NEW COATINGS FOR STIR BAR SORPTIVE EXTRACTION OF POLAR EMERGING ORGANIC CONTAMINANTS

Núria Gilart, Rosa Maria Marcé, Francesc Borrull*, Núria Fontanals

Departament de Química Analítica i Química Orgànica, Universitat Rovira i Virgili, Campus Sescelades Marcel·lí Domingo, s/n, 43007 Tarragona, Spain

* Phone: (+34) 977 55 95 60

Fax: (+34) 977 55 84 46

E-mail: francesc.borrull@urv.cat

Keywords: stir bar sorptive extraction; polar coatings; sol-gel technology; monolithic materials; polar contaminants

Abstract

Stir bar sorptive extraction (SBSE) is a sample preparation technique that allows the sorptive extraction and preconcentration of emerging organic contaminants (EOCs) from complex matrices. Since its introduction, this technique has been widely applied in the areas of environmental, food and biological research, followed by gas chromatography (GC) or liquid chromatography (LC). However, the single commercially available coating for SBSE, based on polydimethylsiloxane, has become its principal limitation and, as a consequence, the use of SBSE has been reduced to the extraction of apolar or moderately polar compounds. In recent years, there has been growing interest in developing more polar in-house coatings for SBSE and, therefore, extend the applicability of this sorptive extraction. In this context, different approaches for achieving the synthesis of polar coatings for SBSE have been developed, with sol-gel technology and monolithic materials being notable examples, among others. This review focuses on the most common and novel strategies for synthesising new coatings for SBSE to enhance the extraction of polar EOCs and their applications.

1. Introduction

Over the last few decades, scientific concern about environmental pollution has increased and environmentally friendly methodologies have gained popularity, including modified and less hazardous sample pre-treatments [1]. In addition, environmental analysis has focused on the extraction and determination of a wide range of emerging organic contaminants (EOCs) with an apolar or moderately polar character because sample preparation techniques were not capable of extracting many compounds with such different chemical properties simultaneously. Thus, the aim of sample pre-treatments has been to extract more polar contaminants, simplify the manipulation of the sample, reduce the sample and organic solvent volumes used, miniaturise the analytical devices, as well as achieving the maximum removal of interferences from complex matrices [2].

Apart from conventional extraction techniques for environmental liquid or solid samples (solid-phase extraction (SPE), ultrasonic solvent extraction or microwave-assisted extraction, among others), great efforts have been concentrated on the development of extraction techniques with lower solvent consumption and low sample handling, such as solid-phase microextraction (SPME), stir bar-sorptive extraction (SBSE), microextraction by packed sorbent, single-drop microextraction, liquid-phase microextraction or supported liquid membrane extraction [3,4].

Regarding liquid samples, SPE is a well-established technique in environmental analysis. While the main advantage of SPE is the high availability of commercial sorbents, other sorptive techniques, such as SPME and SBSE, are still restricted in this respect, limiting the range of analyte classes that can be extracted. In particular, SBSE is an enrichment technique based on SPME principles [5], first introduced by Baltussen *et al.* [6]. The SBSE device consists of a magnetic stir bar covered with a polymeric coat which enables the distribution of the analytes between the sample and the small amount of extracting phase [7,8]. In contrast to SPME, higher extraction phase volumes are found in SBSE stir bars (24-126 µL)

than in SPME fibres (maximum 0.5 µL), which leads to a higher amount of analytes being extracted from the samples [9]. Many publications have demonstrated the applicability of SBSE in different research areas due to its versatility in both sampling (immersion and headspace (HS)) and desorption modes (liquid (LD) or thermal desorption (TD)) [4,8,10].

In SBSE, to promote the transfer of the analytes onto the extracting phase, several variables affecting the extraction step should be evaluated, including extraction time and temperature, sample pH, addition of an inert salt, stirring rate and sample volume. As for TD, desorption time and temperature are the most important variables to be tested, while organic solvent nature, desorption time and volume are the most common variables studied in LD [4,5]. Moreover, another parameter to take into account in SBSE is the coating, being an essential factor in enhancing the retention of the analytes. However, the only commercially available coating for SBSE, until recently, is polydimethylsiloxane (PDMS). This fact is its main disadvantage as it limits extraction to apolar compounds [4,9].

In the present review, the current state of the synthesis of novel coatings for SBSE is extensively described, as well as their application in the analytical field for the extraction of polar pollutants from complex matrices.

2. Commercially available coatings for SBSE

For years, PDMS has been the only commercially available extracting phase for SBSE, commercialised under the name Twister® by Gerstel. Current reviews [4,10-12] highlight a great number of publications in which PDMS coating has been applied to the extraction of many EOCs from environmental, food and biological matrices. Nevertheless, this fact has become the principal disadvantage of SBSE, focusing on the extraction of apolar or moderately polar analytes (generally for those with log $K_{o/w}$>3) [11]. As a consequence, the present trend in both analytical

chemistry and environmental analysis is controlling and determining EOCs, mainly with polar behaviour, in the environment.

In this respect, very recently, SBSE stir bars with polar coatings have been marketed by Gerstel. These new stir bars are coated with poly(ethyleneglycol) (PEG) modified silicone (EG Silicone Twister®) and polyacrylate (PA) with a proportion of PEG (Acrylate Twister®). It should noted that EG Silicone Twister® is widely commercially available, while Acrylate Twister® is still undergoing pilot tests. The structures of these new coatings are presented in Table 1, which shows the enhancement of polarity through hydroxyl and ester groups from PEG and PA structures, respectively. Although they have been synthesised to improve PDMS stir bar performance, both Acrylate and EG Silicone Twisters® are PDMS-based, which might influence the proper retention of polar compounds. Currently, few publications have reported the use of these polar commercial coatings. These are detailed in Table 1.

In 2011, Fries [13] was the first to use Acrylate Twister® for SBSE to extract benzothiazole from wastewaters, using TD coupled to gas chromatography-mass spectrometry (GC-MS). The authors emphasised that the proposed analytical method enabled the improvement of extraction efficiencies compared to SPME, as well as saving time and costs, since no filtering, clean-up steps or organic solvents were required. Recently, Sgorbini *et al.* [14] evaluated both EG Silicone and Acrylate Twisters® for the SBSE of volatile organic compounds (VOCs) from food and cosmetic samples analysed by GC-MS and subsequently compared to the PDMS coating. When both polar coatings were used under immersion and HS modes, it was observed that these coatings provided better performance by immersion in comparison to HS mode. Moreover, EG Silicone Twister® provided higher percentage concentration factors for most of the target analytes than Acrylate Twister®, being able to extract a wider range of analytes with different polarities (log $K_{o/w}$ between -0.2 and 4.6) and improving PDMS limitations. In our research group, these novel polar coatings were first applied for the SBSE of

pharmaceuticals and personal care products (PPCPs) by immersion from wastewaters, followed by liquid chromatography-tandem mass spectrometry (LC-MS/MS) [15]. In this study, all three commercial stir bars were evaluated in terms of recovery values and matrix effect. While the matrix effect was generally low using this extraction technique, there were significant differences with the recovery values obtained. EG Silicone Twister® provided the best results when moderately polar and apolar compounds were extracted, compared to PDMS and Acrylate Twister®, which were able to extract only the more apolar compounds (% recovery values (%R) < 43%). However, it was demonstrated that even EG Silicone Twister® is still limited in terms of more polar analytes, achieving %R ranging from 24% to 80% for compounds with log $K_{o/w}$ > 3. Finally, a recent publication [16] has also described the use of EG Silicone Twister® for SBSE of a group of bisphenols in personal care products (PCPs) by SBSE(TD)-GC-MS, avoiding the need for a derivatisation step, which is frequently necessary using PDMS coating.

Even though there are still few publications reporting the use of these polar commercial stir bars, their SBSE performance could be improved in order to increase polar compound retention. For this reason, the following sections present the new polymeric phases recently developed in-house with polar behaviour and their analytical applications.

3. Novel in-house coatings for SBSE

Over the last few years, interest in novel SBSE coatings has grown significantly in order to promote the retention of polar compounds from complex matrices. To overcome the limitation of the commercial PDMS stir bar, the main requirements of the new SBSE coatings are the polarity of the coatings and mechanical stability. In Fig. 1, the most common approaches for synthesising in-house coatings for SBSE are detailed, such as sol-gel technology, the synthesis of monolithic materials, polyurethanes foams (PUFs), among others.

3.1. PDMS modified coatings

The first in-house SBSE coatings were based on PDMS and obtained, basically, by sol-gel technology. Using this methodology, high thermally and mechanically stable films with a long lifetime were obtained because of the strong chemical bonding between the coating and the surface of the glass bar [4,7,17].

As shown Fig. 1 (A), the sol-gel procedure consists of several reactions: starting with the hydrolysis of the coating precursors, followed by the polycondensation of the hydroxylated compounds and, finally, the chemical bonding of the coating to a glass bar, which is pre-treated to generate the superficial silanol groups [8,17,18]. Moreover, depending on the precursors used in the sol-gel reaction, the chemical properties of the final coating can be influenced to achieve the desired polarity. However, the sol-gel SBSE coatings are generally PDMS-based and a decrease in the affinity to polar compounds may be observed because of its apolar nature. Table 2 shows the structure of the monomers used in the synthesis of several sol-gel SBSE coatings and their subsequent application.

Liu *et al.* [19] were the first to synthesise an SBSE coating using the sol-gel procedure. In this study, the low polarity of the hydroxyl-terminated PDMS led to the extraction of a group of apolar compounds (n-alkanes, polycyclic aromatic hydrocarbons (PAHs)) and organophosphorus pesticides (OPPs) from aqueous samples. The authors highlighted the thermal stability and uniformity of the resulting coating, which are the principal advantages of this approach.

In order to promote the polarity of the SBSE coatings, Yu *et al.* [20,21] developed several in-house coatings by sol-gel technology using more polar sol-gel precursors. Among them, a novel combined stir bar coated with PDMS and poly(vinylalcohol) (PVA) was prepared to extract OPPs from honey [20]. With a higher surface area (21.25 m^2 g^{-1}) but lower thickness (30 μm) than the commercial PDMS stir bar (0.5 mm thick), this novel coating was able to reach equilibrium in

just 15 min for all of the compounds studied, providing slightly more sensitive and less time-consuming performance than SPME. In the same respect, the same authors also synthesised a similar coating based on PDMS, PVA and carbowax (CW) to determine volatile organic sulphur compounds (VOSCs) in waters [21]. The addition of CW and PVA enhanced the polarity of the coating and promoted the retention of more polar VOSCs. The authors stated that this novel coating showed a higher sorption capacity than carboxen-PDMS SPME fibres or PDMS stir bars. In another study, a novel sol-gel polar precursor, cyanopropyltriethoxysilane (CNPrTEOS), was combined with PDMS for the SBSE of two non-steroidal anti-inflammatory drugs (NSAIDs) from aqueous samples [22]. The cyano moieties present in the PDMS/CNPrTEOS coating were responsible for the extraction of relatively more polar compounds, such as diclofenac, while the PDMS moieties contributed to the extraction of a more apolar compound, such as ketoprofen.

Of the sol-gel precursors, a common PDMS modifier for enhancing polarity is β-cyclodextrin (β-CD). Several authors have frequently used PDMS and β-CD for the syntheses of coatings for the SBSE of brominated flame retardants in soil dust [23], steroid hormones in aqueous samples [24] and estrogens in pork and chicken [25], among others. As shown in Table 2, the structure of β-CD, which is a cyclic oligosaccharide, has become the main functional component for extracting these EOCs from complex matrices by SBSE thanks to its hydrophobic interior cavity and its hydrophilic exterior structure which is full of hydroxyl groups. For instance, Yu *et al.* [23] compared the synthesised coating based on PDMS/β-CD with the conventional PDMS and the former provided higher extraction efficiencies for brominated flame retardants when soil dust samples were analysed. Other authors have developed novel sol-gel SBSE coatings based on PDMS/β-CD/DVB to extract estrogens from pork and chicken samples [25], and based on PDMS/β-CD/phenyltrimethylsiloxane (PTMS) to extract steroid hormones from aqueous samples [24]. Using PDMS/β-CD/DVB to extract estrogens from tissue samples after a solid-liquid extraction, high recovery values were achieved (>70%) for all of the target analytes, due to the β-CD and DVB structures, enabling both hydrophilic

and Π-Π interactions, respectively. Furthermore, the sol-gel coating based on PDMS/β-CD/PTMS [24] provided higher selectivity and polarity due to the β-CD and PTMS structures compared to the commercial PDMS stir bar for extracting steroid hormones from water samples. To demonstrate this, the recovery values for all of the target compounds using the in-house coating were higher than 75%, while using the PDMS stir bar, the values ranged from 25% to 95% in ultrapure water.

Very recently, a sol-gel amino modified multi-walled carbon nanotubes-PDMS (AMMWCNTs-PDM) was first synthesised and used as a novel coating for the SBSE of phenols from environmental waters and soils [26]. Carbon nanotubes (CNTs) are very promising as adsorbents in SPE and SPME due to their thermal and chemical stability, their ease of functionalisation and large surface-to-volume ratio. The proposed SBSE coating offered higher extraction efficiencies for the studied analytes than the commercial PDMS coating, due to the Π-Π, electrostatic and hydrogen bonding interactions.

Apart from sol-gel technique, other coatings based on PDMS have been synthesised using a different strategy, in which a magnetic stirring rod was inserted into a Teflon mold containing the polymerisation mixture, including PDMS, a modifier and a curing agent, for several hours at high temperature. For instance, Barletta *et al.* [27] used activated carbon (ACB) as a modifier to extract polar pesticides from juice samples and Melo *et al.* [28] decided to use polypyrrole (PPY) as a modifier to determine antidepressants in plasma samples. In the latter study, the modifier PPY was demonstrated to be extremely suitable for the extraction of the studied compounds, as it was able to establish hydrogen bonding and Π-Π interactions with recovery values in 1 mL of plasma samples between 38% and 83% [28].

All of the above examples show how the polarity of SBSE coating using modifiers with polar functional groups is enhanced. However, all of them lack selectivity. Therefore, sol-gel technology was also proposed for synthesising molecularly

imprinted polymers (MIPs) for SBSE, but few publications have been reported. For instance, Si *et al.* [29] prepared a selective coating for molecularly imprinted stir bar sorptive extraction (MISBSE) by the sol-gel technique using nicosulfuron (sulfonylurea herbicide) as a template, methacrylic acid (MAA) as the functional monomer and methacryloxypropyltrimethoxysilane (MPTMS) as the crosslinker. The authors emphasised the high mechanical strength and efficiency of the developed sol-gel MIP coating, which provided good recoveries (96%) and high selectivity in comparison with non-imprinted polymer (NIP) when 25 mL of tap water was extracted over 2 h. Another example of an MISBSE coating using sol-gel technique is a dummy MIP for the extraction of bisphenol A from tap water [30]. In this study, a structural analogue similar to bisphenol A was used as a template in order to avoid possible leakage of the residual template molecules, which could interfere with the determination of trace amount of bisphenol A. As a result, a homogenous and stable coating surface was obtained with a thickness of 57 μm, showing high selectivity toward bisphenol A and high recovery values (>80%) in comparison with those obtained using the conventional PDMS coating (<20%). Although these two studies highlighted the promising MISBSE performance in terms of recovery values and selectivity, a washing or clean-up step was not included in their performance, making them susceptible to interfering compounds when analysing complex matrices.

3.2. Monolithic coatings

Over the last few years, there has been growing interest in the use of monolithic materials as SBSE coatings due to their numerous advantages: large pore structures, high permeability, high availability of commercial monomers with different polarities and functionalities and, in particular, simple and inexpensive preparation. Furthermore, monoliths have widely been applied as alternative stationary phases in LC and capillary electrochromatography (CEC) as well as extraction sorbents for several extraction techniques, such as SPE and SPME [31,32].

The preparation of a monolith consists of a polymerisation mixture, including adequate monomers (functional monomers and crosslinker), porogenic solvents and initiators, in an appropriate ratio, which is introduced into the desired mould and is initiated thermally or by UV radiation. Therefore, depending on the shape and size of the mould, SBSE coatings with a higher volume of extracting phase can be obtained and, consequently, an increase in capacity and recovery values may be observed [4,7]. In the synthesis of a monolithic coating for SBSE, apart from the mould, other important parameters should be taken into account to obtain the desired final product, such as the choice of monomers for enhancing the polarity of the coating and the porogenic solvent used for forming large pores in the monolithic structure and promoting high permeability. Therefore, the monolithic approach has become a successful option for obtaining chemically and physically stable coatings for SBSE [8].

In the monolithic approach, two different strategies have been developed for fixing the coating to the glass bar: chemical or physical attachment. The procedures for synthesising monolithic coatings using either chemical or physical attachment are detailed in Fig. 1 (B) and Fig. 1 (C), respectively, and are discussed in the following sections.

3.2.1. Monolithic coatings by chemical attachment

The chemical attachment of a monolithic SBSE coating has been extensively used, consisting of the treatment of the glass surface of the bar in order to create double bonds through a silanisation agent and, then, the subsequent growing of the polymer to obtain the final coating, as shown Fig. 1 (B). Huang *et al.* [33] synthesised the first chemically attached monolithic coating for the SBSE of PAHs and steroid hormones from seawater and urine samples, respectively. The proposed monolithic coating was based on octyl methacrylate (OcMA) as the functional monomer and ethylene dimethacrylate (EDMA) as the crosslinker. Both

monomers with ester groups in their structure (Table 2) favoured the transfer of the polar analytes to the coating. In this study, the final dimension of the monolithic coating was evaluated and it was demonstrated that higher thickness led to higher adsorptive capacity. However, the desorption step took 2 h to release the extracted analytes, which is quite long in terms of desorption time. Moreover, the monomers to porogen ratio was also studied (40/60, 45/55 and 50/50, (%, w/w)) and it was observed that a decrease of the porogen content led to a polymer with small pore size and low permeability and, in view of this, the monomers to porogen ratio was kept to 40/60 (%, w/w).

Since 2007, Huang and coworkers have synthesised several polar monoliths as SBSE coatings by chemical bonding. For instance, a novel polar stir bar coated with vinylimidazole (VI) and DVB was developed for the extraction of sulphonamides from milk [34]. Due to the imidazole groups in the monomer structure, hydrogen bonds and hydrophobic interaction were established with the polar analytes (log $K_{o/w}$<1.6), providing higher extraction capacity and lower MDLs than the commercial PDMS stir bar. Furthermore, Huang *et al.* [35] synthesised three in-house monolithic coatings for the SBSE of polar aromatic amines (PAAs) from lake and sea waters. The proposed coatings were based on VI and DVB, vinylpyrrolidone (VPD) and DVB and, finally, vinylpyridine (VP) and EDMA. Their SBSE performance was subsequently compared between them, as well as with the commercial PDMS coating. Fig. 2 shows the extraction of PAAs from water samples using the in-house and the commercial PDMS SBSE coatings under the same conditions (2.5 h and 1h as extraction and desorption times, respectively). The target compounds, PAAs with log $K_{o/w}$ <2.7, were successfully extracted using all three in-house coatings, in contrast to the PDMS coating, which completely failed, since only hydrophobic interactions contributed to the extraction of PAAs. Of the three in-house coatings, the VI/DVB provided the best extraction efficiencies for all PAAs (57-114 %), due to the imidazole and phenyl groups in its structure.

More recently, a new monolithic SBSE coating was synthesised using two less common monomers but with high polar functionalities: vinylphthalimide (VPH) as the functional monomer and *N,N'*-methylenebisacrylamide (MBAA) as the crosslinker [36]. This novel coating was applied for the SBSE of two benzimidazoles (oxfendazole and mebendazole) in milk and honey samples. Thanks to the hydrophilic and Π-Π interactions established by these monomers, promising SBSE performance was achieved for both compounds with recovery values between 71% and 102% when 5 mL of milk and 2.5 g of honey were extracted for 2.5 h, with a significant improvement compared to the conventional PDMS coating. Moreover, the authors evaluated the porogen content and observed that lower porogen content in the polymerisation mixture led to lower peak areas of the analytes due to a decrease in the pore size and thus, in the permeability of the polymer.

In order to enhance the extraction of polar compounds with carboxyl or amino functional groups, anion- or cation-exchange monolithic coatings have been required for SBSE over the last few years. In this respect, the combination of the monomers acrylic acid (AA) with EDMA and methacrylic acid-3-sulphopropyl ester potassium salt (MASPE) with DVB (structures shown in Table 2) have been used to synthesise cation-exchange monolithic SBSE coatings and apply them to the analysis of soluble cations in milk [37] and nitroimidazole antibiotics in honey [38], respectively. Using MASPE/DVB coating, the authors highlighted that the sulphonic and phenyl groups present in the monolithic structure were essential for the extraction of polar nitroimidazole antibiotics from honey, which had a log $K_{o/w}$ ranging from -0.38 to 0.31. This novel coating with strong cation-exchange behaviour enabled better SBSE performance than the PDMS coating, with high extraction efficiencies (%R > 71%), great enhancement of the peak height and, as a result, lower MDLs. However, with the analytes being retained by ion-exchange interactions, no washing or clean-up step with organic solvent was included in the SBSE protocol to remove interferences from the matrix, which is the recommended protocol for ion-exchange materials.

3.2.2. Monolithic coatings by physical attachment

As mentioned earlier, the synthesis of monolithic SBSE coatings can be also achieved using physical attachment. While the polymerisation procedure for obtaining the desired product was the same as those described previously, the immobilisation of the coating on the glass bar was significantly easier than with the chemical attachment, without losing mechanical stability. As can be seen in Fig. 1 (C), the stir bar set-up consists of a glass bar introduced in an iron spring to give stability to the whole monolithic coating. Subsequently, the stir bar and the spring were together placed in a glass tube (with the desired dimensions) and immersed in the polymerisation mixture.

To demonstrate the viability of this novel monolithic approach, our research group pioneered this strategy and synthesised several monolithic SBSE coatings. Bratkowska *et al.* [39,40] developed two monolithic coatings for extracting polar PPCPs from environmental waters by SBSE(LD)-LC-MS/MS. The monolithic coatings were based on VPD [39] and MAA [40] as functional monomers and DVB as the crosslinker. Using the VPD/DVB coating, great results were obtained for all the studied compounds in terms of recovery values in 50 mL of ultrapure water (42-110%) after being extracted for 4 h. In addition, better SBSE performance was achieved using the MAA/DVB coating, which provided excellent recovery values in ultrapure water (61-107%). In both cases, the highly polar analytes, such as paracetamol and caffeine, were poorly recovered (9-45%). These promising results were compared with those obtained using the commercial PDMS coating, in which the studied analytes were hardly recovered. Therefore, the high potential of these two monolithic coatings for the extraction of polar compounds was demonstrated, which may be attributed to the nitrogen and oxygen atoms and to the phenyl groups, being able to establish hydrogen bonds and hydrophobic interactions, as can be seen in Table 2. Following the corresponding procedure, the same research group synthesised another monolithic SBSE coating using two novel monomers: poly(ethyleneglycol) methacrylate (PEGMA) as the functional monomer and

pentaerythritol triacrylate (PETRA) as the crosslinker [41]. This monolithic material contained a great number of hydroxyl and ester groups, providing a polar SBSE coating for extracting PPCPs from wastewater samples. Using PEGMA/PETRA coating, even the recovery values for the studied analytes in ultrapure water were slightly lower than those achieved with the MAA/DVB and VPD/DVB coatings, the analytes were almost fully extracted in just 1 h. Moreover, these results were much better than those provided by the commercial polar coatings (EG Silicone Twister® and Acrylate Twister®) under their optimised SBSE conditions.

3.2.3. MIPs as monolithic coatings for SBSE

As mentioned previously in section 3.1, MIPs have recently gained popularity as SBSE coatings in order to promote selectivity. In this respect, a higher number of studies have been reported in which MIPs were synthesised as monolithic coatings for MISBSE application rather than using the sol-gel methodology. The classic approach for obtaining MIPs was the copolymerisation of an appropriate template, functional monomer and crosslinker in a suitable porogenic solvent. Subsequently, the MIP could be chemically or physically attached to a glass bar. Thus, Xu *et al.* [42] were the first to synthesise a monolithic SBSE coating with a MIP for ractopamine chemically attached. In this study, the silanisation reagent, the crosslinker, the functional monomer and the template were 3-(methacryloxy)propyltrimethoxysilane (MPTS), EDMA, MAA and ractopamine, respectively. Finally, the MISBSE coating was successfully applied for the extraction of a group of β_2-agonists from pork, liver and feed samples, achieving recovery values between 74% and 93%. The same research group applied this synthetic procedure to obtain several coatings for the MISBSE of triazine herbicides from food and soil samples [43], and trimethoprim from biological samples [44], among others. The authors highlighted the good mechanical and chemical stability, selectivity and physical properties (homogenous and porous) of the resulting MISBSE coatings. It should be highlighted that, in these studies, the proposed MISBSE procedures were not able to offer a washing step to reduce interfering

compounds and, consequently, losses in selectivity and sensitivity could be observed. Therefore, efforts should focus on the development of completely selective MISBSE coatings through effective washing and loading steps.

An interesting study was developed by Turiel *et al.* [45], who proposed both physical and chemical attachment of a monolithic coating for the MISBSE of thiabendazole from citrus samples. While the chemical attachment of the coating was the same as those described above, physical attachment was achieved by pre-treating the glass bar with a commercial epoxy adhesive and then immersing it in a vial containing MIP particles. Although the physical attachment of the MIP coating was easier to perform than the chemical one, the former procedure was not completely able to obtain a homogenous immobilisation of the MIP particles onto the glass bar surface. Besides, the chemically attached MISBSE coating allowed the performance of selective loading and washing steps to remove all of the interferences bonded by non-specific interactions to the MIP.

3.3. Other sorptive materials and formats

Apart from these two main approaches, other novel strategies and synthetic routes have been developed to obtain coatings for SBSE, such as PUFs or immersion precipitation technique.

PUFs are defined as plastic materials and are easily obtained by combining all of the required reagents (an isocyanate, a polyol (or polyalcohol), expansion agents, catalysts and surfactants), as described in Fig. 1 (D). After polymerisation, the PUFs were cleaned with an organic solvent and cut to the desired shape and dimensions. Thus, these materials offered high chemical stability, flexibility and simplicity, being really promising as SBSE coatings. Nogueira's research group was the first to develop and apply PUFs, using different polyol types, in the SBSE of organic compounds from aqueous matrices [46]. In this study, high stability and mechanical resistance to organic solvents were the main advantages of PUF

coatings, providing better SBSE recoveries for the studied compounds (25-70%) than the PDMS coating (5-25%). In addition, the same research group developed several SBSE coatings based on PUFs for extracting triazine herbicides [47] or acidic pharmaceuticals [48] from water samples.

A novel and simple synthesis of SBSE coatings was developed by Guan *et al.* [49], who were the first to develop a high thermally stable polar coating based on poly(phthalazine ether sulfone ketone) (PPESK) using the immersion precipitation technique. As detailed in Fig 1. (E), the synthesis consisted of the precipitation of the polymer (PPESK) when the glass bar was immersed in the polymer solution in a water bath at room temperature. The PPESK coating was applied to extract organochlorine compounds from seawaters and OPPs from juices. When the PPESK coating was evaluated, better selectivity towards both organochlorine compounds and OPPS was observed in comparison with the PDMS coating, due to its high number of carbonyl and aromatic groups enabling both hydrogen bonds and hydrophobic interactions. Moreover, the novel PPESK coating also presented higher extraction capacity for OPPs (%R=7-66%) than an SPME fibre coated with PPESK (%R<7%), thanks to its higher thickness (250 μm for PPESK coating and 30 μm for PPESK SPME fibre).

Since 2009, other formats have been designed to solve one of the main drawbacks of the in-house coatings for SBSE, namely the direct contact of the coating with the vessel when immersion sampling is applied. To solve this problem, several in-house and alternative sorptive extractions have been proposed recently, such as rotating disk sorptive extraction (RDSE), stir rod sorptive extraction (SRSE), stir cake sorptive extraction (SCSE) and two adsorptive microextraction techniques (AμE) (bar adsorptive microextraction (BAμE) or multi-sphere adsorptive microextraction (MSAμE)). Fig. 3 details the different sorptive extraction devices of each novel technique. The first attempt to improve SBSE was RDSE (Fig. 3 (A)), in which the coating is immobilised onto the upper surface of the rotating disk. This novel format prevented damage by physical contact and, consequently, was used to perform at

least 50 experiments. However, the only extracting phase used in RDSE was PDMS for extracting nonylphenol, pesticides and chromogenic organic compounds from waters [50-52]. With respect to SRSE (Fig. 3 (B)), a metal rod containing a magnet at the end is coated with the sorptive material, usually a monolithic polymer, and fixed in the sample vessel. For instance, Luo *et al.* [53] synthesised a polar monolith based on VP and EDMA for the SRSE of NSAIDs from water and sewage sludge samples, providing successful recovery values (>76%) and no damage to sorptive material after at least 60 experiments. More recently, in 2011, Huang *et al.* [54] also applied monolithic materials to develop the novel SCSE, similar to RDSE. As shown in Fig. 3 (C), the monolith is synthesised in a circular mould with the desired thickness containing an iron wire to stir and enhance the transfer of the analytes to the extracting phase without friction loss of the monolith. Different monoliths have been synthesised to be applied in SCSE, such as one based on VI and DVB for extracting steroid hormones from milk [54] and a polymeric ionic liquid-based monolith for extracting six preservatives from juices [55]. In both studies, the authors highlighted the feasibility of the novel technique, obtaining good recovery values (63-117%) and, in particular, higher longevity of the extracting phase than in SBSE.

With respect to adsorptive microextraction (AμE) techniques, Nogueira's research group has developed novel approaches in this area, such as the BAμE and MSAμE techniques [2]. As detailed in Fig. 3 (D), BAμE consists of a floating bar covered with a powdered sorbent, while MSAμE consists of coating polystyrene spheres (attached by a thread) with powdered sorbent. The most commonly used sorptive materials are activated carbons and polystyrene-DVB for extracting polar solutes and metabolites from aqueous samples [56,57]. For example, when caffeine and acetaminophen, two extremely polar EOCS, were extracted using both MSAμE and BAμE with activated carbons, high recovery values were obtained (>80%), whereas the conventional PDMS coating for SBSE was completely unable to extract them [56]. However, these techniques have not been widely applied and few publications are available in the literature.

5. Conclusions

SBSE is a well-accepted sorptive extraction technique for preconcentrating a great variety of compounds from many different complex matrices. Despite the high number of SBSE applications in the literature, most have been aimed at extracting compounds with low polarities, due to the only commercial coating for SBSE being based on PDMS with an apolar nature. In recent years, promising strategies have been proposed to overcome this limitation, such as sol-gel technology, monolithic materials, among others. These novel approaches have provided high versatility to SBSE, since a broad range of commercial monomers with different polarities can be used during the coating synthesis, promoting the extraction of more polar EOCs.

Moreover, other important factors to take into account in SBSE have been extensively evaluated, such as mechanical, thermal or chemical stability and the physical dimensions of the coatings, providing successful SBSE performance in comparison with the conventional PDMS coating. Although promising in-house polar coatings for SBSE have been developed, new polar monomers and novel formats need to be exploited more in order to extract polar EOCs from complex matrices.

Acknowledgements

The authors thank the Ministry of Science and Innovation (CTQ2011-24179) and the Department of Innovation, Universities and Enterprises (Project 2009 SGR 223) for financial support. N. Gilart would also like to thank the Department of Innovation, Universities and Enterprises and the European Social Fund for a predoctoral grant (FI-DGR 2011).

References

[1] M. Farré, S. Pérez, C. Gonçalves, M.F. Alpendurada, D. Barceló, TrAC, Trends Anal. Chem. 29 (2011) 1347.
[2] J.M.F. Nogueira, Anal. Chim. Acta 757 (2012) 1.
[3] L. Ramos, J. Chromatogr. A 1221 (2012) 84.
[4] A. Prieto, O. Basauri, R. Rodil, A. Usobiaga, L.A. Fernández, N. Etxebarria, O. Zuloaga, J. Chromatogr. A 1217 (2010) 2642.
[5] M. Kawaguchi, R. Ito, H. Nakazawa, A. Takatsu, in J. Pawliszyn (Editor), Comprehensive Sampling and Sample Preparation, 2012, p. 797.
[6] E. Baltussen, P. Sandra, F. David, C. Cramers, J. Microcol. Sep. 11 (1999) 737.
[7] I. Rykowska, W. Wasiak, Acta Chromatogr. 25 (2013) 27.
[8] R. Lucena, Anal. Bioanal. Chem. 403 (2012) 2213.
[9] F. Sánchez-Rojas, C. Bosch-Ojeda, J. Cano-Pavón, Chromatographia 69 (2009) 79.
[10] M. Kawaguchi, A. Takatsu, R. Ito, H. Nakazawa, TrAC, Trends Anal. Chem. 45 (2013) 280.
[11] M. Kawaguchi, R. Ito, K. Saito, H. Nakazawa, J. Pharm. Biomed. Anal. 40 (2006) 500.
[12] F. David, P. Sandra, J. Chromatogr. A 1152 (2007) 54.
[13] E. Fries, Anal. Chim. Acta 689 (2011) 65.
[14] B. Sgorbini, C. Cagliero, C. Cordero, E. Liberto, P. Rubiolo, M.R. Ruosi, C. Bicchi, J. Chromatogr. A 1265 (2012) 39.
[15] N. Gilart, N. Miralles, R.M. Marcé, F. Borrull, N. Fontanals, Anal. Chim. Acta 774 (2013) 51.
[16] J.I. Cacho, N. Campillo, P. Viñas, M. Hernández-Córdoba, J. Pharm. Biomed. Anal. 78-79 (2013) 255.
[17] A. Kabir, K.G. Furton, A. Malik, TrAC, Trends Anal. Chem.45 (2013) 197.
[18] W.A.W. Ibrahim, W.N.W. Ismail, A.S.A. Keyon, M.M. Sanagi, J. Sol-Gel Sci. Technol. 58 (2011) 602.
[19] W.M. Liu, H.M. Wang, Y.F. Guan, J. Chromatogr. A 1045 (2004) 15.
[20] C.H. Yu, B. Hu, J. Sep. Sci. 32 (2009) 147.

606 [21] C.H. Yu, X. Li, B. Hu, J. Chromatogr. A 1202 (2008) 102.
607 [22] W.A.W. Ibrahim, A.S.A. Keyon, N. Prastomo, A. Matsuda, J. Sol-Gel Sci.
608 Technol. 59 (2011) 128.
609 [23] C.H. Yu, B. Hu, J. Chromatogr. A 1160 (2007) 71.
610 [24] S.V. Duy, P.B. Fayad, B. Barbeau, M. Prevost, S. Sauve, Talanta 101 (2012)
611 337.
612 [25] C. Hu, M. He, B.B. Chen, B. Hu, J. Agric. Food Chem. 60 (2012) 10494.
613 [26] C. Hu, B. Chen, M. He, B. Hu, J. Chromatogr. A 1300 (2013) 165.
614 [27] J.Y. Barletta, P. Gomes, A.J. dos Santos-Neto, F.M. Lancas, J. Sep. Sci. 34
615 (2011) 1317.
616 [28] L.R. Melo, A.M. Nogueira, F.M. Lancas, M.E.C. Queiroz, Anal. Chim. Acta
617 633 (2009) 57.
618 [29] B.J. Si, J. Zhou, Chin. J. Chem. 29 (2011) 2487.
619 [30] N. Sheng, F. Wei, W. Zhan, Z. Cai, S. Du, X. Zhou, F. Li, Q. Hu, J. Sep. Sci.
620 35 (2012) 707.
621 [31] R.D. Arrua, M. Talebi, T.J. Causon, E.F. Hilder, Anal. Chim. Acta 738 (2012)
622 1.
623 [32] L. Xu, Z.G. Shi, Y.Q. Feng, Anal. Bioanal. Chem. 399 (2011) 3345.
624 [33] X.J. Huang, D.X. Yuan, J. Chromatogr. A 1154 (2007) 152.
625 [34] X.J. Huang, N.N. Qiu, D.X. Yuan, J. Chromatogr. A 1216 (2009) 8240.
626 [35] X.J. Huang, N.N. Qiu, D.X. Yuan, Q.M. Lin, J. Chromatogr. A 1216 (2009)
627 4354.
628 [36] X.J. Huang, L.L. Chen, D.X. Yuan, X.B. Luo, J. Sep. Sci. 34 (2011) 3418.
629 [37] X.J. Huang, J.B. Lin, D.X. Yuan, Analyst 136 (2011) 4289.
630 [38] X.J. Huang, J.B. Lin, D.X. Yuan, J. Sep. Sci. 34 (2011) 2138.
631 [39] D. Bratkowska, R.M. Marcé, P.A.G. Cormack, F. Borrull, N. Fontanals, Anal.
632 Chim. Acta 706 (2011) 135.
633 [40] D. Bratkowska, N. Fontanals, P.A.G. Cormack, F. Borrull, R.M. Marcé, J.
634 Chromatogr. A 1225 (2012) 1.
635 [41] N. Gilart, P.A.G. Cormack, R.M. Marcé, F. Borrull, N. Fontanals, J.
636 Chromatogr. A 1295 (2013) 42.

[42] Z.G. Xu, Y.F. Hu, Y.L. Hu, G.K. Li, J. Chromatogr. A 1217 (2010) 3612.
[43] Y.L. Hu, J.W. Li, Y.F. Hu, G.K. Li, Talanta 82 (2010) 464.
[44] Z.G. Xu, Z. Du, Y.L. Hu, Y.F. Hu, Y.P. Pan, G.K. Li, Chin. J. Anal. Chem. 40 (2012) 1002.
[45] E. Turiel, A. Martín-Esteban, J. Sep. Sci. 35 (2012) 2962.
[46] N.R. Neng, M.L. Pinto, J. Pires, P.M. Marcos, J.M.F. Nogueira, J. Chromatogr. A 1171 (2007) 8.
[47] F.C.M. Portugal, M.L. Pinto, J.M.F. Nogueira, Talanta 77 (2008) 765.
[48] A.R.M. Silva, F.C.M. Portugal, J.M.F. Nogueira, J. Chromatogr. A 1209 (2008) 10.
[49] W. Guan, Y.J. Wang, F. Xu, Y.F. Guan, J. Chromatogr. A 1177 (2008) 28.
[50] A. Giordano, P. Richter, I. Ahumada, Talanta 85 (2011) 2425.
[51] P. Richter, A. Canas, C. Munoz, C. Leiva, I. Ahumada, Anal. Chim. Acta 695 (2011) 73.
[52] P. Richter, C. Leiva, C. Choque, A. Giordano, B. Sepulveda, J. Chromatogr. A 1216 (2009) 8598.
[53] Y.B. Luo, H.B. Zheng, J.X. Wan, Q. Gao, Q.W. Yu, Y.Q. Feng, Talanta 86 (2011) 103.
[54] X.J. Huang, L.L. Chen, F.H. Lin, D.X. Yuan, J. Sep. Sci. 34 (2011) 2145.
[55] F.H. Lin, S.Y. Nong, X.J. Huang, D.X. Yuan, Anal. Bioanal. Chem. 405 (2013) 2077.
[56] N.R. Neng, A.R.M. Silva, J.M.F. Nogueira, J. Chromatogr. A 1217 (2010) 7303.
[57] C. Almeida, J.M.F. Nogueira, J. Chromatogr. A 1265 (2012) 7.

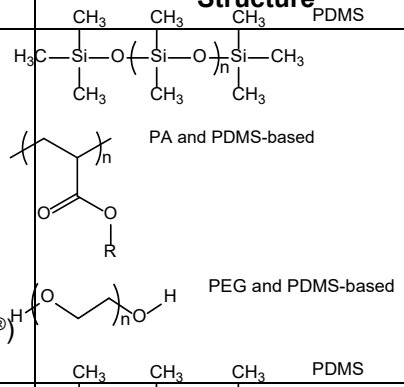
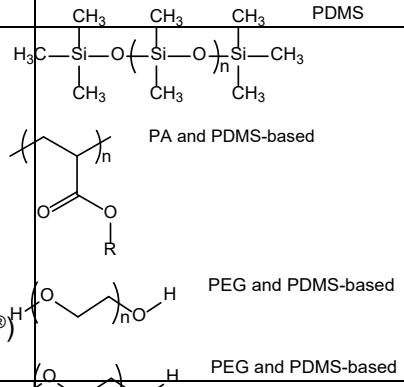
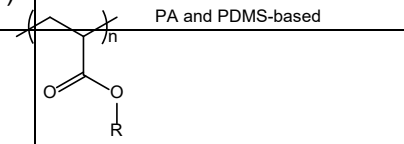
Figure captions

Fig. 1. Schematic representation of the most common strategies to obtain coatings for SBSE.

Fig. 2. HPLC chromatograms of five polar aromatic amines (PAAs) in a standard solution and being extracted using four in-house coatings and the commercial PDMS coating for SBSE. Peaks: 1 = *p*-Nitroaniline (*p*-NA); 2 = aniline (A); 3 = 2,4-dinitroaniline (2,4-DNA); 4 = *o*-chloroaniline (*o*-CA); 5 = 3,4-dichloroaniline (3,4-DCA). Reproduced from [35] with permission of Elsevier.

Fig. 3. Schematic representation of several novel sorptive extraction formats and devices: a) Rotating disk sorptive extraction (RDSE); b) Stir rod sorptive extraction (SRSE); c) Stir cake sorptive extraction (SCSE) and d) Adsorptive micro-extraction techniques (AμE). Reproduced [??] with permission of Elsevier.

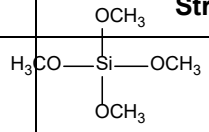
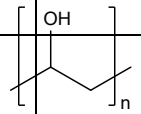
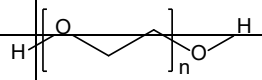
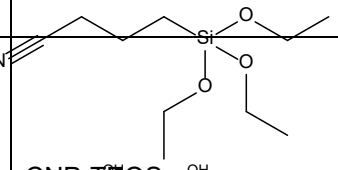
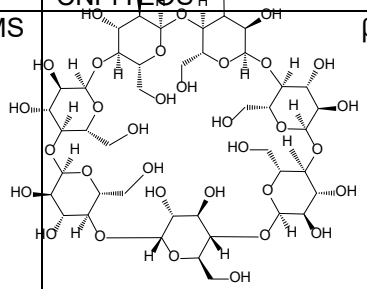
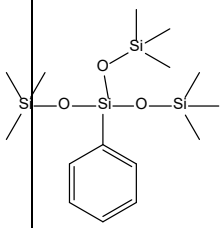
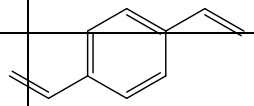
681 **Table 1.** Structures and application of novel commercially available coatings for SBSE.
682

Coating Phase*	Structure	Analyte	Matrix	Sampling Mode	Desorption	Analysis	Ref.
PDMS (Twister®) PA (Acrylate Twister®) PEG (EG Silicone Twister®)		VOCs	Food and cosmetic	Immersion /HS	TD	GC-MS	[14]
PDMS (Twister®) PA (Acrylate Twister®) PEG (EG Silicone Twister®)		PPCPs	Wastewater	Immersion	LD	LC-MS/MS	[15]
PEG (EG Silicone Twister®)		Bisphenols	PCPs	Immersion	TD	GC-MS	[16]
PA (Acrylate Twister®)		Benzothiazole	Untreated wastewater	Immersion	TD	GC-MS	[13]

*Commercial name in brackets
GC-MS: gas chromatography-mass spectrometry; HS: head space; LD: liquid desorption; LC-MS/MS: liquid chromatography-tandem mass spectrometry; PA: polyacrylate; PCPs: personal care products; PEG: poly(ethylene)glycol; PPCPs: pharmaceuticals and personal care products; TD: thermal desorption; VOCs: volatile organic compounds;

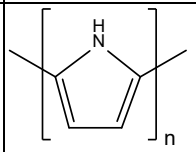
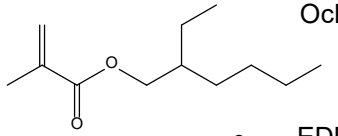
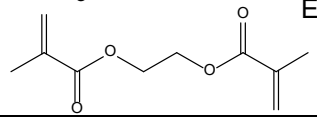
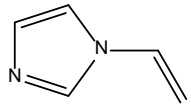
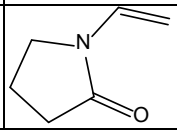
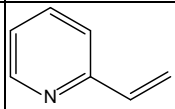
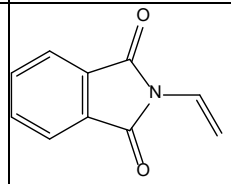
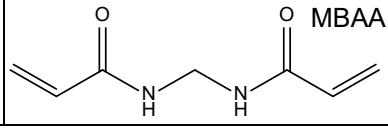
683
684
685
686

687 **Table 2.** Structures, synthesis approach and applications of some in-house coatings for SBSE.
688

Polymer	Structure	Preparation technique	Analytes	Matrix	Analysis	Ref.
PDMS/MTMS	 MTMS	Sol-gel	n-alkanes, PAHs, OPPs	Water	GC-FID	[19]
PDMS/PVA	 PVA	Sol-gel	OPPs	Honey	GC-FPD	[20]
PDMS/CW/PVA	 CW	Sol-gel	VOSs	Water	GC-FPD	[21]
PDMS/CNPrTEOS	 CNPrTEOS	Sol-gel	NSAIDs	Water	CE-UV	[22]
PDMS/β-CD/PTMS	 β-CD  PTMS	Sol-gel	Steroid hormones	Water	LDTD-APCI-MS/MS	[24]
PDMS/β-CD/DVB	 DVB	Sol-gel	Estrogens	Pork and chicken	LC-UV	[25]

689

690 **Table 2.** Continued.
691

Polymer	Structure	Preparation technique	Analytes	Matrix	Analysis	Ref.
PDMS/PPY	PPY 	Copolymerisation	Antidepressants	Plasma	LC-UV	[28]
OcMA/EDMA	OcMA  EDMA 	Monolith (Chemical attachment)	PAHs/Steroid hormones	Sea /Urine	LC-UV	[33]
VI/DVB	VI 	Monolith (Chemical attachment)	PAAs	Lake and sea	LC-UV	[35]
VPD/DVB	VPD 	Monolith (Chemical attachment)	PAAs	Lake and sea	LC-UV	[35]
VP/EDMA	VP 	Monolith (Chemical attachment)	PAAs	Lake and sea	LC-UV	[35]
VPH/MBAA	VPH  MBAA 	Monolith (Chemical attachment)	Benzimidazoles	Milk and honey	LC-UV	[36]

692
693
694

695 **Table 2.** Continued
696

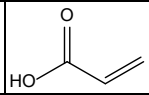
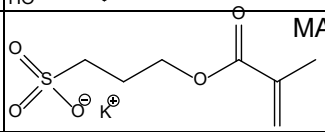
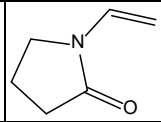
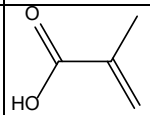
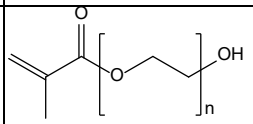
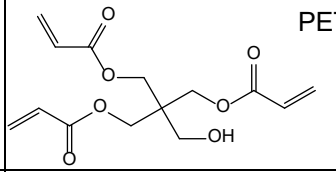
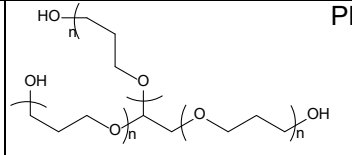
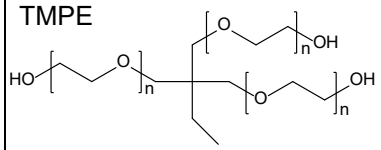
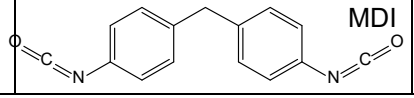
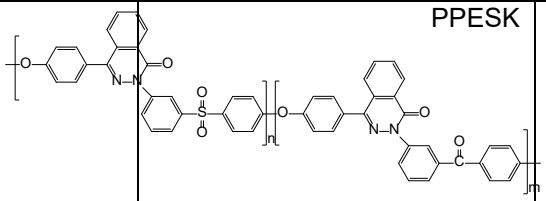
Polymer	Structure	Preparation technique	Analytes	Matrix	Analysis	Ref.
AA/EDMA	AA 	Monolith (Chemical attachment)	Soluble cations	Milk	IC-ECD	[37]
MASPE/DVB	MASPE 	Monolith (Chemical attachment)	Nitroimidazoles	Honey	LC-UV	[38]
VPD/DVB	VPD 	Monolith (Physical attachment)	PPCPs	Environmental waters	LC-MS/MS	[39]
MAA/DVB	MAA 	Monolith (Physical attachment)	PPCPs	Environmental waters	LC-MS/MS	[40]
PEGMA/PETRA	PEGMA  PETRA 	Monolith (Physical attachment)	PPCPs	Environmental waters	LC-MS/MS	[41]
PPG/TMPE/MDI	PPG  TMPE  MDI 	PU foams (Physical attachment)	Triazine herbicides	Water samples	LC-UV	[47]

Table 2. Continued.

Polymer	Structure	Preparation technique	Analytes	Matrix	Analysis	Ref.
PPESK	 PPESK	Immersion precipitation	Organochlorine compounds/OPPs	Sea waters/Juices	GC-ECD/GC-TSD	[49]

ACB: activated carbon; β-CD: β-cyclodextrin; CE-UV: capillary electrophoresis-ultraviolet detection; CNPrTEOS: cyanopropyltriethoxysilane; CW: carbowax; DVB: divinylbenzene; EDMA: ethylene dimethacrylate; GC-ECD: gas chromatography-electron capture detector; GC-FID: gas chromatography-flame ionisation detection; GC-FPD: gas chromatography-flame photometric detection; GC-MS: gas chromatography-mass spectrometry; GC-TSD: gas chromatography- thermionic specified detector; IC-ECD: ion chromatography-electrochemical detector; LC-MS/MS: liquid chromatography-tandem mass spectrometry; LC-UV: liquid chromatography-ultraviolet detection; LDTD-APCI-MS/MS: laser diode thermal desorption-atmospheric pressure chemical ionization-tandem mass spectrometry; MAA: methacrylic acid; MASPE: methacrylic acid-3-sulphopropyl ester potassium salt; MBAA: *N,N'*-methylenebisacrylamide; MDI: 4,4'-methylene bisphenyl diisocyanate; MTMS: methyltrimethoxysilane; OcMA: octyl methacrylate; PDMS: polydimethylsiloxane; PEGMA: poly(ethyleneglycol) methacrylate; PETRA: pentaerythritol triacrylate; PPESK: polyphatalazine ether sulfone ketone; PPG: glycerol propoxylate; PPY: polypyrrole; PTMS: phenyltrimethylsiloxane; PVA: poly(vinylalcohol); TMPE: trimethylolpropane ethoxylate; VI: vinylimidazole; VP: vinylpyridine; VPD: vinylpyrrolidone; VPH: vinylphthalimide;

Figure 1

(A) Sol-gel process
(B) Monoliths (chemical attachment)
(C) Monoliths (physical attachment)
(D) PUs
(E) Immersion Precipitation
1 Hydrolysis of the glass bar
1) NaOH
2) HCl
2 Hydrolysis (1) and polycondensation (2) of coating precursors
Acidic medium
3 Growing sol-gel network with a sol-gel active organic polymer (OH-TPDMS)
OH-TPDMS
4 Chemical bonding of the coating to the silanated glass bar
[ART2-56]
1 Hydrolysis of the glass bar
1) NaOH
2) HCl
2 Silanisation of the glass bar
1) γ-MAPS
3 Immersion of the glass bar in the polymerisation mixture
Functional monomer + Crosslinker + Porogen
4 Traditional polymerisation (chemical attachment)
Thermal initiation
(oil or water bath)
or UV initiation (UV lamp)
↑ Time (≈ 24 h)
5 Remove from the vial and result SBSE coating
Final coating
[ART2-58]
1 Polymerisation mixture
Functional monomer + Crosslinker + Porogen
2 Immersion of the glass tube and bar
3 Traditional polymerisation (physical attachment)
Thermal initiation
60°C for 36-48 h
4 Removal of the glass tube and resulting SBSE coating
Final coating
[ART2-40]
1 Polymerisation mixture
1 or more polyols + Silicone + Isocyanate + Water + Catalyst
2 Formation of PU foam
Oven
(60°C for 24h)
3 Cleaning and giving shape to the PU foam
A desired PU cylinder
4 Insertion of the glass bar in the PU cylinder
Final coating
[ART2-328]
1 Selection of the polymer: Poly(phthalazine ether sulfone ketone) (PPESK)
2 Dissolve PPESK in a suitable solvent
PPESK + N-methyl-2-pyrrolidone (NMP) (solvent)
3 Precipitation of the coating
Water bath (at room T° for 12h)
4 Cleaning of the final coating by drying
Final coating
[ART2-327]

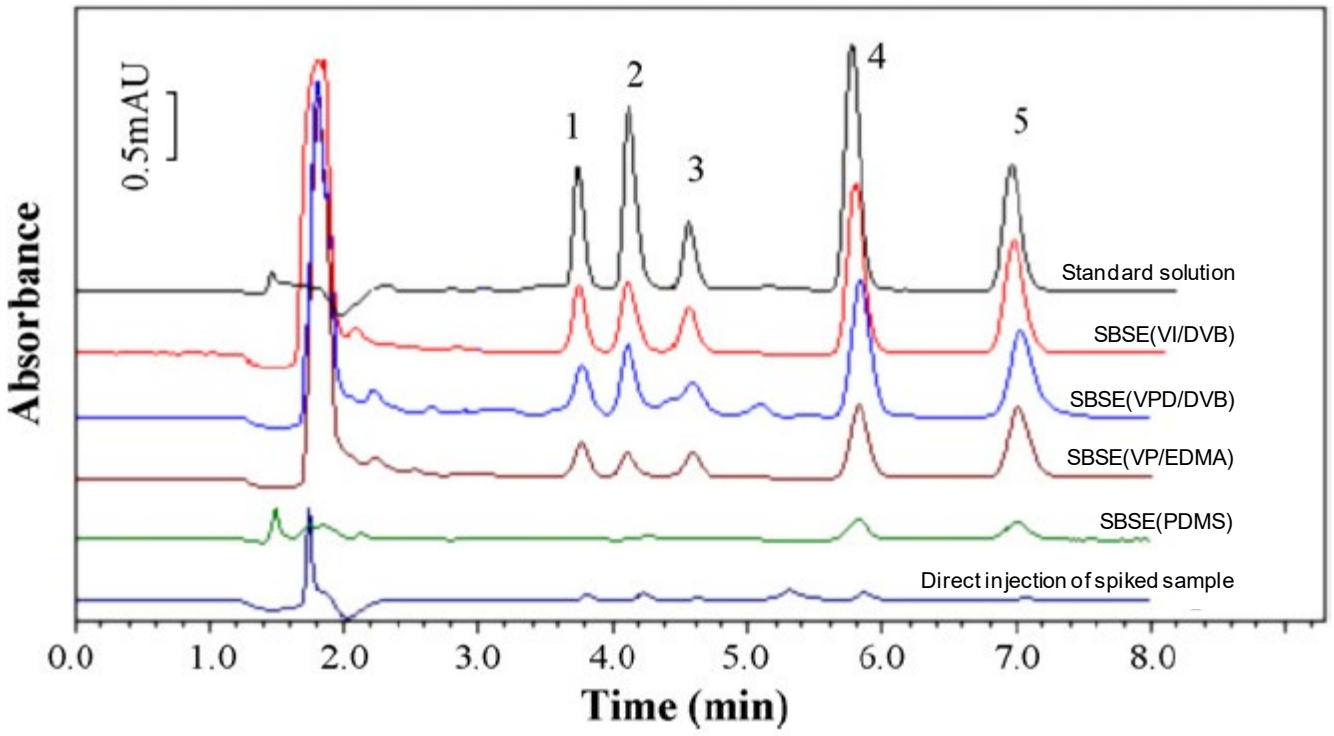


Figure 2

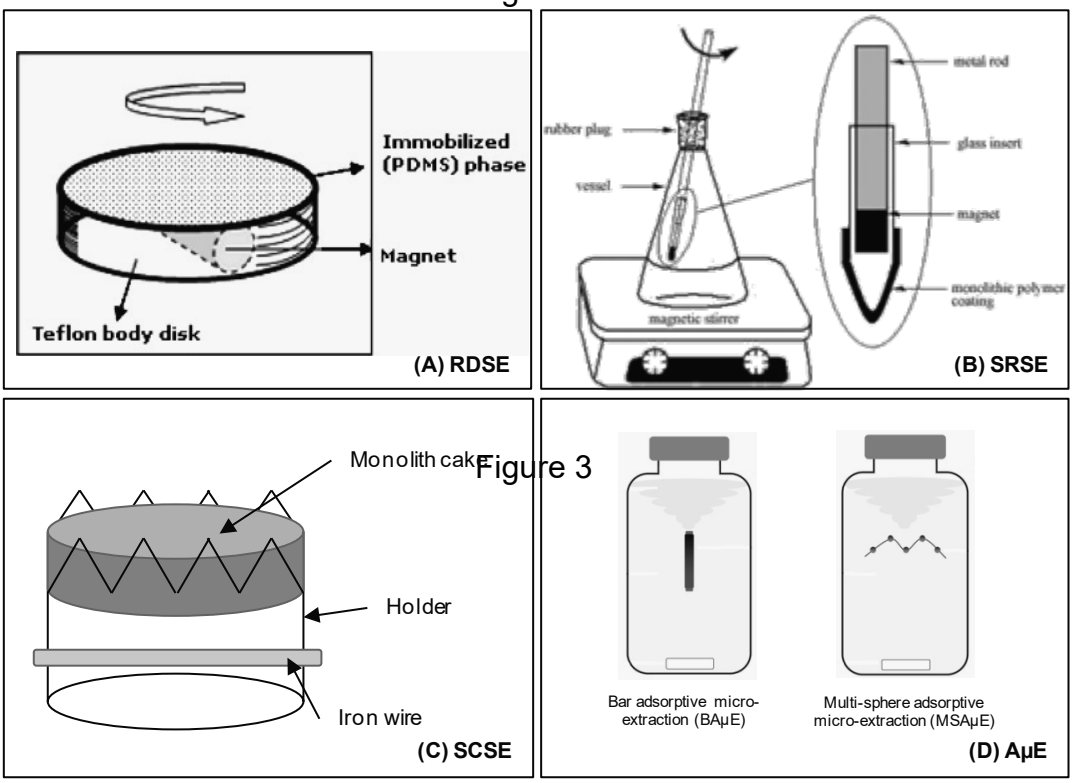


Figure 3