as the electrolyte and ClO_4^- as the counter ion), PPY-TS (sodium p-toluenesulphonate, NaTS, as the electrolyte and TS^- as the counter ion), PPY-DS (sodium dodecylsulphate ,SDS, as the electrolyte and DS^- as the counter ion), and PPY-PSS (poly sodium 4-styrenesulfonate, PSS, as the electrolyte and PSS^- as the counter ion). The nature and size of the counter ions were reported to have a significant effect on the properties of the coatings. PPy with small anions as counter ions (*i.e.* ClO_4^-) were observed to demonstrate anion exchange properties, while use of large counter ions (*i.e.* PSS^-) resulted in cation exchange, since an increase in the size of the counter ion resulting in a corresponding decrease in the mobility of the counter anion [160]. In addition, the physical properties of the coatings, such as morphology, porosity, thermal stability, and mechanical properties, were noted to also be influenced by counter ions. SEM images in Figure 6 show different morphologies of PPy attained with the use of different counter ions and surfactants, corroborate the observed phenomenon. A comparison of the extraction efficiency of the prepared PPy fibers and a commercial PDMS fiber showed that PPy fibers have better extraction efficiency for polar compounds due to hydrogen bonding and the presence of polar functional groups in PPy fibers [160]. Among the prepared PPy fibers, differences in their extraction efficiencies for the studied compounds were also observed. PPy-DS showed better efficiency toward less polar compounds, as addition of DS increases the hydrophobicity of the coating. The thermal stability of the PPy coating is about 200 ºC, which limits GC applications of the fiber to volatile compounds. Some counter ions (mainly surfactant) can significantly increase the thermal stability of the PPy coating. Mohammadi et al. [161] investigated the thermal stability of the PPy-DS SPME fiber for determination of PAHs in water samples. The obtained results demonstrated that the addition of SDS as counter ion to the PPy fiber increased the thermal stability of the fiber up to 300 ºC. The addition of sodium polyphosphate, as electrolyte and counter ion, was also shown to increase the thermal stability of the PPy fiber [162,163]. Preparation of PANI as a new SPME fiber was reported by Bagheri et al. [164] in 2005 for extraction of selected phenols from water samples. PANI was electropolymerized on the platinum wire, and H_2SO_4 was used as electrolyte and counter ion. The obtained results showed good extraction efficiency (low ppb level of detection by GC-FID) and repeatability for the PANI SPME fiber. The presence of a polar functional group, hydrogen binding, and π-π interactions designate PANI as a suitable coating for extraction of polar compounds.

Provided the ability to control the thickness of the coating by some parameters such as electrodeposition time, concentrations of monomer and counter ions, and the applied voltage, Piri-Moghadam et al. [6] recently developed a new geometrical configuration of SPME, namely miniaturized SPME fiber (coated-tip), for extraction of small volumes of samples (*i.e.* ≤ 10 µL) and single cells. To prepare the miniaturized fiber, a medical grade stainless steel (SS) acupuncture needle with a diameter of 120 μm was selected as the substrate. Then, the SS needle, as the anode, was electrochemically etched to the tip with a diameter of 10-30 μm in a conical geometry. Then, a thin layer of PPy (*i.e.* 5 µm), as the biocompatible material, was electrochemically deposited on the etched substrate. Several PPy SPME fibers were prepared by different counter ions including $HClO_4$, HCl, TFA, H_3PO_4, HNO_3, and H_2SO_4 to prepare a robust fiber. In order to improve the stability and porosity and therefore extraction efficiency of the PPy coating, cationic and anionic surfactants such as SDS and cetyltrimethylammonium bromide (CTAB) were used as counter ions in the presence of TFA. The results showed that addition of SDS and CTAB resulted in the enhanced physical stability and sensitivity of the coated-tip. PPy prepared in the presence of CTAB showed the highest extraction efficiency owing to the nano-structured networks. The biocompatibility of the developed fiber was also evaluated in blood and urine samples, with no matrix effects observed. The developed coated-tip was used for analysis of 1-10 µL of whole blood, plasma, and urine sample, coupled with LC/MS/MS, and directly coupling to MS via nano-ESI emitters. In addition, the PPy coated-tip was applied to single cells of Allium cepa L, owing to the small dimension of the tip, for target analysis of quercetin and luteolin flavonoids, as seen in Figure 1b. The obtained results showed good efficiency of the developed device, with low ppb levels of detection and significant stability.

In-tube SPME is yet another geometry that can be developed with the use of electrochemical techniques. The Djozan et al. reported by oxidation of the aluminum tube to prepare a thin layer of Al_2O_3 as the coating of in-tube SPME device [147]. Electrochemical deposition of PPy inside the needle was reported by Bagheri et al. [165] in 2009. However, the developed device was called "inside needle capillary adsorption trap" (INCAT), but due to its similarities with in-tube SPME, it can also be used as an in-tube SPME device. A thin layer of PPy-DS, with a thickness of 18 µm, was electrodeposited and used for headspace extraction of some selected PAHs from water samples. Electrochemical deposition of a conductive polymer inside a tube, to be used as on-line in-tube SPME coupled to HPLC, was also reported [144]. PANI was coated inside the copper tube and used as a control device to be compared to MIX, NIX, and pure sol-gel for evaluation of the selectivity of the prepared MIX (previously discussed in sol-gel section) for extraction of naproxen from urine samples. Incorporation of the PANI was also shown to result in a significant decrease in gelation time. Preparation of a PANI-PPy composite inside stainless steel tube was also reported [166] for on-line in-tube SPME-HPLC for determination of parabens in water, milk, and juice samples. Recently, Piri-Moghadam et al. [10] also reported a biocompatible in-tube SPME device for rapid analysis of single drops (*i.e.* 2 µL) of untreated complex matrices, including urine and whole blood samples, by coating a thin layer of PPy inside a medical grade spinal needle, and coupling to different instrumentations including LC-MS/MS and direct coupling to mass spectrometry.

Although conductive polymers can be electrodeposited on any conductive surface, their application as a membrane and stir bar has not been fully investigated to date.

4.3.1.3. Incorporating the desired materials

To improve the properties of conductive polymers, including extraction efficiency and stability, the desired materials can be incorporated in the coating. The incorporation of modifiers has not been fully investigated to date, with only a few applications, including addition of nanoparticles and MWCNTs, available in the literature. An aniline-silica nanocomposite was electrodeposited on a stainless steel wire as an unbreakable SPME fiber [167], with the addition of nanoparticles showing improved thermal and physical fiber stability. The developed PANI-nanosilica fiber was used for extraction of PAHs, with the obtained results demonstrating the enhanced sensitivity of the prepared fiber in comparison to the PANI fiber. Other reported composites include the incorporation of MWCNTs in PPy [168], MOFs-PANI nanocomposite and CP-IL based coatings [169–172] to improve the sensitivity of the coating [173].

4.3.2. Limitations of electrochemical methods

As the electrochemical technique, cannot be applied as a general technique to prepare any coating, the availability of few polymers that can be used to prepare coatings by the electrochemical method is the limitation of this technique. However, it was reported that conductive polymers have good extraction efficiency, and their properties, such as hydrophobicity and porosity, can be modified by selection of suitable counter ions and surfactants, although their extraction efficiencies have yet to be fully validated and compared to available commercial fibers.

4-4- Electrospinning method

Electrospinning is the innovative technique to prepare nanofibers via an electrically charged jet of the polymer solution. This technique is an electrostatic spraying (electrospray), and has been used in several areas such as mass spectrometry, paining, inkjet, printing, and production of particles of various sizes [174]. Formhals first patented a process for producing filaments using electrostatic force in 1934 [174,175] that employed spinning of cellulose acetate fiber, with acetone used as solvent. A study of the jet produced from droplets of the solution was performed by Taylor in 1960's (so-called taylor cone). This technique has been widely known as electrostatic spinning until 1993, with few applications regarding preparation of nanofibers found in the literature until then. In the 1990s, various research groups (notably Reneker and co-workers) investigated the preparation of nanofibers from a wide range of organic polymers by employment of this technique, with the first use of the term of electrospinning [176]. More detail regarding the electrospinning technique and its history, from 1600-1995, can be found in the literature [174,175].

As shown in Figure 7-a,b, the fabrication of nanofibers via electrospinning requires a spinneret with a metallic needle, a high voltage power supply, and a grounded collector. The desired polymer/composite solution is loaded into an electrically charged syringe connected to a pump. A major step of the electrospinning technique is the selection of an appropriate solvent, as a suitable solvent is needed to evaporate quickly enough to maintain the integrity of the fibers, but not too quickly as to allow the fiber to harden before it reaches the nanometer range. The viscosity and surface tension of the solvent are also important factors to consider in the fabrication of the nanofibers; otherwise, the jet cannot be formed, or becomes too small to allow spraying of the polymer solution. In order to initiate spraying of the polymer solution, the viscosity and surface tension of the polymer need to be overcome, and an adequate power supply that maintains the jet constant must be present. Tip to collector distance (TCD) is another critical parameter, and should be large enough for the solvent to evaporate in time for the fibers to form on the collector.

The first application of the electrospinning technique to prepare an SPME fiber was reported by Zewe et al. [177] in 2010 for extraction of nonpolar and polar compounds (*i.e.* BTEX and selected phenols). A polymeric negative photoresist, SU-8 210, was selected as coating material and stainless steel was chosen as the substrate and collector for electrospinning. A negative photoresists consist of a base polymer and a photoreactive cross-linking agent, which is polymerized and cross-linked under exposure to UV light. To prepare the polymer solution, the SU-8 2100 was dissolved in cyclopentanone, and electrospinning performed by applying a voltage of 9 V for 30s while the tip-to-collector distance (TCD) was kept at 10 cm. The electrospun fiber was then pyrolyzed to convert the SU-8 polymer to carbon. The extraction efficiency of the prepared nanofibers was compared with commercial PDMS/DVB and PA fibers, with results showing a 2-10 times higher efficiency for the electrospun fiber for both non-polar (BTEX) and polar (phenol) compounds with the exception of o-xylene, demonstrating the high surface area of the nanofibers prepared by electrospinning method. Bagheri and co-workers also developed the electrospun SPME fibers in 2011 [178], and further improved the properties of the prepared nanofibers including sensitivity and stability [179–184].

4.4.1. Advantages of electrospinning method

4.4.1.1. High extraction efficiency

One of the main strengths of electrospun materials is the high surface area and aspect ratio (length-to-diameter of nanofibers), owing to the nano-fibrous network of the prepared materials (Figure 7c). As previously discussed, Zewe et al. [177] demonstrated that electrospun fibers were able to provide enhanced sensitivity compared to commercial PDMS/DVB, PDMS, and PA fibers for BTEX and selected chlorophenols. There are several publications related to application of electrospun SPME fibers/membranes that demonstrate their nano-fibrous structure and capacity resulted in low limits of detection.

4.4.1.2. Different electrospun-derived SPME geometries

As with other techniques, electrospinning can also provide fiber and membrane geometries, which can be accomplished by selection of different wires or sheets as collector, as seen in Figure 7 a,b. Bagheri et al. [178] developed four electrospun SPME fibers using polyurethane (PU), polycarbonate (PC), polyamide (PA), and polyvinyl chloride (PVC) polymers. Formic acid and DMF:THF (40:60) were selected as appropriate solvents for PA, and PVC, respectively. DMF was selected as a suitable solvent for dissolving PC and PU polymers (15 % w/v for all polymers). The nanofibers were coated on a stainless-steel wire under the following conditions: voltage of 16 kv, flow rate of 0.5 μL min^{-1}, and TCD of 10 cm. The reported SEM images showed the porous structure of the nanofibers, with diameters in the range of 150-600 nm. The electrospun SPME fibers were employed for extraction of selected cholorobenze compounds from water samples, with an LOQ of 50 ng L^{-1} reported for the PU fiber, demonstrating the high efficiency of the prepared sorbents owing to the large surface area of the nano-fibrous coating. Preparation of a thermal-resistant electrospun SPME fiber for extraction of PAHs from water samples was also reported with the use of polyetherimide (PEI) as the coating [180]. The obtained results confirmed the thermal stability of the fiber by evaluation of the thermal desorption of analytes at different temperatures, up to 290 ºC, with no observed decomposition of the fiber.

The electrospun-derived thin film was presented in 2011 [179]. A composite of polypyrrole-polyamide was prepared on aluminum foil, as the SPME substrate and the collector in the electrospinning system. Nylon 6 was first dissolved in formic acid, followed by addition of ferric chloride and a pyrrole monomer to the solution. To prepare electrospun thin film, an aluminum foil in a dimension of 10 × 10 cm was selected as collector with 10 cm of TCD. The prepared thin film was applied for extraction of malathion from water samples and the results shown high efficiency, ppt levels of detection, and good repeatability. There are several publications of the electrospun-derived sorbents that showcase their efficiency as extraction media [179,182,183,185–194].

4.4.1.3. Incorporating the desired material

Different materials including conductive polymers, magnetic nanocomposites, nanoparticles, and aptamers have been added to electrospinning polymers to tune the properties of the nanofibers. As discussed earlier, preparation of electrospun composites of conducive polymers such as PPy/PA [179] and PANI/nylon-6 [185] have been reported with aims to improve the extraction efficiency of the nanofibers, which benefit from the sorptive properties of the conductive polymers.

Addition of silica nanoparticles to PA polymers was also reported [195] for extraction of chlorobenzenes from water samples. The obtained results demonstrated up to 3-fold improvements in the extraction efficiency of the prepared fiber owing to the addition of nanosilica particles. Qiu et al. [196] developed sulfonated nanoparticles doped in a copolymer of Poly(lactic acid-co-caprolactone) as the biocompatible SPME fiber for in-vivo SPME of pharmaceuticals in fish and vegetables. The electrospun SPME fiber was prepared by dissolving the co-polymer and sulfonated γ-Al_2O_3 nanoparticles in hexafluoroisopropanol, and electrospinning the mixture by applying 10 kv, TCD of 12.5 cm, and a flow rate of 2 mL h^{-1}. The accuracy and sensitivity of the developed biocompatible SPME fiber was in a good agreement with results obtained by liquid extraction.

A magnetic polyurethane (PU) nanocomposite via electrospinning was developed for extraction of fluoxetine from aquatic and biological samples [197]. First, MNPs were synthesized by $FeCl_3.6H_2O$ and $FeCl_2.4H_2O$ in the acidic solution. Next, the MNPs were added to a solution of PU polymer, already dissolved in an appropriate solvent, and electrospinning was conducted at a voltage of 16 kv with a flow rate of 0.5 mL min^{-1} on an aluminum foil collector. The attained results demonstrated the sensitivity and repeatability of the prepared membrane for extraction of fluoxetine in comparison to a previously developed method [197]. Other interesting modifications, such as the incorporation of aptamers in the preparation of a selective coating [198], as well as the preparation of core-shell polybutylene terephthalate/polypyrrole coatings [181], demonstrate the versatility of the electrospinning technique as a promising approach for the design of a new generation of coatings.

4.4.2. Limitations of electrospun-based materials

The major limitation of electrospun SPME fibers is the thermal instability of the most of the prepared coatings. Moreover, the number of available polymers that can be prepared by electrospinning technique and be suitably used for SPME coatings is limited. Similar to the sol-gel and electrochemical techniques, to date, no inter-laboratory validation efforts and comparisons with commercial fibers for a wide range of polarities have been undertaken to fairly evaluate electrospun fibers and membranes. Electrospun SPME coatings have yet to be used for complex matrices, such as whole blood samples, without any treatment in order to evaluate their matrix effect and wide range applicability. In addition, electrospun fibers/thin films have yet to be fully evaluated against other available materials such as commercial fibers, sol-gel, and conductive polymers from several analytical aspects for a wide range of compounds.

4-5- Other coatings

There are some interesting materials including ILs, MOFs and particle loaded coatings that are not prepared according to the main techniques already discussed, but there is an increasing trend in their applications as SPME coatings, and therefore they are briefly discussed here.

4.5.1. Ionic liquids

ILs-based sol-gel coatings were already discussed in section 4.2.1.3, herein the ILs-based SPME coatings that are prepared by conventional methods are summarized. After the first application of ionic liquids as a disposable SPME fiber [119], several attempts have been done to prepare more robust coatings with longer lifetime to be used for several extractions. Anderson’ group in 2008 reported preparation of a stable polymeric ionic liquids (PILs) SPME coating for extraction of esters and fatty acid methyl esters from aqueous solution [199]. Three homologous polymeric imidazolium-based IL coatings were synthesized by radical polymerization in the presence of

AIBN. To prepare a SPME fiber, a fused silica support was dipped in a solution of PILs in acetone. The main strength of the new developed PILs is physical and thermal stability of the coating with 150 times extractions with no significant decrease in the performance with the RSD% of 14-18. On the other hand, long and time consuming process (several days) of coating preparation is the limitation of this technique. To improve the mechanical stability of the fiber, a fused silica support was replaced by super elastic nitinol (NiTi) wire followed by coating the crosslinked PIL, reported by Ho et. al [200]. To prepare stable coating, the nitinol was functionalized to have a chemical binding to the PIL. The NiTi wire was oxidized in a boiling (30% w/w) H_2O_2 solution and derivatized in vinyltrimethoxysilane (VTMS) to be fucntionalized with vinyl moieties. On-fiber co-polymerization of the vinyl-functionalized NiTi support with the IL monomers and dicationic IL crosslinkers was performed by UV exposure, resulted in a covalent binding of the PIL to the NiTi substrate. It was reported that the prepared bonded PIL on the nitinol wire was used for 70 extraction/desorption cycles while the unmodified coating was receded from the nitinol after one extraction [200]. ILs and PILs along with their mechanism of the extraction was discussed in the literature [201,202].

The extraction efficiency of the PILs can be improved by functionalization of the IL/PILs to have π- π interactions[203], and selection of appropriate counter anion [204]. Nacham et al. [205] presented an interesting application of PILs as SPME fiber for extraction of DNA from complex matrices. Eight different PILs were synthesized via on-fiber UV initiated polymerization using different monomers and crosslinkers (several anions and a variety of functional groups) and real-time PCR was used for evaluation of their performance in extraction of DNA from crude bacterial cell lysate. Investigation of the results showed that incorporation of benzyl moieties within the cross-linker decreased DNA extraction efficiency. On the other hand, incorporating polar functional groups into the cationic structure, such as a carboxylic acid or alcohol moieties enhanced the DNA extraction compared to the PIL sorbents lacking polar moieties. It was revealed that substitution of halide-based anions with NTf_2^- anions of similar cationic composition resulted in a significant decrease in DNA extraction performance. Therefore, electrostatic interactions and exchangeable anions have an important roles in DNA extraction (more detail can be found in [205]). Mousavi et. al [206] also reported preparation of Silica-based ionic liquid coating (silica-based 1-vinyl-3-octadecylimidazolium bromide) on blade for 96-blade system for high throughput extraction of amino acid as polar compounds, log p ranging from -1.06 to -4.2, owing to the several interactions including hydrophobic, π-π, electrostatic, hydrogen bonding and ion-dipole interactions. Modification of PILs with CNTs and graphene were also reported [170,207–210], however it seems similar problem associated with sol-gel based CNTs and graphene coatings regarding the aggregation of CNTs occurred with PIL-CNT base fiber, as well. Application of PILs for coupling to HPLC was also reported which will extend its application to non-volatile compounds [211,212].

4.5.2. Metal organic frameworks

MOFs are crystalline three-dimensional coordination polymers (metal ion and organic ligands) with unique properties including permanent porosity, high surface area known, uniform structured nanoscale cavities, uniform pore topologies, thermal stability ranging from 200 to 400 °C that make them suitable as the coating materials of SPME [213]. Owing to the crystalline structure of the MOFs, the molecules are ordered in such a way that the pores and cavities have the same diameter. The first application of MOFs as SPME coating was reported by Cui et al. in 2009 [214]. for preparation of the MOF-199 coating, $Cu(NO_3)_2{\cdot}3H_2O$ and 1,3,5-Benzenetri carboxylic acid (H3BTC) were dissolved in ultrapure water and ethanol, respectively and mixed in a Teflon liner. The stainless-steel support was then dipped into the solution in the Teflon liner followed by sealing the liner and autoclave at 120 °C for 8 h. The prepared SPME fiber was used for extraction of gaseous benzene homologues followed GC-FID analysis. The obtained results proved the high extraction efficiency of the MOF-100 by reporting the significantly high enrichment factors, 19613 for benzene to 110 860 for p-xylene, owing to the high surface area and porosity of MOF-100. Comparison of the MOF-100 based SPME fiber with the PDMS and PDMS/DVB commercial fibers was also proved the superior sensitivity of MOF-100. Several development of MOFs as SPME coating have been reported including covalent binding of MOFs UiO-66 to the SPME support via covalent bonding to amino functionalized support [215], covalent bonding of MOF-5/graphene oxide hybrid composite to stainless steel support [216], aluminum based MOFs-polymer monolith [217], thin film MOFs by cathodic electrodeposition [218], MOF/PANI nanocomposite [173], MOF-199/graphite oxide hybrid composites [219] and MOF-IL. More detail about MOFs as coating materials of SPME can be found in the literature [213].

4.5.3. Particle-loaded coatings prepared by spraying and dipping methods

Vuckovic et al. [220] reported preparation of 5-μm coated silica particles (C18 or C16-amide) fiber as the efficient coating for analysis of drug in complex matrices using thin layer of Locktite 349 glue and rolling the wire support in the particles. Cudjoe et al. [12] applied similar method of preparation on blade support by dipping the glue-coated metal surface into a vial containing C18 particles to form a thin film of coating that could be coupled to the 96-configuration as a high-throughput device. To facilitate the method of preparation, Mirnaghi et al. [44] developed a method of preparation of a C18-PAN 96-blade SPME, as biocompatible coating, using three different methods, including dipping, brush painting, and spraying. As it was already discussed, PAN is used as binder and glue (about 10% w/w PAN particles with DMF) to immobilize the desired particle on the support. The prepared blades using dipping, brush painting, and spraying methods were applied for extraction of the target compounds from PBS sample to evaluate the extraction efficiency and stability of the developed methods. The results showed that the blades prepared using spray coating have the highest absolute recoveries and stability in long-term use.

The particle loaded blades prepared by spray coating method were employed for extraction of wide range of compounds in complex matrices such as bio-fluids [221] and metabolomics [222–224], *in vivo* and *ex vivo* studies [225]. For instance, Mousavi et al. [222] applied spraying method for preparation different coating materials using variety of particles including C18, polystyrene-divinylbenzene-weak anion exchange (PS-DVBWAX), hydrophilic-lipophilic balance (HLB), phenylboronic acid (PBA), silica based-reversed phase-weak cation exchange (Si-RPWCX), surface modified styrene divinylbenzene with pyrrolidone group (StrataX), as well as the lab made silica based ionic liquid (Si-IL), and tris-amide functionalized porous silica (HILIC) particles for extraction of wide range of hydrophobic and hydrophilic cellular metabolites produced by Escherichia coli by the developed 96-blade SPME LC-MS method. Gionfriddo et al. [226] recently developed a new biocompatible coating based on polytetrafluoroethylene amorphous fluroplastics (PTFE AF 2400) as a binder, similar to PAN, to immobilized HLB particles by dipping the stainless steel support in the slurry of PTFE AF/HLB as the thermal and chemical stable coating for GC and LC applications. Table 2 and 3 presents different feature of the available coating materials and their applications in variety of sample matrices.

5. Future perspectives and concluding remarks

Current trends regarding employed coating materials in SPME were investigated by comparison of the main available coatings to date, including commercial, sol-gel, electrochemical, and electrospun derived materials. Commercial coatings have been used for a wide range of applications due to the availability of several fibers, ranging from polar to nonpolar, mixed mode, overcoated (protection layer), and biocompatible. Given the several worldwide evaluations of these commercial fibers, and the various validation efforts using official methods and standards, commercial fibers can be easily employed as reliable, accurate, and repeatable fibers for a variety of applications. In addition to commercially available coatings, different technologies have been used for preparation of new materials, mainly aimed at overcoming some of the drawbacks of commercial fibers, such as thermal instability. Sol-gel technology has been successfully applied to prepare thermally stable fibers. However, this technique still needs to be fully investigated through a validation process that adopts official methods, including the use of inter-laboratory studies, so that these robust fibers can be commercialized, particularly for GC applications.

Alternatively, electrochemical coating has also demonstrated its potential to open doors towards a new generation of coatings, such as coated tip (miniaturized SPME fibers), in view of the fact that a thin layer of coating can be easily engineered by controlling the electrochemical parameters and the concentration of the monomer and electrolytes. This technique can also be used to etch the substrate into any desired shape and thickness, an advantage of this method for preparation of fibers with a small diameter (*i.e.* thickness ≤ 50 µm) that can be used to facilitate extraction by radial diffusion. The biocompatibility of PPy is also a major strength of these materials, in particular for in vivo investigations and bio-SPME uses. As a future perspective, particles such as HLB and DVB can be loaded into the PPy network to improve the extraction efficiency of the coatings. New materials can be prepared in thin film geometry as well. Similarly, inter-laboratory validation and commercialization can be a future trend of electrochemical-based materials.

The electrospinning technique has also been used to prepare SPME fibers and membranes to improve extraction efficiency, owing to the nano-fibrous structure of the final materials which increases the surface area of the fiber. However, most of the reported fibers are burdened by thermal instability over 200 ºC, which limits their GC applications. While Polyetherimide has been shown to provide good thermal stability, it still needs to be fully investigated in terms of accuracy and lifetime of the fiber. A comparison of the extraction efficiency of the Polyetherimide fiber with commercial fibers should be performed to evaluate its suitability for future studies and commercialization. The electrospinning technique seems to be more applicable in the membrane and blade geometry for LC applications. Application of some biocompatible materials, such as polyvinyl alcohol (PVA), will make such materials suitable and versatile devices for clinical and bio-applications. Similar to the electrochemical technique, electrospun materials can also be loaded by particles to improve their efficiencies. In addition, particle loaded coatings prepared with spraying method provide high extraction efficiencies capable of extraction of wide range of compounds (HLB as coating) are useful for metabolomics studies.

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Figure captions

Figure 1. Different geometries of SPME; a) Fiber, b) Coated-tip (miniaturized fiber, coating length 150 µm and tip diameter of 10-30 µm in the cone shape) applied to the single cell of Allium cepa L, c) Arrow (modified fiber), d) In-tube, e) Thin film, f) 96-blade Blade configuration (thin film on a blade support), g) In-tip, and h) Magnetic nanoparticles

(Reprinted with permission from [42], [44], [10] Copyright [2012], [2011], [2016] American Chemical Society; Reprinted with permission from [6] and [15] @ Wiley 2016 and 2011; Reprinted with permission from [7] and [14] @ Elsevier 2015 and 2009.

Figure. 2: Effect of shapes and sizes of an extraction device (a) on the kinetics (b) and efficiency (c) of extraction evaluated by numerical modeling. SPME fibers was assumed to have radius from 5-30 µm and1 mm length, SPME Tip-1 was considered to have top radius of 30 µm and the bottom radius was varied from 5-30 µm and 1 mm length. The SPME Tip-2 was considered to have 0.5 mm length with 15 µm top radius and the bottom radius was varied from 5-15 µm.

Figure 3. Application of commercial SPME fibers for a) In-vivo SPME and b) Food analysis, and c) Saliva metabolome (Score plots of PCA performed on saliva samples collected first from the female individual on the diet (black squares, three replicates), next from the male individual (red diamonds, three replicates), and from QCs (blue dots, seven replicates). (Reprinted with permission from [69] @ Wiley 2011; Reprinted with permission from [72] @ Elsevier 2016; Reprinted with permission from [60] @ Future Science 2013.

Figure 4. Different stages, routes involving in the sol-gel process and the final product

(Reprinted from [77] with permission of Springer 2016)

Figure 5. Modification of the sol-gel based coatings by incorporating a) Crown ether, b) MWCNTs, c) ILs, and d) MNPs

(Reprinted with permission from [114], [15] @ Wiley 2005,2010; Reprinted with permission from [120] @ Elsevier 2010; Reprinted [116] from with permission of Springer 2011)

Figure 6. Effect of counter ion and surfactant on the morphology of the PPy coating, a) $HClO_4$, b), NaTS, c) PSS, d) TFA, d) TFA/SDS, and e) TFA/CTAB

(Reprinted with permission from [160] @ Elsevier 2004, Reprinted with permission from [6] @ Wiley 2016)

Figure 7. Electrospinning set-up for preparation of SPME a) Fiber, and b) Thin film; c) SEM images of the prepared electrospun coating

(Reprinted with permission from [178],[194] @ Wiley 2011,2015)

Figure 1

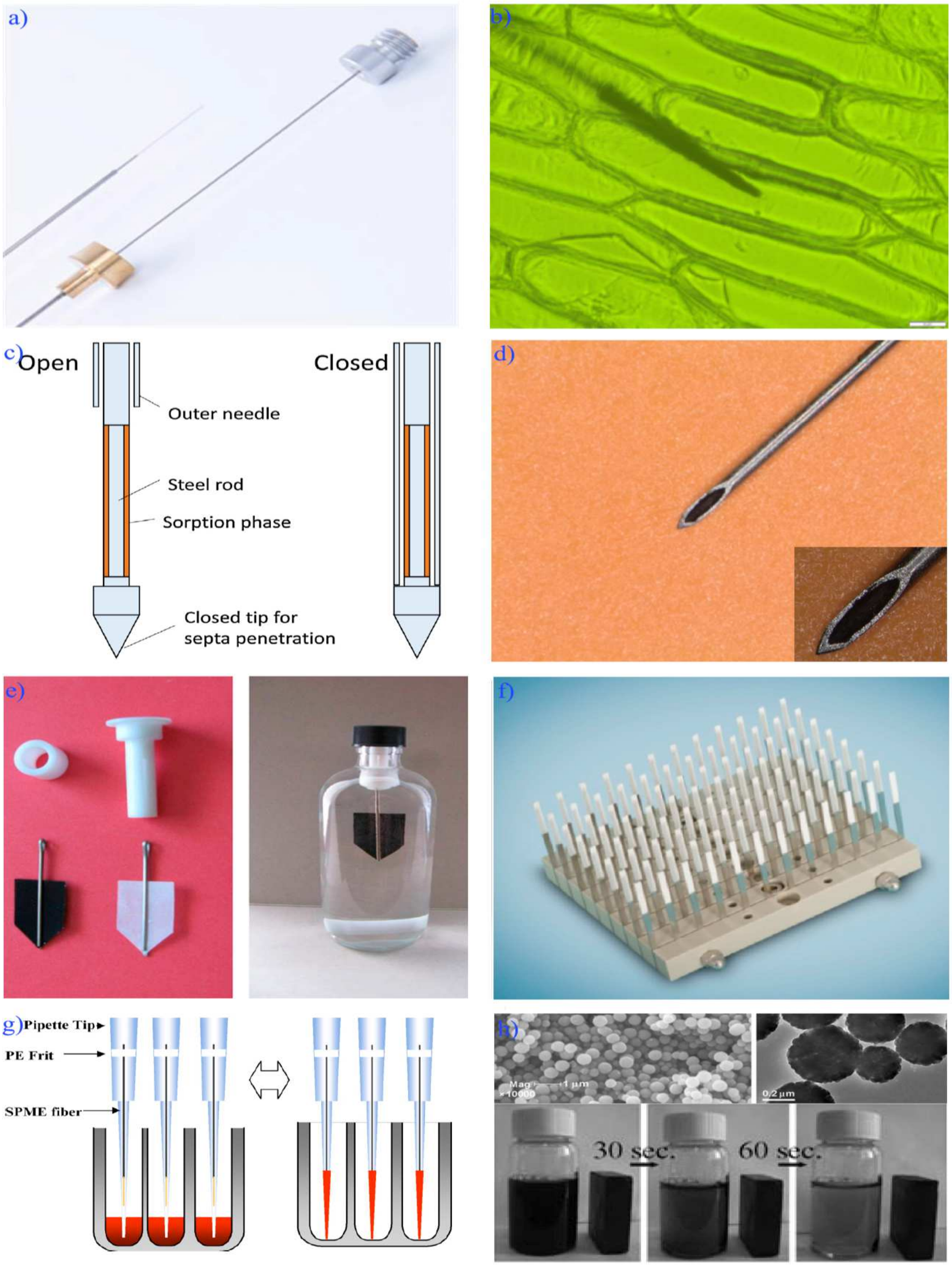

a)
b)
c)
Open
Closed
Outer needle
Steel rod
Sorption phase
Closed tip for
septa penetration
d)
e)
f)
g)
Pipette Tip
PE Frit
SPME fiber
h)
Mag
1 µm
×10000
0.2 µm
30 sec.
60 sec.

Figure 2

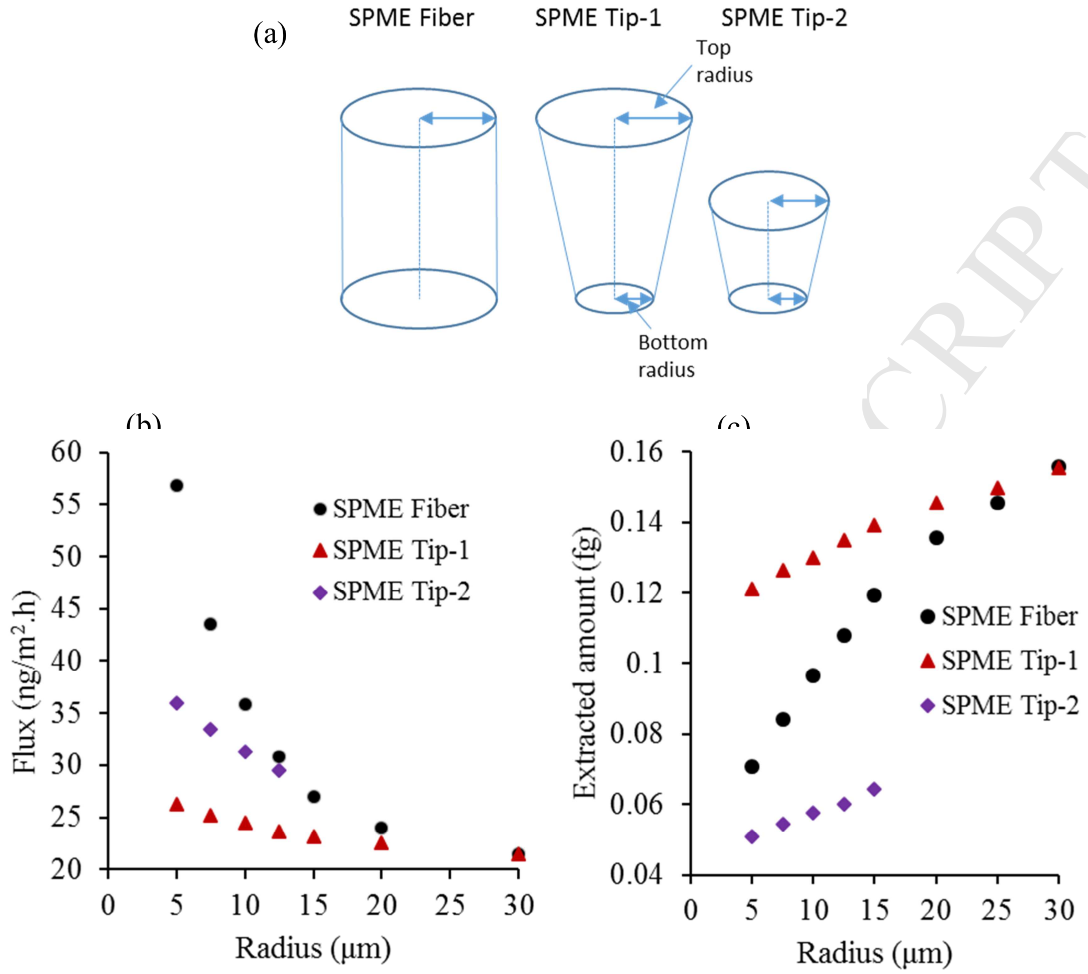
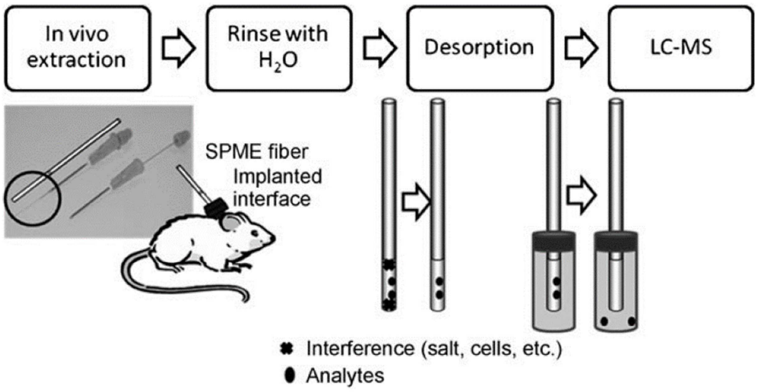
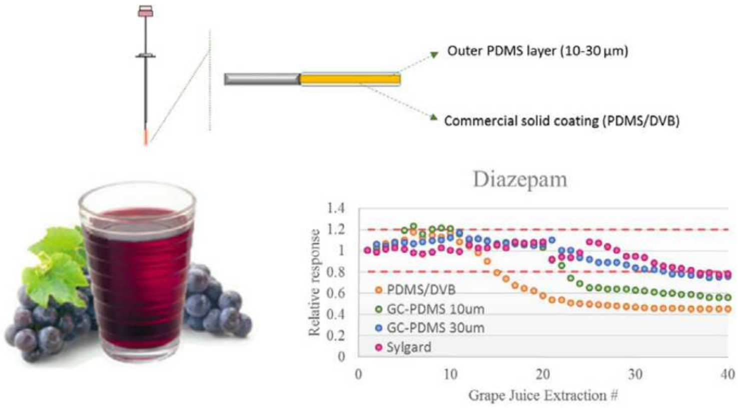

(a)
SPME Fiber
SPME Tip-1
SPME Tip-2
Top radius
Bottom radius
(b)
Flux (ng/m^2.h)
60
55
50
45
40
35
30
25
20
0
5
10
15
20
25
30
Radius (µm)
SPME Fiber
SPME Tip-1
SPME Tip-2
(c)
Extracted amount (fg)
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0
5
10
15
20
25
30
Radius (µm)
SPME Fiber
SPME Tip-1
SPME Tip-2

Figure 3

a)


In vivo extraction
Rinse with H_2O
Desorption
LC-MS
SPME fiber
Implanted interface
Interference (salt, cells, etc.)
Analytes

b)


Outer PDMS layer (10-30 µm)
Commercial solid coating (PDMS/DVB)
Diazepam
Relative response
0
0.2
0.4
0.6
0.8
1
1.2
1.4
PDMS/DVB
GC-PDMS 10um
GC-PDMS 30um
Sylgard
0
10
20
30
40
Grape Juice Extraction #

c)

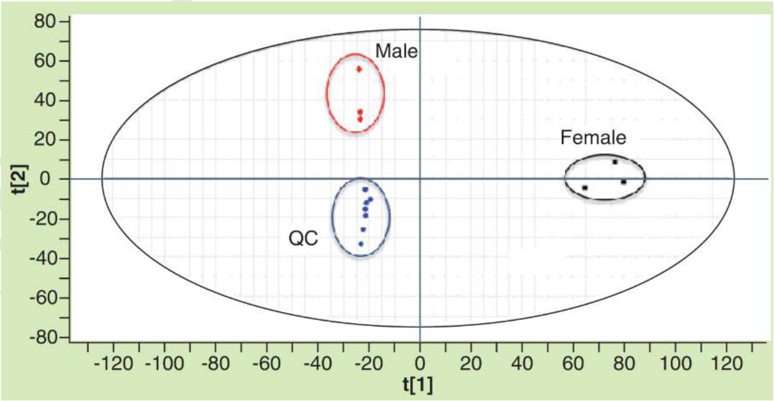

80
60
40
20
0
-20
-40
-60
-80
t[2]
Male
Female
QC
-120
-100
-80
-60
-40
-20
0
20
40
60
80
100
120
t[1]

Figure 4

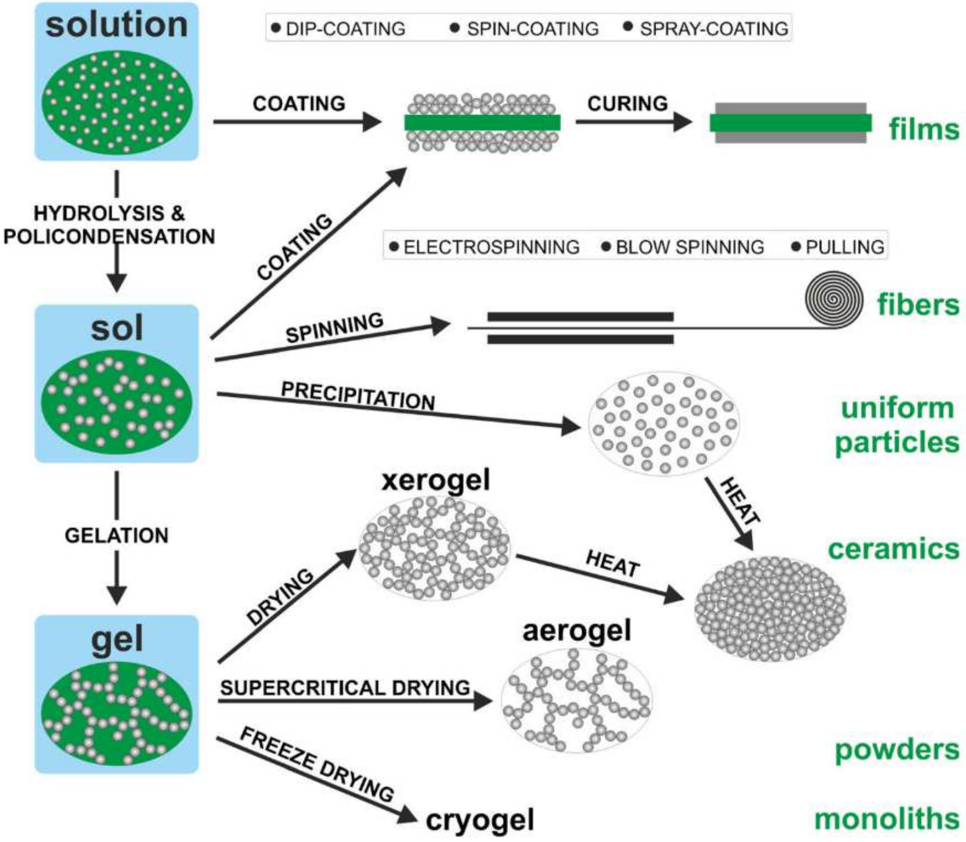
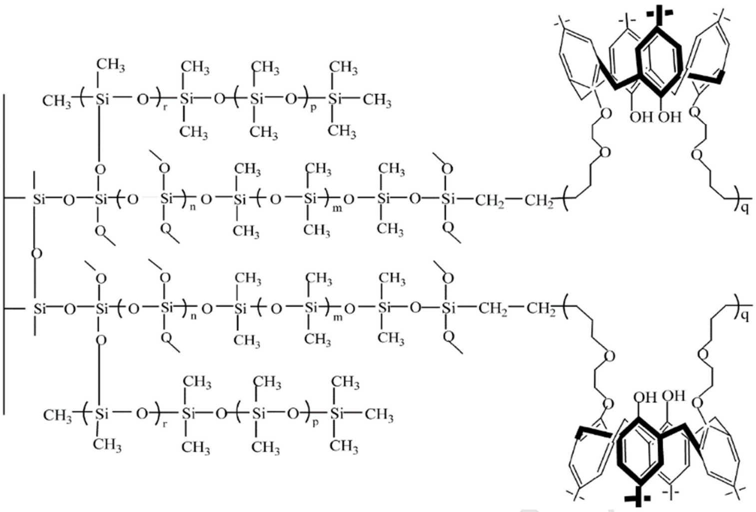
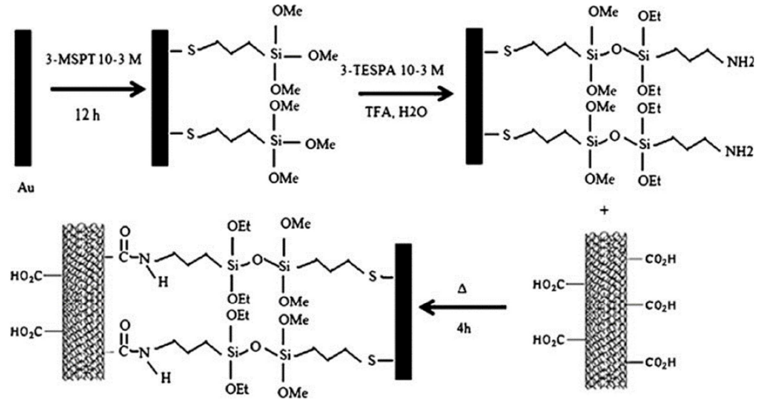

solution
• DIP-COATING • SPIN-COATING • SPRAY-COATING
COATING
CURING
films
HYDROLYSIS & POLICONDENSATION
COATING
• ELECTROSPINNING • BLOW SPINNING • PULLING
sol
SPINNING
fibers
PRECIPITATION
uniform particles
xerogel
HEAT
GELATION
ceramics
DRYING
HEAT
gel
aerogel
SUPERCRITICAL DRYING
powders
FREEZE DRYING
cryogel
monoliths

Figure 5

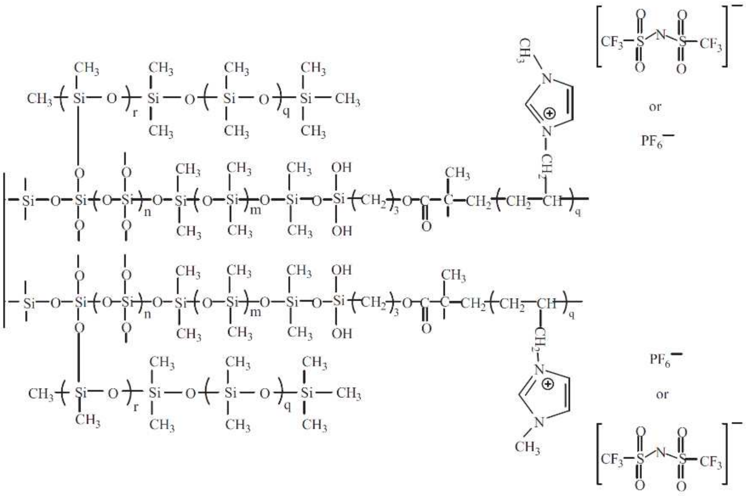
a)


CH3
Si
O
r
p
q
m
n
CH2
OH OH

b)


3-MSPT 10-3 M
12 h
Au
3-TESPA 10-3 M
TFA, H2O
OMe
OEt
NH2
Δ
4h
CO2H
HO2C

c)


CH3
Si
PF6⁻
or
CF3
OH

d)

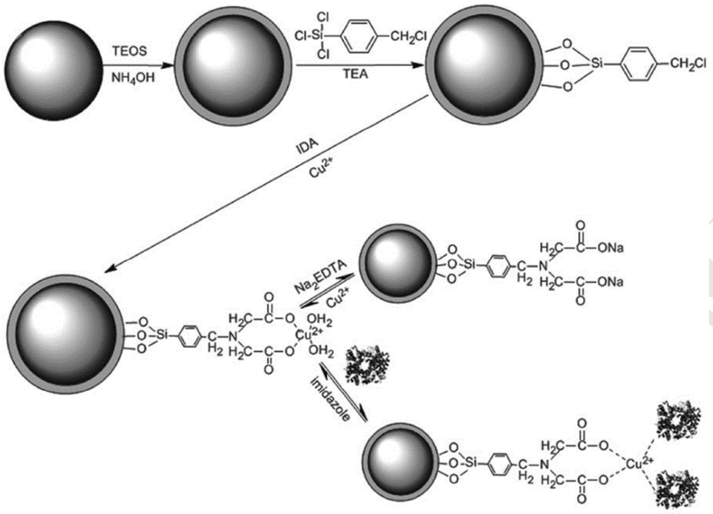
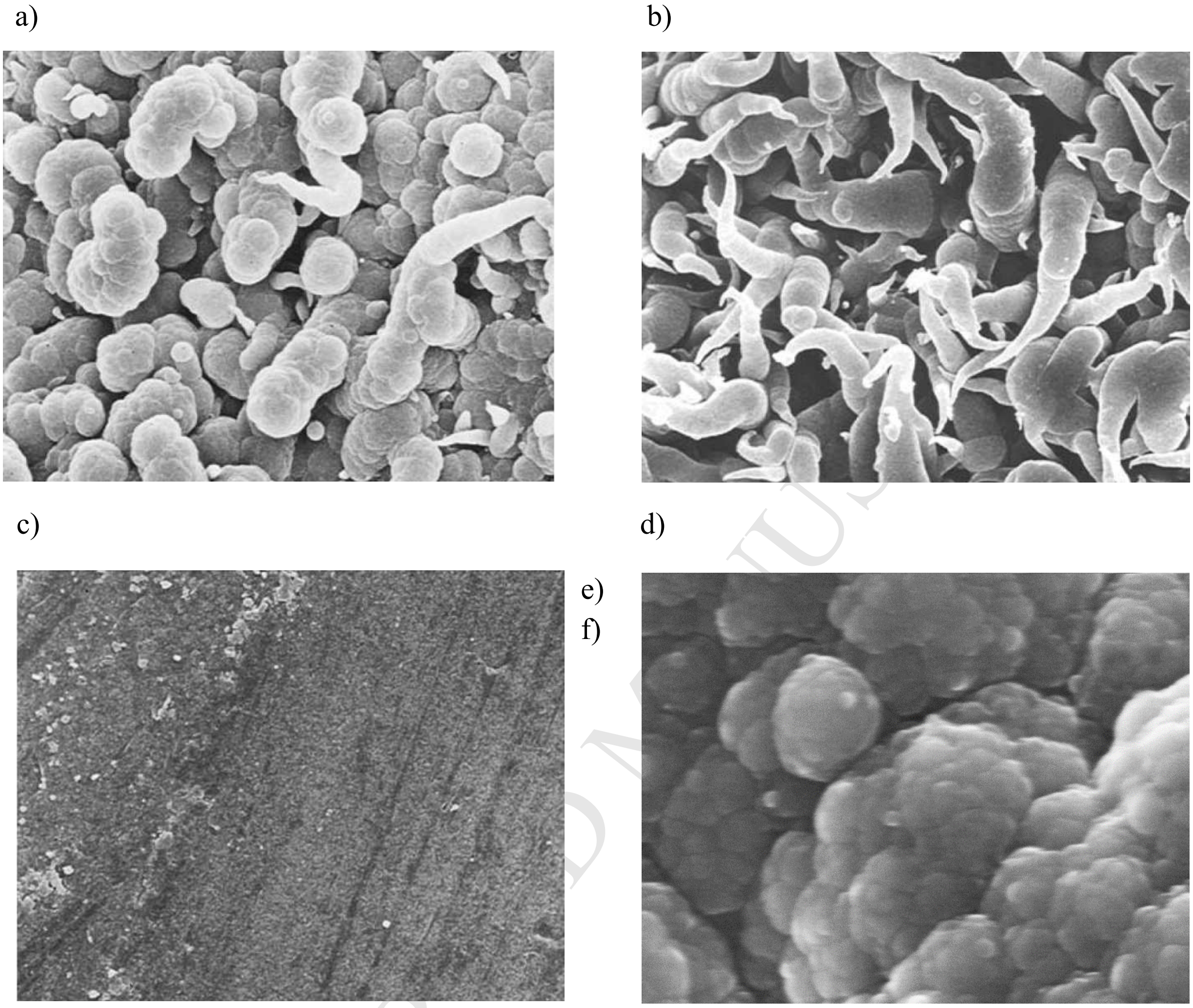

TEOS
NH$_4$OH
Cl-Si(Cl)(Cl)-C$_6$H$_4$-CH$_2$Cl
TEA
O-Si-CH$_2$Cl
IDA
Cu^{2+}
Na$_2$EDTA
Cu^{2+}
ONa
ONa
H$_2$C
H$_2$
N
OH$_2$
Cu^{2+}
imidazole

Figure 6



a)

b)

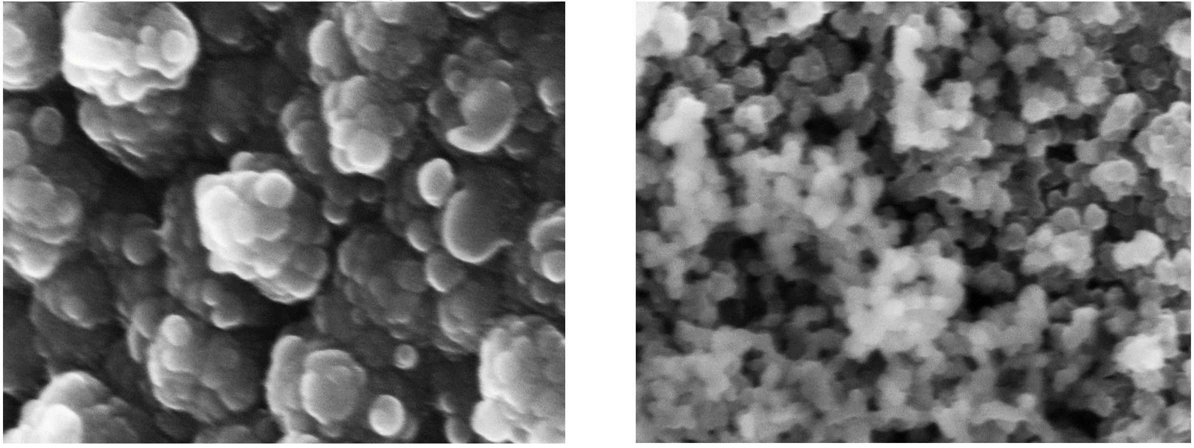
c)

d)

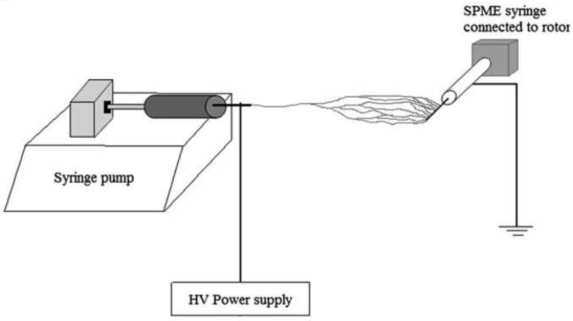
e)

f)

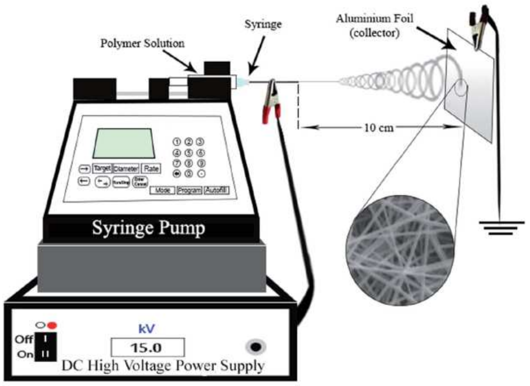
Figure 7



a)


SPME syringe
connected to rotor
Syringe pump
HV Power supply

b)


Polymer Solution
Syringe
Aluminium Foil
(collector)
10 cm
Target
Diameter
Rate
Mode
Program
Autofill
Syringe Pump
Off
On
kV
15.0
DC High Voltage Power Supply

c)

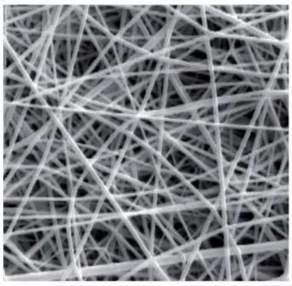


Table 1- Specification of different geometries of SPME

Geometry	Coating volume	Total recovery	Sample matrix	Equilibrium time	Detection strategy (offline/online)
Fiber	~ 0.6 µL (coating thickness 100 µm and length of 1 cm)	Negligible depletion, <2% (depending on the sample volume, coating and analytes, it can be higher)	Biofluid, water, tissue and food	Few minutes to several hours (depends on coating thickness and analytes)	Online: GC and LC (dedicated autosampler and interface) Offline: solvent desorption
Miniaturized fiber (coated-tip)	~ 0.0002 µL (coating thickness 10 µm and length of 500 µm)	Negligible depletion (<2%) in small volume, exhaustive in single cells	Biofluid, water, single cell and small organisms	Few minutes (due to the radial diffusion)	Offline: solvent desorption
Arrow	~ 16 µL (coating thickness 250 µm and length of 3 cm)	Up to exhaustive (depends on the sample volume)	Biofluid, water, tissue and food	Few minutes to several hours (longer than fiber and thin film due to the thicker coating)	Online: GC Offline: solvent desorption
Thin film (TFME)	40 µL (coating thickness 100 µm and dimension of 2 cm × 2 cm)	Up to exhaustive (depends on the sample volume)	Biofluid, water and tissue	Few minutes to several hours (Similar to fiber)	Online: GC (via TDU) and direct coupling of thin film to MS Offline: solvent desorption
In-tube	~ 1.5 µL (length of tube 10 cm, coating thickness 20 µm)	Negligible depletion up to 50 % (depends on the sample volume)	Biofluid and water (mainly water and clean samples)	Few minutes to hours	Online LC Offline: solvent desorption
MNPs	Depends on the amount of NPs	Up to exhaustive (depends on the sample volume)	Biofluid, and water	1-30 min	Offline: solvent desorption
In-tip	Similar to fiber	Similar to fiber	Biofluid and water	~ 1 hour (based on aspiration/dispense cycles)	Offline: solvent desorption

Table 2- Comparison of the of the different SPME coatings

	Commercial	**Sol-gel based**	**Electrochemical derived**	**Electrospun**	**Other coatings**
Coating materials	PDMS, PDMS/DVB, … (section 4.1)	Alkoxy metals (mainly silica-based)	Mainly conductive polymers	Polymers with appropriate solubility [174]	ILs, MOFs, particle loaded coatings
Available geometries	Fiber and thin film	Fiber, in-tube, thin film, and MNPs	Fiber and in-tube	Fiber and thin film	Fiber, thin film
Applications	Environmental, food, biofluids, in-vivo and metabolomics	Environmental and biofluids	Environmental, biofluids, food and single cell	Environmental and biofluids	Environmental, biofluids, in-vivo and metabolomics
Biocompatibility	C18, Mixed mode C18 with benzenesulfonic acid (PAN as biocompatible binder and glue)	Sol-gel based materials are biocompatible, but their biocompatibility and matrix effect as SPME coatings yet to be investigated [88]	Polypyrrole	Poly(lactic acid-co-caprolactone)	PAN as binder and glue (similar to commercial coatings)
New perspective	In-vivo applications and metabolomics studies	-	Coated-tip geometry for small volume of samples, small organism and single cells	-	In-vivo applications and metabolomics studies
Advantages	- Wide range of applications - Inter-laboratory validations	- Available in all the geometries of SPME - High thermal, chemical stability	- Rapid and cost-effective -Easy controlling the coating thickness	High extraction efficiencies due to the nano-fibrous network	- Wide range of applications
Limitations	Low operating temperature of some coatings 240 ºC -280 ºC)	Lack of inter laboratory validation and comparison to commercial coatings from several aspects	Limited number of coating materials	-Low operating temperature (most of the materials about 200 ºC) - limited number of coating materials	- Limited to the available particles - PAN is not thermal stable - ILs: Time consuming procedure of preparation

Table 3- Application of different SPME coatings in variety of sample matrices

Technique	SPME probe	Analytes	Matrix	Instrument	Lifetime	LOD μg L^{-1}	RSD%*	Ref
Commercial	PDMS/DVB fiber (Inter-laboratory validation, SPME and LLE)	Pesticides (25 compounds)	Surface and ground water	GC/MS	-	0.01-1	1-26	[48]
	DVB/CAR/PDMS fiber (Globl inter-laboratory validation)	VOCs (61 compounds)	Surface water and municipal wastewater	GC	-	-	8-35	[49]
	PDMS fiber (Intel-laboratory study)	Pesticides (12 compounds)	Water sample	GC/MS	-	-		[50]
	Carbowax/DVB fiber (Intel-laboratory study)	Triazine herbicides and degradation product	Drinking water sample	GC-NPD, GC/MS	-	0.004-0.040	6-17	[51]
	PDMS fiber (US EPA 8272)	PAHs	Sediment pore water	GC/MS	-	0.06-9	<33	[52]
	PDMS/DVB/PDMS fiber	Triazole pesticieds	Grape pulp	GC/MS	Up to130 runs	-	<33	[3]
	PDMS/DVB/PDMS fiber	Pesticides	Spinach, tomato and carrot	GC/MS	Up to 100 runs	-	-	[74]
	PDMS/DVB/CAR/PDMS fiber	Metabolome	In-vivo of plant tissue	GC/MS	-	-	6.6-19.5	[71]
	Biocompatible C18 fiber	Carbamazepine and carbamazepine-10,11-epoxide	In-vivo sampling of mice	LC/MS	-	1	<17	[68]
	Biocompatible mixed-mode fiber (C18 with benzenesulfonic acid); SPME and microdialysis	Neurotransmitter	Brain (In-vivo sampling of rat)	LC/MS	-	-	-	[59]
	Biocompatible C18 fiber	Metabolomics	Human saliva	LC/MS	-	-	-	[60]
	Biocompatible C18 fiber	Eicosanoids	In-vivo sampling of rat blood	LC/MS	-	-	<10	[61]
	Biocompatible mixed-mode fiber (C18 with benzenesulfonic acid); Compariosn of SPME, ultrafiltration and solvent precipitation	Elusive metabolome	In-vivo SPME of blood of mice	LC/MS	-	-	<35	[69]
	Biocompatible C18 fiber	Exposome	In-vivo sampling of fish	LC/MS	-	-	-	[225]
	PDMS/DVB thin film	Pesticides (23 compunds)	Surface water	TDU-GC/MS	Over 100 runs	0.01-0.25	4-22	[43]
	PDMS thin film	PAHs	Lake water	GC/MS	-	0.002-0.02	2.8-13.6	[16]
	PDMS/DVB thin film	Pesticides	Water sample	Portable GC/MS	-	-	-	[27]
	PDMS/DVB In-tip SPME	MK-0533	Human plasma	LC/MS	-	5	1-13.7	[14]
	CW/TPR fiber	Free and total of chlorhexidine	Human saliva	LC/MS	-	20	9.6	[30]
Sol-gel	MTMOS/PDMS fiber	PAHs, alcohols and phenolic compounds	Aqueous sample	GC-FID	- (Thermal stability over 320 ºC)	-	0.5-9.2	[86]
	MTMOS, OH-TSO and fullerol fiber	PCBs and PAHs	Water sample	GC-ECD and GC-FID	190 (Thermal stability up to 360 ºC)	0.005-0.125	1.1-8.9	[89]
	Calix[4] open-chain crown ether, OH-TSO, TEOS	Polar aromatic and aliphatic	Water and wine samples	GC-FID	-	0.01-110	<7	[114]

	and VTEOS fiber	compounds						
	SWCNTs, TEOS, TSO-OH	PBDEs	Reservoir water and wastewater	GC-ECD	Over 200 runs	0.00008-0.0008	2.2-7.5	[115]
	Graphene, TEOS, PDMS	PBDEs	Canal water	GC/MS	Up to 200 runs	0.0002-0.005	3.2-5	[118]
	Zirconia-PDMDPS CME (in-tube)	PAHs, ketones, aldehydes	Water sample	GC-FID	- (pH resistant)	0.02-0.57	1.2-7.2	[93]
	Titania-Poly THF CME	Polar analytes (phenols, alcohols, amines, aromatic carboxylic acids)	Water sample	LC-UV	- (pH resistant)	0.019-2.03	0.7-4	[94]
	Germania-PDMS CME	PAHs, aldehydes, ketones, alcohols, phenols and free fatty acids	Water sample	GC-FID	- (pH resistant)	11-139	1.3-7.2	[95]
	3MPTMOS-PEG CME (copper tube substrate)	PAHs	River water	LC-Flu	Up to 100 runs	2.8-8.3	0.005-0.5	[98]
	Sol-gel ILs CME (TEOS, PDMS, polyTHF, PEG, BMPO)	PAHs, aldehydes, ketones and alcohol	Water sample	GC-FID	-	3.2-17.4	4.2-5.0	[130]
	3TMSPA CME (metal and plastic substrate)	Triazines	River water	LC-UV	-	10	7.4-16.5	[100]
	TMSPMA CME (Selective coating, MIX)	Traizine	River water	LC-UV	-	1-5	2.7-6.6	[142]
	PANI/EPPTMOS (Selective coating)	Naproxene	Urine and plasma	LC-UV	-	5	2.9	[144]
	Poly-THF-MTMOS on cellulose fabric (FPSE)	Estrogens	Urine and Water samples	LC-FLD	-	0.02-0.04	2	[39]
	Poly-THF-MTMOS on cellulose fabric	Alkyl phenols	Water and soil samples	LC-UV	-	0.16-0.19	0.9-1.5	[102]
	MTMOS-PEG on cellulose fabric	Anti-inflammatory drugs	Surface and waste water	GC/MS	-	0.8-5	3.5-18	[103]
	MTMOS/PDMDPS on polyester fabric	Benzotriazole UV stabilizers	Sewage sample	LC/MS	-	6-60	2-30	[104]
	Magnetic (Fe_3O_4) octadecylsilane particles	Fat-soluble vitamins	Juice and milk	LC-UV	-	0.91.1	2.2-5.6	[110]
	Phenyl-functionalized silica-coated MNPs	Chlorobenzene	Well, spring and wastewater	GC-ECD	-	6-500	4.1-5.8	[111]
	Core-shell MNP with surface MIP (selective nano-sorbent)	Dimetridazole	Egg, milk powder and pid feed samples	UV-Vis	-	100	1.85-4.54	[112]
	Magnetic SiO_2/TiO_2 nanocomposite hollow fiber	Anti-inflammatory drugs	Human hair	LC-DAD	-	10-100	3.1-6.6	[113]
Electrochemical	Anodized aluminum wire	aliphatic alcohols, BTEX, petroleum products	Gaseous samples	GC-FID	-	0.03-0.3	2.4-8.1	[145]
	Poly(3-methylthiophene)	Arsenate ions	Water sample	ICP-MS	-	-	-	[156]
	PPy and PPPy fibers	VOCs, PAHs, Beta-blockers, amines, organo arsenic and alcohols	Water sample	GC-FID, LC-UV and LC/MS	-	0.1-1	0.8.8.3 (except for ionic analytes)	[158]
	PPy fiber	Ionic analytes	Water sample	LC/MS	-	-	<10	[159]
	PPy fiber (different counter ions)	Polar and ionic compounds	Water sample	LC/MS, GC-FID	-	-	2.5-11.2	[160]
	PPy (different counter ions and surfactant)	carbamazepine, propranolol, testosterone, diazepam, and pindolol, quercetin,	Urine, blood, plasma, single cell of onion	LC/MS, Nano-ESI-MS	-	0.3-25	1-19	[6]

		luteolin						
	PANI fiber	Phenols	Well and drinking water	GC-FID	-	0.69-3.7	4.8-17	[164]
	PANI in-tube (PANI and PANI-sol-gel MIX)	Naproxen	Urine and plasma	LC-UV	-	5	2.9-6.8	[144]
	PANI-PPy composite in-tube	Methyl, ethyl, and propyl parabens	Water, milk and juice	LC-UV	-	0.02-0.04	4.4-7.0	[166]
	PPy in-tube (for analysis of single droplet of sample)	Carbamazepine, pindolol, dialepam and propranolol	Urine and blood	LC/MS, Direct coupling of in-tube to MS	Over 50 runs	0.4-10	1-18	[10]
	PANI-Silica nanocomposite fiber	PAHs	River and drinking water	GC/MS	Over 150 runs	0.001-0.003	6-13	[167]
	PPY-DS fiber	PAHs	River and sea water	GC-FID and GC/MS	Over 50 runs	0.05-0.16	2.6-7.6	[161]
	Polyphosphate-doped PPy fiber	Organochlorine pesticides	Well water	GC/MS	Over 70 runs	0.000015-0.00066	4.7-13	[162]
	Thiophene-ILs fiber	Polar analytes	Water samples	GC/MS	- (Thermal stability 300-370 °C)	-	-	[169]
	PANI-IL fiber	Fatty alcohols	Tea and lemon drink	GC-FID	Over 114 runs	6.1-18.3	6-12.2	[171]
	MOF/PANI fiber	Chlorobenzene	Drinking and river water	GC/MS	-	0.0001-0.0002	4-10	[173]
Electrospinning	Pyrolyzed SU-8 fiber	BTEX and phenols	Water sample	GC-FID	20-30	0.04-1	3.3-20	[177]
	PU fiber	Chlorobenzene	River and drinking water	GC/MS	-	0.01	3-8	[178]
	PANI-nylon-6 thin film	Chlorobenzene	River and drinking water	GC/MS	-	0.019-0.033	5-14	[185]
	PPy-PA thin film	Malathion	River water	GC/MS	-	0.05	2	[179]
	PA fiber	Phenol and chlorophenols	River and drinking water	GC/MS	-	0.002-0.01	1.7-6.7	[184]
	Polyetherimide fiber	PAHs	River and drinking water	GC/MS	- (Thermal stability up to 290 °C)	0.001-0.005	1.1-7.1	[180]
	PA-PEG fiber	Chlorophenols	River and paddy	GC/MS	-	0.0008-0.025	2.1-12.2	[193]
	Cote-shell of c (PVP-PBT/PPy thin film	Triazines	Well and paddy water	GC/MS	-	0.05-0.09	4-8	[181]
	Silica-PA fiber	Chlorobenzene	River and drinking water	GC/MS		0.005-0.03	4-12	[195]
	Magnetic PU thin film	Fluoxetine	Urine, blood, milk, drinking and river water	Flu	-	1	2	[197]
	Pyrolyzed SU-8 fiber	ß-blockers	Water sample	LC	Up to 100 runs	1	7.7-33	[189]
	Amino-functionalized PDMS	Speciation inorganic and organometallic arsenic species	Water sample	LC-ICPMS.	-	-	-	[192]
	Poly(lactic acid-co-caprolactone) with sulfonated nanoparticles and polynorepinephrine sheath (biocompatible fiber)	Pharmaceuticals	In-vivo SPME of fish and vegetable	LC/MS	-	0.02-0.08 ng g^{-1}	1.9-15.6	[196]
Other materials	PILs fiber	Esters and FAMEs	Water sample, wines	GC-FID	Up to 150 runs	2.5-50	1-19.6	[199]
	Crosslinked PILs	Phthalate esters	Coffee	GC/MS	-	-	5.7-22.7	[200]
	PILs fiber (tuned selectivity)	PAHs	Water sample	GC-FID	Up to 70 runs	0.003-0.6	1-15	[203]
	PILs fiber (with different	Volatile fatty acids	Water sample	GC-FID	-	0.02-7.5	2.4-14	[204]

counter ions)	and alcohols (selective extraction of polar compounds)						
PILs fiber	Extraction and purification od DNA	Crude bacterial cell lysate with	qPCR amplification	Up to 50 runs	-	-	[205]
Nafion modified ILs-CNTs fiber	Carbamate pesticides	Water, apple and lettuce	GC-FID	Over 150 runs	0.015-0.027	4.7-8.2	[209]
Silica-based ILs thin film (96-blade)	Amino acids	Grape pulp	LC/MS	Up to 20 runs	0.01-1	3-13	[206]
Crosslinked PILs fiber (compatible with LC)	Pharmaceutical drugs, phenolics, and insecticides	Drinking and lake water	LC-UV	155 runs	0.2-2	4.5-19.2	[212]
MOFs 199 fiber	Gaseous benzene homologues	Inddor air	GC-FID	-	0.0080.023	2.9.4	[214]
MOFs fiber (UiO 66)	PAHs	Water and soil samples	GC/MS	90 runs	0.0003-0.0006	1.5-8.9	[215]
MOF-5/GO composite fiber	Triazole Fungicides	Fruit and Vegetable (grape, apple, cucumber, celery cabbage, pear, cabbage, and tomato)	GC-μECD	120 runs	0.05-1.58 ng g^{-1}	3.7-11.4	[216]
MOF fiber (cathodic electrodeposition)	Exogenous estrogens	Milk	LC	Over 120 runs	0.17-0.56	3.5-6.1	[218]
MOF-199/GO composite	Organochlorine pesticides	River water, soil, water convolvulus and longan	GC-ECD	Over 140 runs	0.002-0.006	5.2-12.8	[219]
RP-amide C16-coated silica particle	Diazepam, lorazepam, nor-diazepam, and oxazepam	Human hair and blood	LC/MS	-	0.8-3	2-19	[220]
PAN–PS–DVB and PAN–PBA thin film (96-blade)	Dazepam, oxazepam, caffeine, riboflavin, and sucrose	PBS and human plasma	LC/MS	Over 100 runs	0.1-25	4.3-14.2	[221]
Several thin film including C18, PS-DVB- WAX, HLB, PBA, Si-RP- WCX, StrataX, Si- IL, and HILIC) particles (thin film)	Metabolomics	Escherichia coli (In-vivo)	LC/MS	-	-	-	[222]
PS-DVB-WAX/HLB thin film (96 blade)	In-vivo metabolomics	E. Coli (bactericidal action of cinnamaldehyde against E. coli during bacteria growth)	LC/MS	-	-	-	[223]
PS-DVB-WAX:HLB thin film (96 blade)	Metabolomics	E. coli bacteria (in response to natural antibacterial agents)	LC/MS and GCxGC-ToF/MS	-	-	-	[224]
PAN-C18 thin film (blade)	In-vivo ssampling for elusive exposome	Fish	LC/MS	-	-	-	[225]

- RSD % is different for each study (different levels of concentration, inter-day, intra-day, between fiber, batch, …).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- Presentation of different geometries of solid phase microextraction
- Evaluation of effect of geometry on the extraction rate, sensitivity and diffusion
- Description of variety of techniques to prepare SPME coatings
- Comparison of commercial, sol-gel, electrochemical and electrospun derived materials
- Evaluation of strengths, limitations and future perspectives of the available coatings

Md. Nazmul Alam received his Ph.D. in Analytical Chemistry in 2016 at the University of Waterloo under the supervision of Prof. Janusz Pawliszyn. His doctoral thesis was focused on the development of mathematical models for various types of quantification approaches in solid-phase microextraction (SPME). Dr. Alam gained multidisciplinary research experience through his masters in Inorganic Chemistry at the Western University under the supervision of Prof. Bernie Kraatz and postgraduate diploma in Chemical Engineering at the Tokyo Institute of Technology under the supervision of Prof. Yashiro Nakano. Currently he is doing post-doctoral research at the University of Waterloo. His research interests are development of fast sampling methods, mathematical modeling, numerical simulation of mass and momentum transport in chemical analysis.

Hamed Piri-Moghadam completed his PhD in 2014 at Sharif University of Technology under supervision of Prof. Habib Bagheri. As a post-doctoral fellow in Prof. Janusz Pawliszyn's research group at University of Waterloo (2014-2017), he was working on inter-laboratory validation of SPME methods to demonstrate that SPME can be adopted as a standard protocol by commercial analytical testing laboratories. He was also working on development of new biocompatible miniaturized probes of SPME for rapid analysis of small volume of samples (1-10 μL) and single cells using LC-MS/MS and direct coupling to MS. Currently, Hamed is a post-doctoral fellow in Prof. Christina Bottaro's research group (Memorial University of Newfoundland), developing selective and rapid strategies for analysis of target compounds using molecularly imprinted polymers coupled to LC-MS/MS and DESI/MS.

Janusz Pawliszyn, as the inventor of SPME, focuses on development, validation and application of various geometries of SPME to facilitate isolation, extraction and pre-concentration of compounds from complex matrixes and convenient analysis by designing automated and integrated instrumentations. His research is also focusing on the rapid analysis of compounds by designing the dedicated interfaces for direct coupling of SPME to mass spectrometry including coated blade spray, nano-ESI and in-tube geometries. On-site sampling and in-vivo application, as green analytical approaches, usually with the development of biocompatible coating materials, is the center of current methodologies in Professor Pawliszyn`s research group. Professor Pawliszyn is also exploring application of computational and modeling techniques to enhance performance of sample preparation, chromatographic separations and detection. An additional area of his interest involves the development and application of imaging detection combined with microseparation approaches.