Accepted Manuscript

Title: Miniaturized solid-phase extraction techniques

Author: Justyna Płotka-Wasylka, Natalia Szczepańska, Miguel de la Guardia, Jacek Namieśnik

PII: S0165-9936(15)00201-0
DOI: http://dx.doi.org/doi:10.1016/j.trac.2015.04.026
Reference: TRAC 14492

To appear in: *Trends in Analytical Chemistry*

Please cite this article as: Justyna Płotka-Wasylka, Natalia Szczepańska, Miguel de la Guardia, Jacek Namieśnik, Miniaturized solid-phase extraction techniques, *Trends in Analytical Chemistry* (2015), http://dx.doi.org/doi:10.1016/j.trac.2015.04.026.

Miniaturized solid-phase extraction techniques

Justyna Płotka-Wasylka [a,*], Natalia Szczepańska [a], Miguel de la Guardia [b], Jacek Namieśnik [a]

[a] *Department of Analytical Chemistry, Faculty of Chemistry, Gdansk University of Technology, 11/12 Narutowicza Street, 80-233 Gdansk, Poland*
[b] *Department of Analytical Chemistry, Research Building, University of Valencia, 50th Dr. Moliner St., E-46100, Burjassot, Valencia, Spain*

HIGHLIGHTS

- The milestones in development of the solid-phase extraction technique
- Miniaturized solid-phase extraction techniques
- Advantages and drawbacks of solid-phase-based extraction techniques

ABSTRACT

More than 80% of analysis time is spent on sample collection and sample preparation, so sample preparation is a critical part of the analytical process. Traditionally, liquid-liquid extraction was developed and employed to screen for general unknowns. However, solid-phase extraction (SPE) is becoming highly popular as an alternative, due to its simplicity and economy in terms of time and solvent. This review summarizes the current state of the art and the future prospects for green analytical chemistry with special emphasis on environment-friendly sample-preparation techniques based on solid phase. We discuss in detail miniaturized SPE techniques, based on the most relevant, most representative and most recent scientific references.

Keywords:
Dispersive solid-phase extraction
Green analytical chemistry
Immunoaffinity solid-phase extraction
Magnetic solid-phase extraction
Microextraction in a packed syringe
Miniaturized solid-phase extraction
Molecularly-imprinted solid-phase extraction
Solid-phase extraction
Solid-phase microextraction
Stir-bar sorptive extraction

* Corresponding author. Tel.: +48 583 472 110.
E-mail address: arshenia.j@wp.pl; plotkajustyna@gmail.com (J. Płotka-Wasylka)

1. Introduction

Analytical laboratories have an essential role in environmental protection because, without their work, it would not be possible to monitor pollutants in air, water or soil. However, analytical activities involve the use of many reagents and solvents, thus generating toxic residues. For these reasons, green analytical chemistry (GAC) was introduced in 2000 to reduce or to remove the side-effects of analytical practices on operators and the environment [1]. Although it is relatively new area of activity within green chemistry, GAC has attracted a great deal of interest among chemists. It concerns the role of analytical chemists in making laboratory practices more environmentally friendly [2,3].

GAC is focused on developments in instrumentation and methodologies, reduction of the negative impact of chemical analyses on the environment, and also enabling analytical laboratories to be sustainable in terms of costs and energy. Despite the concept of GAC

providing a wonderful ideology, it also poses a number of challenges associated with reaching a compromise between the increasing quality of the results and the improving environmental friendliness of analytical methods. As a result, the guidelines and the principles of green chemistry have been introduced to provide a framework for GAC [3]. Also, components of green analysis are well known and are presented in many critical reviews.

It is well known that more than 80% of analysis time is spent on sample collection and sample preparation, so sample preparation is a critical part of the analytical process and should be part of any curriculum for teaching analytical chemistry [4].

There are different ways to make sample preparation "green" [5]. First, it is necessary to eliminate, or at least to reduce, the amounts of solvents and reagents used in the analysis. Otherwise, solvent recovery and reuse are recommended. Furthermore, green media, such as agro-solvents, ionic liquids (ILs), supercritical fluids or superheated water, are preferable, rather than petrol-based solvents. The scale of analytical operations should be reduced and instruments should be miniaturized. Integration of operations and automation (or robotization) of sample preparation are also important. Moreover, application of factors enhancing the effectiveness of sample preparation (e.g., high temperature and/or pressure, microwave and UV radiation, and ultrasound energy) also impact on the "green" character of the whole procedure. These recommendations are largely met by using miniaturized SPE. There is a large number of review papers focused on different aspects of "green" sample preparation for chromatographic analysis [2,4–6].

Traditionally, liquid-liquid extraction (LLE) was developed and employed to screen for general unknowns. However, solid-phase extraction (SPE) is becoming more popular than LLE for analyte pre-concentration and matrix removal, due to its simplicity and economy in terms of time and solvent [4,7]. SPE has gained wide acceptance because of the inherent disadvantages of LLE, whose drawbacks include [7]:

(1) inability to extract polar compounds;
(2) being laborious and time-consuming;
(3) expense;
(4) tendency to form emulsions;
(5) need for evaporation of large volumes of solvents; and,
(6) disposal of toxic or flammable chemicals.

Moreover, recent regulations concerning to the use of organic solvents have made LLE techniques unacceptable. LLE procedures that require several successive extractions to recover more than 99% of the analyte can often be replaced by SPE methods [8]. Due to the fact that SPE is a more efficient separation process than liquid-liquid extraction, it is easier to obtain a higher recovery of the analyte by using a reduced volume of solvents I the elution step [8]. Furthermore, SPE does not require the phase separation required for LLE, and that eliminates errors associated with variable or inaccurately-measured extract volumes [8].

Due to these advantages, it is no wonder that SPE technique has become the object of improving and creating even better, more modern and greener solutions for sample preparation, so a number of green techniques characterized have been introduced.

Fig. 1 shows the milestones of SPE. However, there are some disadvantages of SPE techniques:

(1) perceived difficulty in mastering its usage (method development);
(2) wide range of chemistries, many choices for manipulating solvent and pH conditions make it difficult to grasp;
(3) often several steps are required (and additional time necessary); and,
(4) greater cost per sample than simple LLE.

To overcome these drawbacks, novel microextraction techniques introduced require less time and labor than multi-step procedures of SPE. These microextraction techniques allow the integration of activities (e.g., sampling, extraction and analyte enrichment to the level above the method limit of detection (LOD), and analyte isolation from the sample matrix that cannot be directly introduced into a measuring instrument) [9]. We can consider as green the

following SPE techniques: magnetic SPE (MSPE), solid-phase microextraction (SPME) and stir-bar sorptive extraction (SBSE).

This review summarizes the current state of the art and the future trends of GAC with special emphasis on environment-friendly sample-preparation techniques based on the solid phase. We discuss in detail miniaturized SPE techniques, based on the most relevant, most representative and most recent scientific references.

2. Solid-phase microextraction (SPME)

SPME is one of the most popular green techniques used for sample preparation in analytical chemistry. SPME was introduced into analytical practice by Pawliszyn and Arthur in 1990 as an attempt to redress limitations inherent in SPE and LLE. Since then, there has been an intensification of research in order to elaborate new methodical solutions in many research facilities around the world, which could increase use of this technique [10]. SPME is a kind of SPE, whereby SPME eliminated its two most substantial faults (i.e., the length of time for extraction and, more importantly, the need to use organic solvents) [10].

Sample preparation using SPME gained appreciation among a large group of analytical scientists, above all thanks to [9, 11]:

(1) the possibility of simultaneous download, concentration and analyte determination, which significantly shortened the time to make an analysis;
(2) high sensitivity (possibility to determine the substance at the ppt level);
(3) small sample size;
(4) simplicity and speed of analysis, where use of complicated equipment, tools and devices or precise operations was not required;
(5) cost minimization, by eliminating expensive and toxic organic solvents and multiuse of SPME fibers;
(6) small fibers, which allows the device to download samples in *in situ* conditions;
(7) possibility of automation;
(8) possibility of joining with other instrumental techniques –most often with gas chromatography (GC), liquid chromatography (LC), high-performance liquid chromatography (HPLC) and capillary electrophoresis (CE) in the off-line or on-line modes.

The numerous advantages of SPME mean that it is almost universal, because it allows analysis of many kinds of sample in different physical states, liquid, gas and solid, often with very complex matrixes, and it provides determination of analytes at trace and ultra-trace levels [12]. All those features make SPME a hot topic in the development of analytical chemistry and one of most chosen techniques for sample preparation and analyte enrichment. Because of that, it is easy to find a large number of articles on new methodical solutions, new materials used to coat fibers and new applications in the food, biological and pharmaceutical fields [12].

SPME includes two fundamental stages [11]:

(1) adsorption of analytes on the sorbent surface; and,
(2) desorption of analytes under high temperature.

In SPME, thin fibers made from the melted silica, coated with a suitable sorption material, are employed to catch the target analytes. Compounds present in the sample are divided between the coated fiber and the matrix. The quantity of absorbed analyte depends on the partition coefficients between the matrix of the samples and the sorbent layer coating the fiber, and on the analyte affinity, the time of contact and other variables.

In the case of GC analysis, the thermal desorption (TD) of analytes from the coated fiber is the second stage of the microextraction process [13]. The fiber with absorbed analyte is subjected high temperature, and, as a result, the amount of compounds on the sorbent falls. The analytes are freed to the gas phase and, together with the carrier gas, are transported to the chromatographic column, where they are identified using a suitable detector [11,12].

Depending on position of the fiber in relation to the sample, microextraction to the stationary phase may happen in two manners [10]:
(1) direct (direct immersion, DI); or,
(2) adsorption from the headspace (HS).

In DI-SPME, the fiber is immersed in the sample, analytes are transferred directly from the matrix to the stationary phase, which is immobilized on the fiber. By the time of extraction from the HS, analytes are transferred from the sample to the gas phase, which is in direct contact with sample. The fiber is place3d in the HS, so the coating of the fiber is not damaged by non-gaseous pollution from sample matrix and solvents. HS extraction allows the sample to be changed without any risk of fiber destruction [24]. Transfer of analytes from sample to the coating of the fiber happens much faster than analytes transported directly from the sample to the stationary phase. Because diffusion factors in the gas phase are larger than in the liquid phase, the thermodynamic balance takes less time [24].

The effectiveness of analyte pre-concentration by SPME technique depends on many different parameters, such as [15]:
(1) fiber type;
(2) thickness of the stationary phase;
(3) fiber length;
(4) mode of extraction;
(5) sample volume;
(6) time and temperature of extraction; and,
(7) salting out.

Selection of a suitable stationary phase, showing the highest affinity to specified analytes, is really hard but also the main task, which analytical chemists have to carry out. Nowadays, among all stationary phases available on the market, we can mention: polydimethylsiloxane (PDMS), divinylbenzene (DVB), carboxen (CAR), polyethylene glycol (PEG) and Carbowax (CW). Also, in analysis, often in order to isolate and to enrich mixtures of compounds of different sorts, which feature with a high polarity, such as alcohols or ethers, stationary phases combine polar and non-polar materials. Among those, the most commonly used composite sorption materials are: PDMS/DVB, PDMS/CAR, and CW/DVB [10,13]. However, taking into consideration the huge number of compounds and their metabolites present in the environment, with different physical-chemical properties, the amount of currently available sorption materials is still insufficient. Also, analytical laboratories have critically evaluated the weaknesses of commercial fibers (e.g., low thermal stability, short expiry date and small selectivity) [10]. In connection with such weaknesses, many research facilities have focused on improving the fibers proposed for SPME based on the use of new classes of materials, which are successfully employed to isolate and to enrich of a wide range of analytes present in complex matrices. Among those new materials may be mentioned:
(1) molecularly-imprinted polymers (MIPs);
(2) metal complex imprinted polymers;
(3) conductive polymers;
(4) ILs and polymeric ILs (PILs);
(5) Immunosorbents (ISs);
(6) metal nanoparticles (NPs);
(7) carbon materials;
(8) materials obtained via the sol-gel process; and,
(9) mesoporous and nanoporous silicates, and aniline-silica nanocomposites.

These new materials open up exciting possibilities for sample treatment in different fields with respect to the kind of samples and the mixtures of analytes to be determined [13,16].

2.1. Other methodological solutions in SPME

2.1.1. In-tube SPME

An alternative to the use of coated fibers is the internally-coated capillary or needle, which is the base of so-called in-tube techniques. In–tube SPME uses open-tubular capillary columns for analyte retention. This technique was primarily developed to provide an automation option for fiber SPME-HPLC. This mode can overcome some problems related to the use of conventional fiber SPME, such as fragility, low sorption capacity, and bleeding of thick-film coatings of fiber [17].

In-tube techniques may be divided into methods with :

(1) extraction coatings, which use coatings as the internal extraction phase immobilized in the needle or in the capillary wall; and,
(2) extraction fillings, which use a sorbent-packed material as extraction phase.

In-tube systems can be used in static mode, where analytes are transferred by diffusion, or dynamic mode, where the analytes are transferred actively by pumping or under gravitational flow of the sample phase through needles or tubes [12]. However, the fundamental assumptions on which the traditional microextraction is based are very similar for stationary-phase and in-tube SPME. However, there is one significant difference. Analyte extraction is performed on the inner capillary column for in-tube SPME and the outer surface of fibers for fiber SPME. In-tube SPME requires removal of particulates by filtration or centrifugation before extraction to prevent plugging of the extraction capillary. However, the SPME fiber does not need particulates to be removed using these methods. It can be simply done by washing the fiber with water before insertion to the desorption chamber of the SPME-HPLC interface [12]. The result is that the in-tube approach requires more complex instrumentation than traditional SPME, but, using longer tubes and an increased amount of sorbent, it can be expected to increase sensitivity. In the literature, there can be found information about the use of in-tube SPME for determination of inorganic and organic contaminants in environmental, clinical, forensic and food analysis [18,19].

2.1.2. Solid-phase dynamic extraction (SPDE)

SPDE is another solution in relation to the SPME, in which the internal surface of the needle is coated with a suitable sorbent. Locating the sorbent layer on the internal side of needle increased the inter-phase contact. Fig. 2 shows the locations of the sorbent layer in SPME and SPDE.

SPDE was used for the first time to determine pesticides in water in 2001 [20]. Since then, a large number of articles were published with information about the possibilities of its use and analytes enrichment in different kinds of samples. Table 1 summarizes some basic information on several aspects associated with isolating and enriching analytes using the SPME and SPDE techniques [21].

From data reported in Table 1, we can conclude that SPDE involves a shorter analysis time and significantly lower sample capacity than classical SPME. In addition, SPDE fibers have better mechanical resistance of sorption element than the former extraction fibers. The main disadvantage of the SPDE and, consequently, the cause of less interest from analysts is the complex process involved in retention and elution of SPDE fibers and also the possibility of carry-over problems, because analytes tend to remain in the inner wall of the needle after TD [21]. SPDE has been successfully applied to the analysis of chlorinated pesticides, ethers and alcohols in water samples, volatile compounds in plants, food, blood and plasma [22]. SPDE is also applicable for forensic analysis {e.g., cannabinoids, amphetamines and synthetic-drug determination in hair samples [22]}.

2.1.3. Micro-SPE (µSPE)

µSPE, also known as porous membrane-protected µSPE, is a simple, effective method for isolation and enrichment of compounds in complex samples. This technique was developed in 2006 as an alternative to multistep SPE [23]. The small sorbent bags (1–4 cm^2) made of a

porous membrane, commonly polypropylene, were filled with a small amount of sorbent [24], but bags were also made of composite materials of polyamide and nylon fibers [25].

Compared to conventional SPME, µSPE has several advantages [26]:

(1) it is effective to extract analytes from suspensions or semi-solid/solid samples, due to the porous membrane preventing particles from contaminating the sorbent phase; µSPE can thus reduce the matrix effect and avoid the blockage generally encountered in SPE columns;
(2) it provides high enrichment factors (EFs);
(3) costs less, as much less organic solvent is required, and each device can be re-used up to 20 times;
(4) it is easy to handle and is less time consuming than conventional SPME, which may indicate it is more convenient for daily operation.

µSPE also addresses some disadvantages of SPME (e.g., analyte carryover and fiber fragility). µSPE was used successfully to extract several persistent organic pollutants, such as organochlorine pesticides (OCPs), polychlorinated biphenyls, and fungicides from waters [27] and estrogens and cannabinoids and their metabolites in urine samples [28]. Also, µSPE is applicable to detection for trace metals, such as Cd, Pb, Se and Cr, in different kinds of environmental sample, comprising very complex matrices [29].

2.1.4. Adsorptive microextraction (AµE)

The latest specialized literature review, containing themes connected with green techniques of samples preparation for analysis, shows a significant increase in interest in AµE in analytical laboratories. This analytical tool could be a great alternative to SBSE, which has significant limitations in sampling, concentration and determination of analytes featuring high values of the $K_{o/w}$ factor [30]. Use of different kinds of sorbent nanostructure allow use of AµE to monitor contaminants at trace levels of wide range of polar and medium-polar compounds and their metabolites in aqueous medium and biological fluids [31]. In practice, AµE of analytes can be done using two geometrical variants (Fig. 3):

- bar AµE (BAµE)
- multi-sphere AµE (MSAµE)

A vast number of currently available sorption materials have provided facilities around the world to perform research on identifying the material with the best physico-chemical proprieties, allowing the highest recovery factor (RF). So far, the most promising results, exceeding the 80%, were obtained using activated carbon (AC) and divynylbenzene mixed with polystyrene (PS-DVB) [30, 31]. In addition, the optimization of process conditions showed that, over and above the kind of sorbent used, analyte recovery strongly depends on certain parameters (e.g., time of extraction and agitation speed) and matrix characteristics (e.g., pH, polarity and ionic strength).

The last stage of the process in AµE may be conducted in two ways: adsorbed analytes may be examined, after desorption with a small amount of solvent, by using:

(1) HPLC-diode-array detection (HPLC-DAD); or,
(2) large-volume injection (LVI) and GC coupled with mass spectrometry (MS) (LVI-GC-MS).

Both BAµE and MSAµE have found a wide range of uses in different kinds of xenobiotics monitored in different kinds of environmental sample, phenolic acids in food material [32], sex hormones, pharmaceuticals and personal-care products, repellents and pesticides in water samples [33] and in antidoping control (e.g., identification of anabolics in urine) [34]. Table 2 summarizes some information concerning the recovery of analytes gained while using AµE and SBSE techniques [30].

According to the data above, analyte-recovery values found by AµE are significantly higher than those gained by SBSE. The RF determined by the $K_{o/w}$ factor, together with the increase of compound polarity, also increases analyte recovery. Based on data used for caffeine, the location of the sorbent does not has a significant influence on the recovery value.

AμE also has interesting features (e.g., high effectiveness, very high selectivity and sensitivity, easy to work with and cost effectiveness) [34].

2.1.5. Stir-cake sorptive extraction (SCSE)

SCSE is an improved version of SBSE. The first information about SCSE was published in 2011 [35].

The stationary phase is placed in specially prepared holder. In the lower part of the cake holder, a mixture, made of iron, coated with glass protection layer, is placed [36]. Compared with SBSE, the extraction medium lasts significantly longer because there is no interaction between the sorptive element and the bottom of the vessel. Fig. 4 shows a cake holder empty and full of sorbent.

SCSE uses monoliths as the extractive medium. According to the character of target analytes, the medium-monolithic cake can be easily designed and prepared to realize effective extraction of analytes. Among the extraction phases most often used in the literature are poly(4-vinylbenzoic acid-divynylbenzene) (VBADB) sorbents made based on polymeric IL and monolithic discs made of MIP [36,37]. Table 3 gives information on some applications of SCSE-based methods in different fields of analytical chemistry.

It is worth noting that procedures in which SCSE has been used for sample collection and preconcentration are characterized by very low LODs and high levels of recovery.

2.1.6. Rotating-disc sorbent extraction (RDSE)

In 2009, Richter and co-workers proposed RDSE as another very useful analytical tool for extraction and pre-concentration of low-polarity analytes [39]. The extraction device includes a Teflon disk, on which the top was filled with stationary phase, using the sol-gel technique. In the bottom, as in SCSE, a magnetic mixer is placed [39,40]. The extraction process is conducted using a rotating disc (Fig. 5).

As SCSE, RDSE increases the exchange-efficiency mass, gaining higher analyte -recovery values, better repeatability and enhanced term of use of the extractive material compared to traditional SBSE [40]. In addition, the disk configuration is easily fabricated in the laboratory, and allows for the immobilization of a larger exposed surface area of the active phase than that achieved with SBSE.

After extraction, disks are dried and analytes desorbed with a small quantity of solvent. An undoubted advantage of this type of disk is that they can be used several times. The possibility of a second use of the sorption material surely decreases the costs of whole analysis [40]. Retained analytes were determined using both chromatography and spectrophotometry, with PDMS being used as the stationary phase [41].

In recently published studies, discs coated with a layer of nylon, polyamide membrane [39], octadecyl chemically-modified silica [41], divinylbenzene/n-vinylpyrrolidone copolymer, were proposed to extract analytes with EFs and high recovery values for different types of compound, including OCPs [42], hexachlorobenzene (HCB) [43], non-steroidal anti-inflammatory drugs [41], personal-care products [43] and some polyaromatic hydrocarbons [39] from water and urine samples.

2.1.7. Stir-rod sorptive extraction (SRSE)

SRSE was proposed recently was an improved SBSE format (like RDSE and SCSE) to avoid the friction loss of the coating material used for extraction. This green technique was developed in 2010 and is used for isolation and enrichment of analytes with different physico-chemical properties in environmental samples, featuring very complex matrices [45]. An SRSE set-up includes a metal rod, on whose edge the magnet and the monolithic polymer coating are placed [46] (Fig. 6).

3. Stir-bar sorptive extraction (SBSE)

Due to its elimination of solvents and reduction of the labor-intensive and time-consuming sample-preparation step, SBSE also fulfills the requirements of GAC. SBSE was introduced in 1999 by Baltussen et al. [47], who proposed a novel application involving the use of polydimethylsiloxane(PDMS) polymer as sorbent for SPE.

SBSE is based on the same principles as SPME, but, instead of a polymer-coated fiber, stir bars are coated with PDMS, an apolar polymeric phase used for hydrophobic interactions with target molecules (commercially available as Twister, Gerstel GmbH). The retention process in the PDMS phase is based on van der Waals forces and the hydrogen bonds that can be formed with oxygen atoms of PDMS, depending on the molecular structure of the target analytes [48].

Sampling is done by introducing the SBSE device into the aqueous sample (DI). The SBSE rod can also be exposed to the HS of a vial containing a gaseous, liquid or solid sample, but this approach is less common.

While stirring, the bar adsorbs analytes to be extracted. The bar is removed from the sample, rinsed with deionized water and dried. Afterwards, the analytes are desorbed from the enriched sorbent phase by TD in the injection port for GC or LC. In the case of analytes that decompose at low temperatures, the analytes are desorbed by liquid desorption (LD).

The SBSE technique offers several advantages, described in many review papers [48,49]. However, some additional limitations must also be considered [48,49] (e.g., since a single apolar polymer covers the stir bar, it may only be applied to semi-volatile, thermo-stable compounds when TD is used as a back-extraction mode). However, SBSE coupled with a derivatization process can address this limitation and expand the application of SBSE to polar and thermally-labile compounds.

One of the advantages of SBSE is that its automation is possible. Gerstel MultiPurpose Sampler (MPS) is a commercially-available device to automate the whole SBSE procedure [50]. The MPS simplifies utilization of SBSE in many analytical areas where the sample-preparation step is necessary. In addition, devices for analyte desorption in multi-shot mode have been introduced [16].

Although the first note on the SBSE was published in 2001 [51], it cannot be considered a novel technique, but, recently a large number of new applications were being continually developed. Because SBSE exhibits a high pre-concentration capacity, abroad spectrum of applications and simplicity, it is becoming one of the most studied and explored sample-preparation techniques [51]. SBSE has been successfully applied to many analytical fields (e.g., environmental, clinical and food analysis) and to different kinds of matrix, including wastewater, environmental water, biological fluids, soils, and gaseous samples [51]. In addition, studies aimed at elaborating novel variants of SBSE are continually being conducted. For example, the research mainly deals with improvements in equipment that allow analyte elution with a liquid phase and application of novel sorption materials to extract polar compounds effectively [51].

New materials used for coating magnetic stirrers [16] include:

(1) polyurethane foams [52];
(2) silicone materials [53];
(3) poly(ethylene glycol)-modified silicone (EG Silicone Twister) [54];
(4) poly(dimethylsiloxane)/polypyrrole;
(5) poly(phthalazine ether sulfone ketone) [55];
(6) polyvinyl alcohol [56];
(7) polyacrylate (Acrylate Twister) [57];
(8) carbon nanotube-poly(dimethylsiloxane) (CNT-PDMS);
(9) alkyl-diol-silica (ADS) restricted access materials [58];
(10) MIPs;
(11) sorbents obtained with sol-gel techniques [59];
(12) monolithic materials [60]; or,

(13) cyclodextrin.

Moreover, two-phase sorptive elements were designed to improve the efficiency of extraction [61]. The two materials applied (e.g., PDMS and polypyrrole) are characterized by different retention mechanisms (absorption and adsorption). These specific two-phase elements may also be applied in HS sorptive extraction (HSSE) [62]. MIPs are other sorptive materials that can be used for very selective extractions of analytes [63].

The development of new coatings is the most relevant improvement to expand the applicability of SBSE, allowing the analysis of polar compounds. Unfortunately, these compounds generally cannot be analyzed using GC, and TD cannot be used. Table 4 presents recent SBSE-based methods that use new coating materials. The data in the table show greater applicability of liquid desorption than TD.

Another advantage of SBSE technique is the possibility to couple it with derivatization procedures. Different derivatization modes can be employed including on-stir, post-extraction, the most commonly used being the *in situ* strategy.

The SBSE has also some disadvantages including: i) limited spectrum of analyte polarities for the available stationary phases, ii) the presence of strong matrix effects and iii) the need of high control of extraction conditions.

Despite of the fact that originally SBSE was intended for environmental analysis, over time, hundreds of applications for almost every field of analytical chemistry have been developed. Table 5 presents information on SBSE application fields which are divided into four groups: environmental analysis, food analysis, clinical and pharmaceutical analysis.

Previously, SBSE has been widely applied to the analysis of Persistent Organic Pollutants (POPs), which include compounds like PAH, organonitrogenated pesticides (ONPs), organochlorinated pesticides (OCPs), organophosphorus pesticides (OPPs), PCBs and polybrominated diphenylethers (PBDE). Soil and water were the most commonly studied matrices using SBSE. However, other matrices as sewage sludge and air were analyzed. During the last two decades, it has been shown that SBSE can be applied for the analysis of almost all of mentioned above pollutants. In recent years, the SBSE application has been also extended to emerging pollutants which may be perceived as a potential or real threat to human health or the environment.

Food analysis is another field of analytical chemistry were SBSE technique is extensively applied. In this field, this extraction is mainly used for the analysis of toxics and pollutants. However, few SBSE-based methods have been validated for the determination of nutrients and major contaminants such as amines and free medium-chain fatty acids [75].

SBSE-based methods have been also developed in the field of pharmaceuticals and clinical analysis. However, the number of application within this filed is lower than in the field of food and environment analysis. This is mainly due to the following reasons [76]:

i) biological matrices are generally very complex, so SBSE may be not the best choice for eliminating interferences because it is not a highly selective or specific extraction technique;

ii) in pharmaceutical production and quality assurance analysis, the concentration of the target analytes is usually in a range in which pre-concentration is unnecessary; a dilution of the initial sample is usually performed, so SBSE is not useful and simpler extraction procedures are used;

iii) in medical and pharmaceutical research, the sample volume is often limited to a few mL or a few µL due to the nature of the sample (e.g., plasma, serum or tissues) and the difficulty of sample collection. Although SBSE requires very low sample volumes, a minimal volume is required to cover adequately the stationary phase and to obtain reliable extractions; and,

iv) many analytes (pharmaceuticals) are polar compounds and they have poor extraction efficiency when PDMS is used as the stationary phase.

3. Magnetic solid-phase extraction technique (MSPE)

In recent years, MSPE with magnetic particles (MPs) as adsorbents became of interest in analytical science. Although, magnetic separation was first reported by Robinson et al. [93] in

1973, the MSPE term was first introduced for analytical purposes by Šafaříková and Šafařík [94] in 1999.

MSPE involves adding MPs to the sample solution [95]. The magnetic core of these MPs is coated with silica or alumina oxides using the sol-gel technique. Appropriate functional groups can be immobilized by silanization [9]. Analytes of interest are adsorbed on the surface of the MPs, and they are then separated from the aqueous solution by an external magnetic field [95]. Separation of MPs with adsorbed analytes makes sense in solution where a complex matrix is present. Next, the target analytes are desorbed by an eluent for further determination [95]. Fig. 7 shows the steps in MSPE.

The separation mechanism of MPs depends on the type of sorbent, and is connected with the interaction of analyte molecules with the surface functional groups immobilized on the magnetic core, as in classical extraction in the solid phase. The following types of interactions have been recognized [96]: hydrogen bonding, ionic, dipole-dipole, dipole-induced dipole and dispersion forces.

The proper isolation of analytes depends on the sorbent chosen. First, the choice of the right sorbent depends on the nature of the sample being tested. The polarity of the analytes, their solubility and the complex matrix composition are also important. In addition, attention should be paid on the predicted concentration of the analyte and interfering substances that are present in the sample. These properties can affect the strength of the interaction of the analyte with the sorbent. Moreover, the choice of a suitable type of solvent used to elute analytes must take into account adequate elution strength and its role in the extraction process and the final determination [96].

The application of MPs simplifies the sample-preparation procedure compared to conventional SPE techniques because MSPE does not need the column to be packed with the sorbent in batch-mode operation, since the phase separation can be quickly and easily accomplished by applying an external magnetic field [9,95].

MSPE has been extensively used in many fields, including:

(1) biomedicine, to separate cells and to isolate proteins, enzymes or peptides [97];
(2) environmental science, for the isolation of metal ions, pesticides, dyes, surfactants, PAHs, drugs, antibiotics, and carcinogenic, and mutagenic compounds in water and sewage samples; and,
(3) food analysis, to extract pesticides, antibiotics, metals and drugs from different kinds of food sample (Table 6).

It is also worth mentioning the use of micromagnetic and nanomagnetic particles for on-line pre-concentration [98] and determination of many analytes of different types from complex matrices [99]. Moreover, ILs have been used as extraction media for coated magnetic NPs (MNPs) and used for the extraction of sulfonylurea herbicides [100]. MIPs are the latest development in MSPE coatings [101].

The application of magnetic (nano)particles in SPE significantly reduces the time taken for analysis by reducing the number of steps in the extraction procedure, and providing simultaneous isolation and enrichment of analytes, and facilitates the separation of the sorbent with analytes adsorbed on the surface by using an external magnetic field. Moreover, MSPE can reduce the use of organic solvents, and thus the formation of toxic and dangerous wastes – in accordance with the principles of green chemistry [9].

5. Immunoaffinity solid-phase extraction (IASPE)

The need for improved selectivity of analytical methods has increased research on the development of antibodies for the recognition of antigen-target analytes. Since the early 1970s, antibodies have been successfully employed in environmental research. Antibodies have been used in biosensors as the active elements, which fill the column in affinity chromatography and immunoanalysis, including the very popular ELISA (enzyme-linked IS assay) [116]. The high specificity and selectivity of antibodies means that they can also be used as sorbents in extraction and enrichment of analytes during sample preparation and,

based on that, IASPE has been developed. ISs are produced by immobilization of relatively matched antibodies (monoploid or polyploidy ones) on a solid-support surface. The conditions for applying antibodies are based on the physico-chemical properties of both antibody and support, which are subject to tight control in order to avoid the risk of antibodies being deactivated [117]. Among the materials used most often to produce supports, we can mention agarose-gel and silica beads. Other solid supports have also been suggested in the literature (e.g., glass, alumina, or polystyrene-divinylbenzene polymers), but they have not shown great advantages compared with silica [117].

Fig. 8 shows the extraction process with ISs. The immunoextraction process may be performed on-line or off-line. Final determination has commonly been made using chromatography techniques (HPLC, GC) or capillary electrophoresis (CE) (Table 7). The latest scientific literature shows that the highest distribution factor with the lowest consumption of sample was obtained using immunoaffinity CE (IA-CE) in an on-line system [118].

The high specificity of imprinted antibodies to target analytes means that immunoextraction can be particularly useful for isolation and enrichment of analytes occurring at very low concentration levels in environmental and biological samples with very complex matrices. The first extensive studies demonstrating the advantages of coupling immunoextraction to a separation technique, HPLC, were made by Farjam et al. They used ISs to isolate and to enrich estrogens and testosterone hormones from urine samples and plasma and aflatoxin from milk samples [117].

However, aptamers have also been used in analyte isolation and enrichment. Aptamers are single-stranded oligonucleotides of DNA, RNA or polypeptides, which show high affinity for tightly-determined molecules, including: proteins, nucleic acids, peptides, amino acids, cells, viruses, small molecules, and ions [125]. Undoubtedly, their best advantage is the possibility of easy modification and accurate design in relation to the molecule with which have to be selectively employed. In addition, aptamers show high selectivity, high specificity and affinity to target analytes with a high reproducibility, superior stability, with simultaneous low production and modification costs as compared to antibodies [126]. Because of that, there can be found in recent literature some information describing the use of aptamers in sample preparation. So far, apta-SPME was successfully used to extract adenosine and thrombin from human plasma [122,127] and ochratoxin A from wheat [126] and wine [127]. However, very advantageous properties, which feature aptamers, give high hopes of a future extension of their application in both clinical and environmental research.

6. Microextraction in a packed syringe (MEPS)

MEPS is a recently developed sample-pretreatment technique based on the miniaturization of conventional SPE [128]. In MEPS, approximately 1 mg of the sorbent is packed inside a syringe (100–250 μL) as a plug or between the barrel and the needle as a cartridge. Commercially-available MEPS uses the same sorbents as conventional SPE columns. When the sample is passed through the solid support, the analytes are adsorbed to the extracting media. The analytes are then eluted with an organic solvent [129].

In the literature, a lot of information is available about methods based on MEPS in non-aqueous CE-MS to detect anesthetic drugs in human plasma and GC-MS with MEPS to characterize PAHs in water samples. Compared to other sample-preparation techniques, MEPS provides significantly shorter extraction times, higher RF values and significantly less sample capacity and solvent use (about 10 μL) than classical SPE [130]. Table 8 gives information on sample capacities and the extraction times required for different techniques [128].

MEPS involves great reductions in time and sample volume required for analyte enrichment. Additionally, the undoubted advantage is that the syringe with sorbent may be used many times, significantly minimizing the costs of the whole analysis.

MEPS has been successfully applied for isolation and quantitative determination of a wide spectrum of analytes including drugs and their metabolites, pesticides and organic pollutants in different kinds of environmental samples (water, wastewater, and soil) and biological samples (urine, salvia, blood, hair, plasma, and serum) [131]. In recent times, MEPS was also used in food analysis for the determination of biologically active flavonols in wines [129] and phenyl flavonoids in beers [132].

There is no doubt that the development of new materials has significantly influenced the spread of all techniques of sample preparation, so MIPs as MEPS sorbents have been employed to isolate organic pollutants from wastewater samples and for identification and quantification of anesthetics in plasma and urine [133], while also offering promising results in LC-MS/MS for the separation of prostate-cancer biomarkers from biofluids. Apart from the use of MIPs as sorbents in MEPS, nanoporous carbon, CNTs and graphene can also improve SPE [128].

7. Molecularly-imprinted solid-phase extraction (MISPE)

Recently, MIPs attracted much attention due to their outstanding advantages [134]:

(1) predetermined recognition ability;
(2) mechanical and chemical stability;
(3) relative ease and simplicity of preparation;
(4) low cost of preparation; and,
(5) potential application to a wide range of target molecules.

MIPs are synthetic polymers with predetermined selectivity towards a given analyte or a group of structurally-related species [135]. In the most common process of preparation, monomers form a complex with a template through covalent or non-covalent interactions and they are joined using a cross-linking agent [134]. Fig. 9 shows the synthesis of MIPs and their selective recognition of a target molecule.

MIPs have been widely used as artificial receptors in separation, sensors, catalysis, and drug development and screening [134]. Of these applications, the most widely used is SPE, for which MIPs are commercialized [134]. MIPs used for SPE can be synthesized by three imprinting techniques (Table 9):

(1) non-covalent imprinting;
(2) covalent imprinting; and,
(3) hybridization of covalent and noncovalent imprinting, also called semi-covalent imprinting.

There are several methods available for the preparation of MIP particles. The first MISPE procedure was reported by Sellergren in 1994 [136]. Since that time, this technique has been developed and is widely used in many research areas.

MISPE can be performed in two modes: off-line and on-line. The most common used MISPE mode is off-line. These methods are similar to off-line SPE with conventional sorbents. A small amount of imprinting polymer (15–500 mg) is usually packed in cartridges, and then, after conditioning, there are loading, washing and elution steps so that analytes can be isolated from the real sample (Fig. 10).

Off-line MISPE offers several advantages, including a simple, easy operation process, the possibility to use different solvents and additives without regard to their influence on the subsequent chromatography analysis, and, consequently, high EF and selectivity can be obtained [134]. Unfortunately, the off-line mode is somewhat time consuming, so increasing analytical errors.

On-line MISPE has been developed to overcome the disadvantages of off-line MISPE. On-line MISPE involves automation of MISPE coupled with the analytical system. This approach avoids sample manipulation between pre-concentration and analysis, thus reducing the loss of target compounds and the risks of contamination, and thus improving accuracy and reproducibility. Additionally, automation of MISPE can greatly reduce the time for pretreatment of real samples, the consumption of reagents and the amount of waste.

Moreover, only a small volume of sample is needed because the whole extract enters the analytical column.

Nowadays, there are two types of on-line MISPE procedures. The first involves placing a pre-column, packed with a small amount of MIP particles, in the loop of an injection valve [134]. Next, the sample is loaded and the interfering compounds are washed out. After this, the analyte is eluted by the mobile phase, separated in a chromatography column and finally determined by an appropriate detection system. This mode is mainly used for multi-analyte determinations where the MIP recognizes several structural analogs [134]. The second on-line MISPE procedure is characterized by the absence of a chromatographic column between the MIP precolumn and the detector. Thus, both pre-concentration and separation of analytes can be directly carried out on one MIP column. This on-line MISPE procedure is usually applied for extraction and determination of a single analyte in real samples.

MISPE has been successfully applied to extraction and determination of analytes in different matrices. Most of the MISPE applications have focused on extracting compounds from environmental and biological samples. However, it was also applied to drug and food analysis (Table 10).

8. Dispersive micro-SPE (DMSPE)

DMSPE was proposed in 2003 as a very efficient procedure to increase the selectivity of analytical processes. DMSPE is a technique of sample preparation where the solid sorbent in the µg range is dispersed in the solution being analyzed [153]. After centrifuging the suspension, the solid-phase sediments are at the bottom of the test tube. Next, an appropriate organic solvent is used to elute the analytes of interest from the solid sorbent prior to analysis of the organic extract. After elution of adsorbed analytes, they are thermally desorbed or directly determined by a suitable technique. Due to the immediate reaction between analytes of interest and the sorbent, sample-preparation time is shortened [153]. Moreover, because the contact between the target analytes and the support is greater than in traditional SPE, it increases the equilibrium rate and provides higher extraction yields.

Generally, the simplicity of operation and the flexibility of the working conditions of SPE methods greatly depend on the proper choice of sorbent materials. The solid sorbents used in DMSPE need to meet several requirements. First, they need to have high capacity and large surface area, to guarantee fast, quantitative sorption and elution, and to be characterized by high dispersibility in liquid samples [153].

Taking into account these requirements, NPs including carbon-based compounds (CNTs, graphene, fullerene) and inorganic NPs (MNPs) seem to be perfect for use in DMSPE. A wide choice of NPs allows them to be used in organic and inorganic analyses. As far as NPs are concerned, MNPs have been proposed in the literature, taking into account that, after extraction, they can be separated from the liquid media by a magnet, which simplifies the process as no centrifugation step is required. Moreover, the surface functionality of MNPs can be easily modified to achieve selective sample extraction.

Due to the many advantages of DMSPE, such as simplicity, good recovery, speed, capability of combination with different detection techniques and low consumption of organic solvents, DMSPE has attracted the interest of scientists for research in separation and pre-concentration. DMSPE with MNPs as solid sorbent (including magnetic carbon NPs and MIPs) have been successfully applied to analysis of different groups of compounds, including acidic and basic pharmaceuticals [154], estrogenic compounds [155], drugs of abuse [156], PAHs [157], and phenolic compounds [158] in different kinds of matrix, such as environmental samples, biological fluids or food (Table 11).

9. Evaluation of miniaturized SPE techniques

Methodological solutions presented in this article, together with properly matched sampling devices for collecting analytes, reduce the number of errors during sample

preparation and limit the negative impact of extraction on the environment and the health of laboratory operators. However, in spite of many such advantages, all of these techniques are also characterized by a number of drawbacks. In short, Table 12 compares the advantages and the drawbacks of the main techniques described in this review.

10. Conclusions

Determination of analytes present in complex samples at very low level of concentration usually requires analytical procedures that include isolation and/or enrichment of target analytes prior to their quantification and, to do it, SPE offers an interesting alternative to classical LLE. However, in order to accelerate sample pretreatment and to reduce the environmentally deleterious effects of sample pretreatments, miniaturization of sorbent-based extraction techniques (e.g., SPME, SBSE, MSPE, IASPE and MISPE) were developed years ago and, at present, offer green extraction options for the treatment of gaseous, liquid and/or solid samples. These techniques have numerous positive features including:

i) simplicity of operation;
ii) relatively low costs of instrumentation;
iii) versatility;
iv) easy coupling to chromatographic systems; and,
v) short time of extraction.

Research concerning these techniques remains active through the development of novel sorbents with improved features regarding selectivity, loading capacity or retention efficiency, with special focus on analytes that were retained only slightly in previously available materials.

Acknowledgements

The research is funded in the framework of program of Polish Ministry of Science and Higher Education, "Iuventus Plus" in the years 2015–17 (Project no: IP2014 037573).

References

[1] J. Namieśnik, Trends in environmental analytics and monitoring, Crit. Rev. Anal. Chem. 30 (2000) 221–269.
[2] S. Armenta, S. Garrigues, M. de la Guardia, Green analytical chemistry, Trends Anal. Chem. 27 (2008) 497–511.
[3] A. Gałuszka, Z. Migaszewski, J. Namieśnik, The 12 principles of green analytical chemistry and the SIGNIFICANCE mnemonic of green analytical practices, Trends Anal. Chem. 50 (2013) 78–84.
[4] J. Pawliszyn, H. L.Lord, Handbook of sample preparation, John Wiley & Sons, Inc., New Jersey, 2010.
[5] J. Płotka, M. Tobiszewski, A. M. Sulej, M. Kupska, T. Góreckib, J. Namieśnik, Green Chromatography, Journal of Chromatography A, 1307 (2013) 1– 20.
[6] C.J. Welch, N. Wu, M. Biba, R. Hartman, T. Brkovic, X. Gong, R. Helmy, W. Schafer, J. Cuff, Z. Pirzada, L. Zhou, Greening analytical chromatography, Trends Anal. Chem. 29 (2010) 667-680.
[7] Y.Picó, M. Fernández, M. J. Ruiz, G. Font, Current trends in solid-phase-based extraction techniques for the determination of pesticides in food and environment, J. Biochem. Biophys. Methods 70 (2007) 117–131.
[8] R.E. Majors, Solid Phase-Extraction, in: Handbook of Sample Preparation, eds. J. Pawliszyn, H. L.Lord, John Wiley & Sons, Inc., New Jersey, 2010, pp. 53-79.
[9] A. Spieteluna, Ł. Marcinkowski, M. de la Guardia, J. Namieśnik, Recent developments and future trends in solid phase microextraction techniques towards green analytical chemistry, Journal of Chromatography A, 1321 (2013) 1–13.
[10] E. A. Souza Silva, S. Risticevic, J.Pawliszyn, Recent trends in SPME concerning sorbent materials, configurations and in vivo applications. Trends, 43(2013) 24-36
[11] C. Duan, Z. Shen, D. Wu, Y. Guan, Recent developments in solid-phase microextraction for on-site sampling and sample preparation. Trends, 30 (2011) 1568-1574
[12] H. Lord, J. Pawliszyn, Evolution of solid-phase microextraction technology. J. Chromatogr. A, 885 (2000)153-193
[13] A. Spietelun, M.Pilarczyk, A. Kloskowski, J. Namieśnik, Current trends in solid-phase microextraction (SPME) fiber coatings. Chem. Soc. Rev. 39 (2010) 4524–4537
[14] B. Bojko, E. Cudjoe, G. A. Gomez-Rios, K. Gorynski, R. Jiang, N. Reyes-Garces, S. Risticevic, E. A.S. Silva, O. Togunde, D. Vuckovic1, J. Pawliszyn, SPME – Quo vadis? Anal. Chim. Acta, 750 (2012) 132-151

[15] Y.-B. Luo, H.-B. Zheng, J.-X. Wanga, Q. Gao, Q.-W. Yu, Y.-Q. Feng, An anionic exchange stir rod sorptive extraction based on monolithic material for the extraction of non-steroidal anti-inflammatory drugs in environmental aqueous samples. Talanta, 86, (2011) 103-108
[16] J. Namieśnik, A. Spietelun, Ł. Marcinkowski, Green Sample Preparation Techniques for Chromatographic Determination of Small Organic Compounds. Int J Chem Eng Appl. 6 (2015) 215-219
[17] B. J. Silva, F. M. Lanc¸as, M. E. C. Queiroz, In-tube solid-phase microextraction coupled to liquid chromatography (in-tube SPME/LC) analysis of nontricyclic antidepressants in human plasma. J. Chromatogr. B, 862 (2008) 181-188
[18] H. Kataoka, Automated sample preparation using in-tube solid-phase microextraction and its application – a review. Anal Bioanal Chem. 373 (2002) 31-45
[19] A. K. Malik, V. Kaur, N. Verma, A review on solid phase microextraction—High performance liquid chromatography as a novel tool for the analysis of toxic metal ions. Talanta, 68 (2006) 842–849.
[20] K. Ridgway, S. P.D. Lalljie, R. M. Smith, Sample preparation techniques for the determination of trace residues and contaminants in foods. J. Chromatogr. A, 1153 (2007) 36-53
[21] Y.-B. Luo, Q. Ma, Y.-Q. Feng, Stir rod sorptive extraction with monolithic polymer as coating and its application to the analysis of froquinolones in honey sample. J. Chromatogr. A, 1217 (2010) 3583–3589
[22] B. Rossbach, P. Kegal, S. Letzel, Application of headspace solid phase dynamic extraction gas chromatography/mass spectrometry (HS-SPDE-GC/MS) for biomonitoring of n-heptane and its metabolites in blood. Toxicol. Lett. 25 (2012) 232-239
[23] M.-Y. Wong, W.-R. Cheng, M.-H. Liu, W.-C. Tian, C.-J. Lu, A preconcentrator chip employing m-SPME array coated with in-situ-synthesized carbon adsorbent film for VOCs analysis. Talanta, 101 (2012) 307-313
[24] M.-M. Wona, E.-J. Chaa, O.-K. Yoona, N.-S. Kimb, K. Kima, D.-S. Lee, Use of headspace mulberry paper bag micro solid phase extraction for characterization of volatile aromas of essential oils from Bulgarian rose and Provence lavender. Anal. Chim. Acta., 631(2009) 54-61
[25] M. Abbasghorbani, A. Attaran, M. Payehghad, Solvent-assisted dispersive micro-SPE by using aminopropyl-functionalized magnetite nanoparticle followed by GC-PID for quantification of parabens in aqueous matrices. J. Sep. Sci. 36 (2013) 311-319
[26] C. Basheer, A. A. Alnedhary, B. S. M. Rao, S. Valliyaveettil, H. Kee Lee, Development and Application of Porous Membrane-Protected Carbon Nanotube Micro-Solid-Phase Extraction Combined with Gas Chromatography/Mass Spectrometry. Anal. Chem., 78 (2006) 2853-2858
[27] M. T. García-Valverde, R. Lucena, S. Cárdenas, M. Valcárcel, Titanium-dioxide nanotubes as sorbents in (micro)extraction techniques. TRAC, 62 (2014) 37-45
[28] C. Montesano, M. Sergi , S. Odoardi, M. C. Simeoni, D. Compagnone, R. Curini, A -SPE procedure for the determination of cannabinoids and their metabolites in urine by LC–MS/MS. J. Pharm. Biomed. Anal. 91 (2014) 169-175
[29] M. Miróa, E. H. Hansen, On-line sample processing involving microextraction techniques as a front-end to atomic spectrometric detection for trace metal assays: A review. Anal. Chim. Acta, 782 (2013) 1–11.
[30] N.R. Neng, A.R.M. Silva, J.M.F. Nogueira, Adsorptive micro-extraction techniques—Novel analytical tools for trace levels of polar solutes in aqueous media. J. Chromatogr. A, 1217 (2010) 7303-7310
[31] N.R. Neng, A.S. Mestre, A.P. Carvalho, J.M.F. Nogueira, Powdered activated carbons as effective phases for bar adsorptive micro-extraction (BAμE) to monitor levels of triazinic herbicides in environmental water matrices. Talanta, 83 (2011) 1643-1649
[32] H. Wang, S. Yu, A. D. Campiglia, Solid-phase nano-extraction and laser-excited time-resolved Shpol'skii spectroscopy for the analysis of polycyclic aromatic hydrocarbons in drinking water Samples. Anal. Biochem. 385 (2009) 249–256
[33] Y.-B, Luo, J.-S. Cheng, Q. Ma, Y.-Q. Feng, J.-H. Li, Graphene-polymer composite: extraction of polyclice aromatic hydrocarbons from water samples by stir rod sorptive extraction. Anal. Methods, 3 (2011) 92-98
[34] W. Liu L. Zhang Li. Fan , Z. Lin, Y. Cai , Z. Wei , G. Chen, An improved hollow fiber solvent-stir bar microextraction for the preconcentration of anabolic steroids in biological matrix with determination by gas chromatography–mass spectrometry. J. Chromatogr. A, 1233 (2012) 1-7
[35] X. Huang, L. Chen, F. Lin, D. Yuan, Novel extraction approach for liquid samples: Stir cake sorptive extraction using monolith. J. Sep. Sci. 34 (2011) 2145-2151
[36] Y. Wang, J. Zhang, X. Huang, Do. Yuan, Preparation of stir cake sorptive extraction based on polymeric ionic liquid for the enrichment of benzimidazole anthelmintics in water, honey and milk Samples. Anal. Chim. Acta, 840 (2014) 33-41
[37] X. Huang, L. Chena, D. Yuana, S. Bi, Preparation of a new polymeric ionic liquid-based monolith for stir cake sorptive extraction and its application in the extraction of inorganic anions. J. Chromatogr. A, 1248 (2012) 67-73
[38] X. Huang, L. Chen, D. Yuan, Preparation of stir cake sorptive extraction based on poly(4-vinylbenzoic acid-divinylbenzene) monolith and its application in sensitive determination of -agonists in milk and swine urine samples. J. Hazard. Mater., 262 (2013) 121-129
[39] A. Cañas, P. Richter, G. M. Escandar, Chemometrics-assisted excitation–emission fluorescence spectroscopy on nylon-attached rotating disks. Simultaneous determination of polycyclic aromatic hydrocarbons in the presence of interferences. Anal. Chim. Acta,852 (2014) 105-111

[40] V. Manzoa, M. Miró, P.Richter, Programmable flow-based dynamic sorptive microextraction exploiting an octadecyl chemically modified rotating disk extraction system for the determination of acidic drugs in urine. J. Chromatogr. A, 1368 (2014) 64-69
[41] V. Manzo, Orielle Navarro, L. Honda, K. Sa´nchez, M. I. Toral, P. Richter, Determination of crystal violet in water by direct solid phase spectrophotometry after rotating disk sorptive extraction. Talanta, 106 (2013) 305-308
[42] A. Giordano, P. Richter, I. Ahumada, Determination of pesticides in river water using rotating disk sorptive extraction and gas chromatography-mass spectrometry. Talanta, 85 (2011) 2425-2429
[43] A.Canas, ˜ P.Richter, Solid-phase microextraction using octadecyl-bonded silica immobilized on the surface of a rotating disk: Determination of hexachlorobenzene in water. Anal. Chim. Acta,743 (2012) 75-79
[44] L. Jachero, B.Sepúlveda, I. Ahumada, E.Fuentes, P.Richter, Rotating disk sorptive extraction of triclosan and methyl-triclosan from water samples. Anal Bioanal Chem., 405 (2013) 7711-7716
[45] Y.-B, Luo, J.-S. Cheng, Q. Ma, Y.-Q. Feng, J.-H. Li, Graphene-polymer composite: extraction of polyclice aromatic hydrocarbons from water samples by stir rod sorptive extraction. Anal. Methods, 3 (2011) 92-98
[46] Y.-B. Luo, Q. Ma, Y.-Q. Feng, Stir rod sorptive extraction with monolithic polymer as coating and its application to the analysis of fluoroquinolones in honey sample. J. Chromatogr. A, 1217 (2010) 3583–3589
[47] E. Baltussen, P. Sandra, F. David, C. Cramers, Stir bar sorptive extraction (SBSE), a novel extraction technique for aquatus samples : theory and principles J. Microcolumn Sep. 10 (1999) 737–747
[48] J.M.F. Nogueira, Novel based sorptive methodologies for statistic microextraction analysis: a review on SBSE and related techniques. Anal. Chim. Acta 757 (2012) 1-10
[49] C. Bicchi, E. Liberto, C, Cordero, B. Sgorbini, P. Rubiolo, Stir bar sorptive extraction (SBSE) and headspace sorptive extraction (HSSE) : an overview. LCGC North America 27 (2009) 376-391.
[50] http://www.gerstel.com/en/mps-gc-ms-autosampler.htm
[51] P. Popp, C. Bauer, L. Wennrich, Application of stir bar sorptive extraction in combination with column liquid chromatography for the determination of polycyclic aromatic hydrocarbons in water samples. Anal. Chim. Acta, 436 (2001) 1–9.
[52] N.R. Neng, M.L. Pinto, J. Pires, P.M. Marcos, M.F. Nogueira, Development, optimisation and application of polyurethane foams as new polymeric phases for stir bar sorptive extraction. J. Chromatogr. A, 1171 (2007) 8-14.
[53] M. Schellin, P. Poop, Application of a polysiloxane-based extraction method combined with large volume injection–gas chromatography–mass spectrometry of organic compounds in water samples. J. Chromatogr. A, 1152 (2007) 175-183.
[54] B. Sgorbini, C. Cagliero, C. Cordero, E. Liberto, P. Rubiolo, M.R. Ruosi, C. Bicchi, New medium-to-high polarity twister coatings for liquid and vapour phase sorptive extraction of matrices of vegetable origin.
J. Chromatogr. A, 1265 (2012) 39-45.
[55] W. Guan, Y. Wang, F. Xu, Y. Guan, Poly(phthalazine ether sulfone ketone) as novel stationary phase for stir bar sorptive extraction of organochlorine compounds and organophosphorus pesticides. J. Chromatogr. A, 1177 (2008) 28-35.
[56] C. Yu, B. Hu, Sol–gel polydimethylsiloxane/poly(vinylalcohol)- coated stir bar sorptive extraction of organophosphorus pesticides in honey and their determination by large volume injection GC. J. Sep. Sci., 32 (2009) 147-153.
[57] E. Fries, Stir bar sorptive extraction: Recent applications, limitations and future trends Anal. Chim. Acta, 689 (2011) 65-68.
[58] J.P. Lambert, W.M. Mullett, E. Kwong, D. Lubda, Stir bar sorptive extraction based on restricted access material for the direct extraction of caffeine and metabolites in biological fluids J. Chromatogr. A, 1075 (2005) 43-49.
[59] A. Kabir, K.G. Furton, Innovations in Sol-gel Extraction Media for Solvent-free Sample Preparation in Analytical Chemistry. Trends Anal. Chem., 45 (2013) 197-218.
[60] X.J. Huang, N.N. Qiu, D.X. Yuan, Q.M. Lin, A new anionic exchange stir bar sorptive extraction coating based on monolithic material for the extraction of inorganic anion. J. Chromatogr. A, 1216 (2009) 4354-4360.
[61] L.P. Melo, A.M. Nogueira, F.M. Lancas, M.E.C. Queiroz, Polydimethylsiloxane/polypyrrole stir bar sorptive extraction and liquid chromatography (SBSE/LC-UV) analysis of antidepressants in plasma samples
Anal. Chim. Acta, 633 (2009) 57-64.
[62] C. Bicchi, C. Cordero, E. Liberto, B. Sgorbini, F. David, P. Sandra, P. Rubilo, Influence of polydimethylsiloxane outer coating and packing material on analyte recovery in dual-phase headspace sorptive extraction. J. Chromatogr. A, 1164 (2007) 33-39.
[63] L.Q. Yang, X.M. Zhao, J. Zhou, Selective enrichment and determination of nicosulfuron in water and soil by a stir bar based on molecularly imprinted polymer coatings. Anal. Chim. Acta, 670 (2010) 72-77.
[64] J.I. Cacho, N. Campillo, P. Viñas, M. Hernández-Córdoba, Stir bar sorptive extraction with EG-Silicone coating for bisphenols determination in personal care products by GC-MS. J. Pharm. Biomed. Anal., 78–79 (2013) 255–260.
[65] Z. Xu, Y. Hu, Y. Hu, G. Li, Investigation of ractopamine molecularly imprinted stir bar sorptive extraction and its application for trace analysis of beta2-agonists in complex samples. J. Chromatogr. A, 1217 (2010) 3612–3618.

[66] S. Wang, J. Wei, T. Hao, Z. Guo, Determination of ractopamine in pork by using electrochemiluminescence inhibition method combined with molecularly imprinted stir bar sorptive extraction
J. Electroanal. Chem., 664 (2012) 146–151.
[67] X. Huang, J. Lin, D. Yuan, A new anionic exchange stir bar sorptive extraction coating based on monolithic material for the extraction of inorganic anion. J. Chromatogr. A, 1217 (2010) 4898–4903.
[68] X. Mao, B. Chen, C. Huang, M. He, B. Hu, Titania immobilized polypropylene hollow fiber as a disposable coating for stir bar sorptive extraction-high performance liquid chromatography-inductively coupled plasma mass spectrometry speciation of arsenic in chicken tissues. J. Chromatogr. A, 1218 (2011) 1–9.
[69] P. Li, B. Hu, X. Li, Zirconia coated stir bar sorptive extraction combined with large volume sample stacking capillary electrophoresis-indirect ultraviolet detection for the determination of chemical warfare agent degradation products in water samples. J. Chromatogr. A, 1247 (2012) 49–56.
[70] L. Lan, B. Hu, C. Yu, Investigation of ractopamine molecularly imprinted stir bar sorptive extraction and its application for trace analysis of beta2-agonists in complex samples. J. Chromatogr. A, 1217 (2010) 7003–7009.
[71] D. Bratkowska, R.M. Marcé, P.A.G. Cormack, F. Borrull, N. Fontanals, Development and application of polar coatings for stir bar sorptive extraction for emerging pollutants from environmental water samples. Anal. Chim. Acta, 706 (2011) 135–142.
[72] D. Bratkowska, N. Fontanals, P.A.G. Cormack, F. Borrull, R.M. Marcé, Preparation of a polar monolithic stir bar based on methacrylic acid and divinylbenzene for the sorptive extraction of polar pharmaceuticals from complex water samples. J. Chromatogr. A, 1225 (2012) 1–7.
[73] C. Hu, M. He, B. Chen, B. Hu, A sol–gel polydimethylsiloxane/polythiophene coated stir bar sorptive extraction combined with gas chromatography-flame photometric detection for the determination of organophosphorus pesticides in environmental water samples. J. Chromatogr. A, 1275 (2013) 25–31.
[74] S. Vo Duy, P.B. Fayad, B. Barbeau, M. Prévost, S. Sauvé, Using a novel sol–gel stir bar sorptive extraction method for the analysis of steroid hormones in water by laser diode thermal desorption/atmospheric chemical ionization tandem mass spectrometry . Talanta, 101 (2012) 337–345.
[75] T. Horák, J. Čulík, M. Jurková, P. Čejka, V. Kellner, Determination of free medium-chain fatty acids in beer by stir bar sorptive extraction. J. Chromatogr. A, 1196–1197 (2008) 96–99.
[76] F.J. Camino-Sánchez, R. Rodríguez-Gómez, A. Zafra-Gómez, A. Santos-Fandila, J.L. Vílchez, Stir bar sorptive extraction: recent applications, limitations and future trends.Talanta 130 (2014) 388–399.
[77] X. Mao, B. Hu, M. He, W. Fan, Stir bar sorptive extraction approaches with a home-made portable electric stirrer for the analysis of polycyclic aromatic hydrocarbon compounds in environmental water. J. Chromatogr. A, 1260 (2012) 16–24.
[78] N. Ochiai, T. Ieda, K. Sasamoto, Y. Takazawa, S. Hashimoto, A. Fushimi, K. Tanabe, Stir bar sorptive extraction and comprehensive two-dimensional gas chromatography coupled to high-resolution time-of-flight mass spectrometry for ultra-trace analysis of organochlorine pesticides in river water. J. Chromatogr. A, 1218 (2011) 6851–6860.
[79] D.R. Klein, D.F. Flannelly, M.M. Schultz, Quantitative determination of triclocarban in wastewater effluent by stir bar sorptive extraction and liquid desorption–liquid chromatography–tandem mass spectrometry. J. Chromatogr. A, 1217 (2010) 1742–1747.
[80] F.J. Camino-Sánchez, A. Zafra-Gómez, J.P. Pérez-Trujillo, J.E. Conde-González, J.C. Marques, J.L. Vílchez, Validation of a GC-MS/MS method for simultaneous determination of 86 persistent organic pollutants in marine sediments by pressurized liquid extraction followed by stir bar sorptive extraction. Chemosphere, 84 (2011) 869–881.
[81] J. Martín, W. Buchberger, E. Alonso, M. Himmelsbach, I. Aparicio, Comparison of different extraction methods for the determination of statin drugs in wastewater and river water by HPLC/Q-TOF-MS. Talanta, 85 (2011) 607–615.
[82] A. Iparraguirre, A. Prieto, P. Navarro, M. Olivares, L.A. Fernandez, O. Zuloaga, Optimisation of stir bar sorptive extraction and in-tube derivatisation-thermal desorption-gas chromatography-mass spectrometry for the determination of several endocrine disruptor compounds in environmental water samples. Anal. Bioanal. Chem., 401 (2011) 339–352.
[83] N. Ramírez, R.M. Marcé, F. Borrull, Development of a stir bar sorptive extraction and thermal desorption–gas chromatography–mass spectrometry method for determining synthetic musks in water samples. J. Chromatogr. A, 1218 (2011) 156–161.
[84] I. Lavagnini, A. Urbani, F. Magno, Overall calibration procedure via a statistically based matrix-comprehensive approach in the stir bar sorptive extraction–thermal desorption–gas chromatography–mass spectrometry analysis of pesticide residues in fruit-based soft drinks. Talanta, 83 (2011) 1754–1762.
[85] K. Ridgway, S.P.D. Lalljie, R.M. Smith, The use of stir bar sorptive extraction—A potential alternative method for the determination of furan, evaluated using two example food matrices. Anal. Chim. Acta, 657 (2010) 169–174.
[86] J.I. Cacho, N. Campillo, P. Viñas, M. Hernández-Córdoba, Stir bar sorptive extraction coupled to gas chromatography–mass spectrometry for the determination of bisphenols in canned beverages and filling liquids of canned vegetables. J. Chromatogr. A, 1247 (2012) 146–153.

[87] J. Ha, Y. Wang, H. Jang, H. Seog, X. Chen, Determination of E,E-farnesol in Makgeolli (rice wine) using dynamic headspace sampling and stir bar sorptive extraction coupled with gas chromatography-mass spectrometry. Food Chem., 142 (2014) 79–86.
[88] P.L. Kole, J. Millership, J.C. McElnay, Stir bar sorptive extraction of diclofenac from liquid formulations: a proof of concept study. J. Pharm. Biomed. Anal., 54 (2011) 701–710.
[89] B.L. Armstrong, A.F. Senyurt, V. Narayan, X. Wang, L. Alquier, G. Vas, Stir bar sorptive extraction combined with GC-MS/MS for determination of low level leachable components from implantable medical devices. J. Pharm. Biomed. Anal., 74 (2013) 162–170.
[90] N. Unceta, A. Ugarte, A. Sánchez, A. Gómez-Caballero, M.A. Goicolea, R.J. Barrio, Development of a stir bar sorptive extraction based HPLC-FLD method for the quantification of serotonin reuptake inhibitors in plasma, urine and brain tissue samples. J. Pharm. Biomed. Anal., 51 (2010) 178–185.
[91] J.T. Huang, L. Alquier, J.P. Kaisa, G. Reed, T. Gilmor, G. Vas, Method development and validation for the determination of 2,4,6-tribromoanisole, 2,4,6-tribromophenol, 2,4,6-trichloroanisole, and 2,4,6-trichlorophenol in various drug products using stir bar sorptive extraction and gas chromatography–tandem mass spectrometry detection. J. Chromatogr. A, 1262 (2012) 196–204.
[92] N. Kaur, J.L. Cabral, A. Morin, K.C. Waldron, Headspace stir bar sorptive extraction-gas chromatography/mass spectrometry characterization of the diluted vapor phase of cigarette smoke delivered to an in vitro cell exposure chamber. J. Chromatogr. A, 1218 (2011) 324–333.
[93] P.J. Robinson, P. Dunnil, M.D. Lilly, The properties of magnetic supports in relation to immobilized enzyme reactors Biotechnol. Bioeng., 15 (1973) 603–606
[94] M. Šafaříková, I. Šafařík, Magnetic solid-phase extraction. J. Magn. Magn. Mater., 194 (1999) 108—112.
[195] G. Giakisikli, A.N. Anthemidis, Magnetic materials as sorbents for metal/metalloid preconcentration and/or separation. A review. Anal. Chim. Acta, 789 (2013) 1–16.
[96] A. Wasik, A. Zygler, A. Kot-Wasik, ABC Techniki SPE, Wydawnictwo Politechniki Gdańskiej, Gdańsk (2011)
[97] X.-W. Chen, Q.-X. Mao, J.-W. Liu, J.-H. Wang, Isolation/separation of plasmid DNA using hemoglobin modified magnetic nanocomposites as solid-phase adsorbent. Talanta, 100 (2012) 107-112.
[98] P.-L. Lee, Y.-C. Sun, Y.-C. Ling, Magnetic nano-adsorbent integrated with lab-on-valve system for trace analysis of multiple heavy metals. J. Anal. At. Spectrom., 24 (2009) 320-327.
[99] A. Idris, N.S.M. Ismail, N. Hassan, E. Misran, A.-F. Ngomsik, Synthesis of magnetic alginate beads based on maghemite nanoparticles for Pb(II) removal in aqueous solution. J. Ind. Eng. Chem., 18 (2012) 1582-1589.
[100] M. Bouri, M. Gurau, R. Salghi, I. Cretescu, M. Zougagh, A. Rios, Ionic liquids supported on magnetic nanoparticles as a sorbent preconcentration material for sulfonylurea herbicides prior to their determination by capillary liquid chromatography. Anal. Bioanal. Chem., 404 (2012) 1529-1538.
[101] Z.M. Zhang, W. Tan, Y.L. Hu, G.K. Li, Simultaneous determination of trace sterols in complicated biological samples by gas chromatography–mass spectrometry coupled with extraction using β-sitosterol magnetic molecularly imprinted polymer beads. J. Chromatogr. A, 1218 (2011) 4275-42783.
[102] Z. He, D. Liu, R. Li, Z. Zhou, P. Wang, Magnetic solid-phase extraction of sulfonylurea herbicides in environmental water samples by Fe3O4@dioctadecyl dimethyl ammonium chloride@silica magnetic particles. Anal. Chim. Acta, 747 (2012) 29–35.
[103] Q. Wu, G. Zhao, C. Feng, C. Wang, Z. Wang, Preparation of a graphene-based magnetic nanocomposite for the extraction of carbamate pesticides from environmental water samples.J. Chromatogr. A, 1218 (2011) 7936–7942.
[104] Y. Liu, H. Li, J.-M. Lin, Magnetic solid-phase extraction based on octadecyl functionalization of monodisperse magnetic ferrite microspheres for the determination of polycyclic aromatic hydrocarbons in aqueous samples coupled with gas chromatography–mass spectrometry. Talanta, 77 (2009) 1037–1042.
[105] J.S. Suleiman, B. Hu, H. Peng, C. Huang, Separation/preconcentration of trace amounts of Cr, Cu and Pb in environmental samples by magnetic solid-phase extraction with Bismuthiol-II-immobilized magnetic nanoparticles and their determination by ICP-OES. Talanta, 77 (2009) 1579–1583.
[106] Q. Li, M.H.W. Lam, R.S.S. Wu, B. Jiang, Rapid magnetic-mediated solid-phase extraction and pre-concentration of selected endocrine disrupting chemicals in natural waters by poly(divinylbenzene-*co*-methacrylic acid) coated Fe_3O_4 core-shell magnetite microspheres for their liquid chromatography–tandem mass spectrometry determination. J. Chromatogr. A, 1217 (2010) 1219–1226.
[107] F. Bianchi, V. Chiesi, F. Casoli, P. Luches, L. Nasi, M. Careri, A. Mangia, Magnetic solid-phase extraction based on diphenyl functionalization of Fe3O4 magnetic nanoparticles for the determination of polycyclic aromatic hydrocarbons in urine samples. J. Chromatogr. A, 1231 (2012) 8–15.
[108] S. Wang, R. Wang, X. Wu, Y. Wang, C. Xue, J. Wu, J. Hong, J. Liu, X. Zhou, Magnetic molecularly imprinted nanoparticles based on dendritic-grafting modification for determination of estrogens in plasma samples. J. Chromatogr. B, 905 (2012) 105–112.
[109] N. Rastkari, R. Ahmadkhaniha, Magnetic solid-phase extraction based on magnetic multi-walled carbon nanotubes for the determination of phthalate monoesters in urine samples. J. Chromatogr. A, 1286 (2013) 22–28.

[110] G. Cheng, M. He, H. Peng, B. Hu, Dithizone modified magnetic nanoparticles for fast and selective solid phase extraction of trace elements in environmental and biological samples prior to their determination by ICP-OES. Talanta, 88 (2012) 507–515.
[111] D. He, X. Zhang, B. Gao, L. Wang, Q. Zhao, H. Chen, H. Wang and C. Zhao, Preparation of magnetic molecularly imprinted polymer for the extraction of melamine from milk followed by liquid chromatography-tandem mass spectrometry. Food Control, 36 (2014) 36–41.
[112] B. Sha-Sha, L. Zhi, Z. Xiao-Huan, W. Chun, W. Zhi, Graphene-based Magnetic Solid Phase Extraction Dispersive Liquid-Liquid Microextraction Combined with Gas Chromatographic Method for Determination of Five Acetanilide Herbicides in Water and Green Tea Samples. Chin. J. Anal. Chem, 41 (2013) 1177–1182.
[113] C. Huang, B. Hu, C. Huang, B. Hu, Silica-coated magnetic nanoparticles modified with γ-mercaptopropyltrimethoxysilane for fast and selective solid phase extraction of trace amounts of Cd, Cu, Hg, and Pb in environmental and biological samples prior to their determination by inductively coupled plasma mass spectrometry. Spectrochim. Acta, Part B., 63 (2008) 437–444.
[114] M.H. Mashhadizadeh, M. Amoli-Diva, K. Pourghazi, Magnetic nanoparticles solid phase extraction for determination of ochratoxin A in cereals using high-performance liquid chromatography with fluorescence detection. J. Chromatogr. A, 1320 (2013) 17–26.
[115] X.-Z. Hu, M.-L. Chen, Q. Gao, Q.-W. Yu, Y.-Q. Feng, Determination of benzimidazole residues in animal tissue samples by combination of magnetic solid-phase extraction with capillary zone electrophoresis. Talanta, 89 (2012) 335–341.
[116] A. E. Prince, T. S. Fan, B. A. Skoczenski, R. J. Bushway, Development of an immunoaffinity-based solid-phase extraction for diazinon. Anal. Chim. Acta, 444 (2001) 37–49
[117]] N. Delaunay-Bertoncini, M.-C. Hennion, Immunoaffinity solid-phase extraction for pharmaceutical and biomedical trace-analysis—coupling with HPLC and CE—perspectives. J Pharm. Biomed. Anal., 34 (2004) 717–736
[118] P. Su, X.-X. Zhang, W.-B. Chang, Development and application of a multi-target immunoaffinity column for the selective extraction of natural estrogens from pregnant women's urine samples by capillary electrophoresis. J. Chromatogr. B, 816 (2005) 7–14
[119] S. Medina-Casanellas, F. Benavente, J. Barbosa, V. Sanz-Nebot, Preparation and evaluation of an immunoaffinity sorbent for the analysis of opioid peptides by on-line immunoaffinity solid-phase extraction capillary electrophoresis–mass spektrometry. Anal. Chim. Acta. 717 (2012) 134– 142
[120] J. Hosogi, H. Tanaka, K. Fujita, T. Kuwabara, S. Ikegawa, N. Kobayashi, N. Mano, J. Goto, LC–MS/MS coupled with immunoaffinity extraction for determination of estrone, 17α-estradiol and estrone 3-sulfate in human plasma. J. Chromatogr. B, 878 (2012) 222–227
[121] E.A. Prokudina, P. Lankova, R. Koblovska, N. Al-Maharik, O. Lapcˇı´k, Development of sorbents for immunoaffinity extraction of isoflavonoids. Phytochem. Lett. 4 (2011) 113–117
[122] L. Xu, S. Qiu, C.-J. Sun, Q.-P. Deng, H.-X. Chen, Y.-L. Zhou, X.-X. Zhang, Determination of epitestosterone in human urine by off-line immunoaffinity solid-phase extraction coupled with high performance liquid chromatography. J. Chromatogr. B, 878 (2010) 1443–1448
[123] N. Gasilova, A.-L. Gassner, H. H. Girault, Analysis of major milk whey proteins by immunoaffinity capillary electrophoresis coupled with MALDI-MS. Electrophoresis, 33 (2012) 2390–2398
[124] J. Rohrich , S. Zorntlein, J. Becker, Analysis of LSD in human body fluids and hair samples applying ImmunElute columns. Forensic Sci Int., 107 (2000) 181–190
[125] L. Mu, X. Hu, J. Wen, Q. Zhou, Robust aptamer sol–gel solid phase microextraction of very polar adenosine from human plasma. J. Chromatogr. A, 1279 (2013) 7-12
[126] A. De Girolamo, M. McKeague, J. D. Miller, M. C. DeRosa, A. Visconti, Determination of ochratoxin A in wheat after clean-up through a DNA aptamer-based solid phase extraction column. Food Chemistry, 127 (2011) 1378-1384
[127] F. Du , M. N. Alam, J. Pawliszyn, Aptamer-functionalized solid phase microextraction–liquid chromatography/tandem mass spectrometry for selective enrichment and determination of trombin. Anal. Chim. Acta. 845 (2014) 45-52
[128] M. M. Moein, A. Abdel-Rehim, M. Abdel-Rehim, Microextraction by packed sorbent (MEPS). TrAC, PII: S0165-9936(15)00023-0
[129] C. L. Silva, J. L. Goncalves, J.S. Câmara, A sensitive microextraction by packed sorbent-based methodology combined with ultra-high pressure liquid chromatography as a powerful technique for analysis of biologically active flavonols in wines. Anal. Chim. Acta. 739 (2012) 89– 98
[130] S. Fu, J. Fan, Y. Hashi, Z. Chen, Determination of polycyclic aromatic hydrocarbons in water samples Rusing online microextraction by packed sorbent coupled with gas chromatography–mass spektrometry. Talanta, 94 (2012) 152– 157
[131] A. El-Beqqali, A. Kussak, M. Abdel-Rehim, Fast and sensitive environmental analysis utilizing microextraction in packed syringe online with gas chromatography–mass speCtrometry. Determination of polycyclic aromatic hydrocarbons in water. J. Chromatogr. A, 1114 (2006) 234–238
[132] J. L. Gonc¸alves, V. L. Alves, F. P. Rodrigues, J. A. Figueira, J. S. Câmara, A semi-automatic microextraction in packed sorbent, using a digitallycontrolled syringe, combined with ultra-high pressure liquidchromatography as a new and ultra-fast approach for the determination of prenylflavonoids in beers. J. Chromatogr. A., 1304 (2013) 42– 51

[133] A. El-Beqqali, A. Kussak, M. Abdel-Rehim, Fast and sensitive environmental analysis utilizing microextraction in packed syringe online with gas chromatography–mass spectrometry: Determination of polycyclic aromatic hydrocarbons in water. J. Chromatogr. A., 1114 (2006) 234–238
[134] Chiyang He, Yuanyuan Long, Junlan Pan, Kean Li, Feng Liu, Application of molecularly imprinted polymers to solid-phase extraction of analytes from real samples. J. Biochem. Biophys. Methods 70 (2007) 133–150.
[135] Xiao Yang, Zhaohui Zhang, Jiaxing Li, Xing Chen, Minlei Zhang, Lijuan Luo, Shouzhuo Yao, Novel molecularly imprinted polymers with carbon nanotube as matrix for selective solid-phase extraction of emodin from kiwi fruit root. Food Chem. 145 (2014) 687–693.
[136] Sellergren B. Direct drug determination by selective sample enrichment on an imprinted polymer. Anal Chem 66 (1994) 1578–1582.
[137] M. Jiang, J.H. Zhang, S.R. Mei, Y. Shi, L.J. Zou, Y.X. Zhu, K. Dai, B. Lu, Direct enrichment and high performance liquid chromatography analysis of ultra-trace Bisphenol A in water samples with narrowly dispersible Bisphenol A imprinted polymeric microspheres column, J Chromatogr A, 1110 (2006) 27–34.
[207] F. Breton, P. Euzet, S.A. Piletsky, M.T. Giardi, R. Rouillon, Integration of photosynthetic biosensor with molecularly imprinted polymer-based solid phase extraction cartridge, Anal Chim Acta, 569 (2006) 50–57.
[139] X.L. Zhu, J. Yang, Q.D. Su, J.B. Cai, Y. Gao, Selective solid-phase extraction using molecularly imprinted polymer for the analysis of polar organophosphorus pesticides in water and soil samples, J Chromatogr A, 1092 (2005) 161–169.
[140] M.L. Mena, P. Martinez-Ruiz, A.J. Reviejo, J.M. Pingarron, Molecularly imprinted polymers for on-line preconcentration by solid phase extraction of pirimicarb in water samples, Anal Chim Acta, 451 (2002) 297–304.
[141] R. Suedee, V. Seechamnanturakit, B. Canyuk, C. Ovatiarnporn, G.P. Martin, Temperature sensitive dopamine-imprinted (N,N-methylene-bis-acrylamide cross-linked) polymer and its potential application to the selective extraction of adrenergic drugs from urine, J Chromatogr A, 1114 (2006) 239–249.
[142] H. Sambe, K. Hoshina, K. Hosoya, J. Haginaka, Direct injection analysis of bisphenol A in serum by combination of isotope imprinting with liquid chromatography-mass spectrometry, Analyst, 130 (2005) 38–40.
[143] J. Yang, Y. Hu, J.B. Cai, X.L. Zhu, Q.D. Su, A new molecularly imprinted polymer for selective extraction of cotinine from urine samples by solid-phase extraction, Anal Bioanal Chem, 384 (2006) 761–768.
[144] K.S. Boos, C.T. Fleischer, Multidimensional on-line solid-phase extraction (SPE) using restricted access materials (RAM) in combination with molecular imprinted polymers (MIP), Fresenius J Anal Chem, 371 (2001) 16–20.
[145] G. Theodoridis, P. Manesiotis, Selective solid-phase extraction sorbent for caffeine made by molecular imprinting, J Chromatogr A, 948 (2002) 163–169.
[146] A.G.V. De Prada, P. Martínez-Ruiz, A.J. Reviejo, J.M. Pingarrón, Solid-phase molecularly imprinted on-line preconcentration and voltammetric determination of sulfamethazine in milk, Anal Chim Acta, 539 (2005) 125–132.
[147] S.N. Zhou, E.P.C. Lai, J.D. Miller, Analysis of wheat extracts for ochratoxin A by molecularly imprinted solid-phase extraction and pulsed elution, Anal Bioanal Chem, 378 (2004) 1903–1906.
[148] Q. Liu, Y.X. Zhou, Z.H. Meng, Q.Q. Wang, X.Y. Hu, Y.T. Liu, Determination of nerve agent degradation products in rice by molecule imprinting polymer-solid phase extraction and capillary electrophoresis, Chin J Anal Chem, 29 (2001) 387–390.
[149] M.L. Zhang, J.P. Xie, Q. Zhou, G.Q. Chen, Z. Liu, On-line solid-phase extraction of ceramides from yeast with ceramide III imprinted monolith, J Chromatogr A, 984 (2003) 173–183.
[150] S.G. Hu, S.W. Wang, X.W. He, Study of paracetamol molecularly imprinted polymers applied to solid phase extraction, Acta Chimi Sin, 62 (2004) 864–868.
[151] X.C. Dong, W.A. Wei, S.J. Ma, H. Sun, Y. Li, J.Q. Guo, Molecularly imprinted solid-phase extraction of (−)-ephedrine from Chinese Ephedra, J Chromatogr A, 1070 (2005) 125–130.
[152] J.C. Xie, L.L. Zhu, X.J. Xu, Affinitive separation and on-line identification of antitumor components from Peganum nigellastrum by coupling a chromatographic column of target analog imprinted polymer with mass spectrometry, Anal Chem, 74 (2002) 2352–2360.
[153] K. Kocot, B. Zawisza, E. Marguí, I. Queralt, M. Hidalgo, R. Sitko, Dispersive micro solid-phase extraction using multiwalled carbon nanotubes combined with portable total-reflection X-ray fluorescence spectrometry for the determination of trace amounts of Pb and Cd in water samples, J Anal At Spectrom, 28 (2013) 736–742.
[154] A. A. Asgharinezhad, N. Mollazadeh, H. Ebrahimzadeh, F. Mirbabaei, N.Shekari, Magnetic nanoparticles based dispersive micro-solid-phase extraction as a novel technique for coextraction of acidic and basic drugs from biological fluids and waste water, Journal of Chromatography A, 1338 (2014) 1–8.
[155] Bárbara Socas-Rodríguez, Javier Hernández-Borges, Pedro Salazar, Miriam Martín, Miguel Ángel Rodríguez Delgado, Core-shell polydopamine magnetic nanoparticles as sorbent in micro-dispersive solid phase extraction for the determination of estrogenic compounds in water samples prior to high-performance liquid chromatography-mass spectrometry analysis, Journal of Chromatography A, In Press, 2015.

[156] A. A. Asgharinezhad, H. Ebrahimzadeh, F. Mirbabaei, N. Mollazadeh, N. Shekari, Dispersive micro-solid-phase extraction of benzodiazepines from biological fluids based on polyaniline/magnetic nanoparticles composite, Analytica Chimica Acta 844 (2014) 80–89.
[157] Emilia M. Reyes-Gallardo, R. Lucena, S. Cárdenas, M. Valcárcel, Magnetic nanoparticles-nylon 6 composite for the dispersive micro solid phase extraction of selected polycyclic aromatic hydrocarbons from water Samales, Journal of Chromatography A, 1345 (2014) 43–49.
[158] W. Cao, S.-S. Hu, L.-H. Ye, J. Cao, J.-J. Xu, X.-Q. Pang, Trace-chitosan-wrapped multi-walled carbon nanotubes as a new sorbent in dispersive micro solid-phase extraction to determine phenolic compounds, Journal of Chromatography A, 1390 (2015) 13–21.

Captions

Fig. 1. The milestones in development of the solid-phase extraction technique

Fig. 2. The setting of the sorbent layer used in the SPME and SPDE.

Fig. 3. Devices for the determination of analytes by absorptive microextraction techniques: (A) BAμE; and, (B) MSAμE.

Fig. 4. Device for analyte extraction using the SCSE technique: (A) empty holder; and, (B) holder filled with monolithic cake.

Fig. 5. Device for RDSE.

Fig. 6. Set-up employed for SRSE

Fig. 7. Steps of MSPE.

Fig. 8. Immunoextraction.

Fig. 9. Synthesis of MIPs and their selective recognition of a target molecule.

Fig. 10. Off-line MISPE procedure using a column packed with MIP particles.

Table 1.
Comparison of some aspects associated with isolation and enrichment of analytes using SPME and SPDE

	SPME	SPDE
Sample size [mL]	0.5–20	0.010,01
Sample type	Gas, liquid, solid	Gas, liquid, solid
Volume of the coating [μL]	>1	0,5
Extraction time [min]	10–90	2–10
Enrichment factor	High	Very high

Table 2.
Information on recovery of analytes gained while using AμE and SBSE

Analyte	Log $K_{o/w}$	Sample type	Technique	Recovery [%]
Morphine	0,90	Urine	BAμE (AC)	40
			SBSE (PDMS)	0
Simazine	1,78	Surface water	BAμE (AC)	100
			SBSE (PDMS)	20
Ibuprofen	3,84	Drinking water	BAμE (AC)	100
			SBSE (PDMS)	45
Mestranol	4,04	Water	BAμE (AC)	78

			SBSE (PDMS)	100
Atrazine	2,20	Pure water	BAμE (AC)	98
			SBSE (PDMS)	28
Caffeine	-0,55	Surface water	BAμE (AC)	76
			MSAμE (AC)	82
Bisphenol A	4,04	Pure water	BAμE (PS-DVB)	98
			SBSE (PDMS)	0

AC, Active carbon; PDMS, Polydimethylsiloxane; PS-DVB, Divynylbenzene mixed with polystyrene; SBSE, Stir-bar sorptive extraction

Table 3.
Information on applications of SCSE-based methods in different fields of analytical chemistry

Analyte	Sample type	Extraction material	Final determination	LOD [μg/L]	Concentration determined [μg/L]	Recovery [%]	Ref.
Oxfendazole (OFE)	Water	AMIIDB	HPLC-DAD	0.051	5.10	101.9 ± 2.4	[36]
	Milk			0.059	4.66	93.1 ± 6.5	
	Honey			0.048	44.76	89.2 ± 6.3	
Clenbuterol	Milk	VBADB	HPLC-MS/MS	0.027	1.49	74.5 ± 7.2	[38]
	Urine			0.012	5.79	58.3 ± 1.8	
Ractopamine	Milk	VBADB	HPLC-MS/MS	0.011	11.4	56.7± 3.3	
	Urine			0.002	5.44	52.4± 5.2	
Methyl 4-hydroxybenzoate	Pear juice	Copolymer 1-vinylbenzyl-3-methylimidazolium chloride and divinylbenzene	HPLC-DAD	0.110	76.9	76.9 ±7.0	[36]
Isobutyl 4-hydroxybenzoate	Orange juice	Copolymer 1-vinylbenzyl-3-methylimidazolium chloride and divinylbenzene	HPLC-DAD	0.334	71.1	69.4±9.4	
Inorganic anions (F^-, Br^-, NO_3^-, PO_4^{3-}, SO_4^{2-})	Spiked water	Copolymer 1-vinylbenzyl-3-methylimidazolium chloride and divinylbenzene	IC-CD	0.11-2.08	-	40.4-118.5	[37]

AMIIDB, d,1-allyl-3-methylimidazolium bis[(trifluoro methyl)sulfonyl]imide (AMII) and divinylbenzene; HPLC-DAD, High-performance liquid chromatography with diode-array detection; HPLC-MS/MS, High-performance liquid chromatography-tandem mass spectrometry; VBADB, Poly(4-vinylbenzoic acid-divinylbenzene)

Table 4.
Recent SBSE-based methods that use new coating materials

Groups of analytes	Sample type	Analytes	Separation and detection technique	SBSE-coating material	Ref.
Thermal desorption					
Industrial residues	Wastewater	Benzothiazole	GC–MS	PA	[57]
Volatile compounds	Green Tea	32 VOCs present in beverages	GC–MS	EG-Silicone	[57]

Bisphenols	Personal care products	BPA, BPF and BPZ	GC–MS	EG-Silicone	[64]
Liquid desorption					
β2-agonists	Pork, liver and feed	Ractopamine, isoxsuprine, clenbuterol and fenoterol	HPLC-UV HPLC-FID	MIP with ractopamine	[65]
Drugs	Pork meat	Ractopamine	ECL	MIP	[66]
Inorganic anions	Purified water	Br^-, NO_3, PO_4^{3-} and SO_4^{2-}	IC	Monolithic material poly(2-(methacryloyloxy) ethyltrimethylammonium chloride-co-divinylbenzene)	[67]
Phenyl arsenic compounds and their possible transformation products	Chicken tissues	cMMA,DMA,p-ASA,4-OH,3-NHPAA,PA,4-NPAA	HPLC–ICP-MS	TiO_2-PPHF	[68]
Chemical warfare agents and degradation products	Environmental water	EMPA, PMPA and MPA	CE	ZrO_2-PDMS	[69]
Drugs	Urine	AMP, mAMP, 3,4-methylenedioxy-AMP, 3,4-methylenedioxy-mAMP and ketamine	HPLC-UV	Titania-OH-TSO	[70]
Emerging pollutants (polar pharmaceuticals and personal care products)	River water, effluent and influent waste water	Paracetamol, caffeine, antipyrine, propranolol, carbamazepine, ibuprofen, diclofenac, methylparaben, ethylparaben, propylparaben, triclocarban, DHB, DHMB and BP3	LC–MS/MS	Hydrophilic polymer based on poly(N-vinylpyrrolidone-co-divinylbenzene)	[71]
Polar pharmaceuticals	Environmental water	Paracetamol, caffeine, antipyrine, propranolol, carbamazepine, naproxen and diclofenac	LC–MS/MS	poly(MAA-co-DVB)	[72]
Organophosphorus pesticides	Environmental waters	Phorate, fenitrothion, malathion, parathion and quinalphos	GC-FPD	PDMS/PTH	[73]
Preservatives	Beverages (cola, orange juice and herbal tea)	BA, SA, MP, EP, PP and, BP	HPLC-UV	APTES/OH-TSO and C_{18}-PDMS	[74]

AMP, Amphetamine; APCI, Atmospheric chemical ionization; APTES, 3-aminopropyltriethoxysilane; BA, Benzoicacid; BP, Butyl p-hydroxybenzoate; BP3, Benzophenone-3; BPA, Bisphenol A; BPF, Bisphenol F; BPZ, Bisphenol Z; CAs, Chloroanisoles; CPs, Chlorophenols; DHB, 2,4-dihydroxybenzophenone; DHMB, 2,2-dihydroxy-4-methoxy benzophenone; ECL, Electrochemiluminescence; EG, Ethylene glycol; EMPA, Ethyl methylphosphonic acid; EP, Ethyl p-hydroxybenzoate; γ-GluMeSeCys, γ-glutamyl-Se-methyl-selenocysteine; GS-Se-SG, Selenodiglutathione; LDTD, Laser-diode thermal desorption; mAMP, Methamphetamine; MIP, Molecularly-imprinted polymer; MP, Methyl p-hydroxybenzoate; MPA, Methylphosphonic acid; MeSeCys, Methylseleno-cysteine; OH-TSO, Hydroxy-terminated silicone oil; PA, Polyacrilate; PDMS, Polydimethylsiloxane; PMPA, Pinacolyl methylphosphonate; poly(MAA-co-DVB), Copolymer of methacrylic acid and divinylbenzene; PP, Propyl p-hydroxybenzoate; PSP-TiO_2, Partially sulfonated polystyrene-titania; PTH, Polythiophene; PTS, Phenyltrimethylsiloxane; SA, Sorbic acid; SeCys2, Selenocystine; SeEt, Selenoethionine; SeMet, Selenomethionine; TiO_2-PPHF, High polar extraction phase of titania immobilized polypropylene hollow fiber; titania-OH-TSO, Titania-hydroxy-terminated silicone oil; 4-t-OP, 4-t-octylphenol; VOCs, Volatile organic compounds; ZrO_2, zirconia

Table 5.
Application of SBSE-based methods in different fields of analytical chemistry

Family of analyzed compounds	Sample type	Analytes	Desorption	Final Determination	Remarks	Ref.

Environmental analysis						
PAHs	Environmental water samples	6 PAHs	Solvent	HPLC-FLD	DI-SBSE: LODs = 0.05–3.41 ng/L R = 88.8–114.3% Head Space-SBSE: LODs = 0.03–2.23 ng/L Continuous flow-SBSE: LODs = 0.09–3.75 ng/L R = 87.1–123.6%	[77]
Pesticides	River water	16 OCPs	Thermal	GC×GC-HRTOF-MS	LODs = 10–44 pg/L Linear range = 60–1000 pg/L	[78]
Fungicides/ preservatives	Wastewater	TCC	Solvent	LC–MS/MS	Recovery at 0.5 µg/L: 92±2% Recovery at 5.0 µg/L: 96±5% (%RSD)>2% LOQ = 10 ng/L	[79]
Organic pollutants	Marine sediments	84 Compounds: OCPs, OPPs, ONPs, ureic pesticides, PAHs, PCBs, PBDEs	Thermal	GC–MS/MS	PLE and SBSE R = 63–119% (%RSD) = 6–38% LOQs = 0.001–0.99 ng/g	[80]
Drugs residues	Wastewater and river water	6 Statin drugs	Solvent	HPLC/Q-TOF-MS	LODs = 0.52–2.00 ng/L	[81]
EDCs	Environmental water samples	20 Compounds: APs, BPA, estrogens and sterols	Thermal	GC–MS	Derivatization after extraction in the desorption tube R = 62–147% (%RSD) = 2–27% LOD: 0.8–84 ng/L	[82]
Odors/synthetic compounds/ detergents	Natural water and wastewater	9 Synthetic musk fragrances	Thermal	GC–MS	LODs = 0.02–0.3 ng/L	[83]
Food analysis						
Pesticides	Fruit-based soft drinks	7 OCPs, 6 OPPs	Thermal	GC–MS	Variance component model approaching was set for calibration R = 38.5–123.4% LOQs = 21 and 43 ng/L	[84]
Furan	Coffee and jarred baby food	Furan	Thermal	GC–MS	R = 97–119% (%RSD) = 2.4–7.9%	[85]
EDCs (bisphenols)	Canned beverages and filling liquids of canned vegetables	BPA, BPF, BPZ, BP	Thermal	GC–MS	Two derivatization procedures R = 86–122% (%RSD)<9.7% LODs = 4.7–12.5 ng/L	[86]

Volatile compounds (aroma)	Rice wine	E,E-farnesol and other volatile compounds: volatile alcohols, 1-butanol-3-methyl acetate, stearol, and phytane	Thermal	GC–MS	R = 96–109% (%RSD)<9.9% LOQs = 0.02–0.05 ng/mL	[87]
Medical and pharmaceutical analysis						
Drugs	Pharmaceutical liquid formulations	DIC	Solvent	HPLC-UV	R = 70% LOD = 16.06 ng/mL LOQ = 48.68 ng/mL	[88]
Antioxidants	HMWP implantable medical devices	2-Tert-butyl-6-(prop-1-en-2-yl)phenol, 2,6-Di-tert-butylphenol, BHT-quinone, BHT, BHT-aldehyde, Metilox	Thermal	GC–MS/MS	R = 90–95% (%RSD) = 9.8–17.8% LOD = 8.3–15.2 pg/mL	[89]
SRI	Brain tissue, plasma and urine	Fluoxetine, citalopram, venlafaxine, norfluoxetine, desmethylcital-opram didesmethylcital-opran and o-desmethylven-lafaxine.	Solvent	HPLC-FLD	R = 89–113% (%RSD) = 13% LOQ (plasma) = 0.2–2 µg/L LOQ (brain) = 2–20 ng/g LOQ (urine) = 1–10 µg/L	[90]
Phenols	Solid drugs	2,4,6-TBA, 2,4,6-TBP, 2,4,6-TCA and 2,4,6-TCP	Thermal	GC–MS/MS	R: TCA (79.4–97.1%); TCP (67.4–89.4%); TBA (68.3–75.7%); TBP (55.5–67.4%) (%RSD): TCA (6.17–15.83%); TCP (6.03–14.9%); TBA (2.08–11.04%); TBP (6.47–15.62%). LOQ: TCA (4 pg); TCP (285.7 pg); TBA (9.0 pg); TBP (371.3 pg)	[91]
CCS	Smoke	17 VOCs	Thermal	GC–MS	(%RSD) = 10.1–12.9%	[92]

APs, Alkylphenols; BPA, Bisphenol A; BP, Bisphenol; BPF, Bisphenol F; BPZ, Bisphenol Z; BHT, Butylated hydroxytoluene; CCS, Components of cigarette smoke; DI, Direct immersion; DIC, Diclofenac; EDCs, Endocrine-disrupting chemicals; HMWPE, High-molecular-weight polyethylene; MAE, Microwave extraction; OCPs, Organochlorinated pesticides; ONPs, Organonitrogenated pesticides; OPPs, Organophosphorus pesticides; PAHs, Polycyclic aromatic hydrocarbons; PBDEs, Polybrominated diphenyl ethers; PCBs, Polychlorinated biphenyls; PLE, Pressurized liquid extraction; R, Recovery; SRI, Serotonin reuptake inhibitor; TBA, Tribromoanisole; TBP, Tribromophenol; TCA, Trichloroanisole; TCC, Trichlocarban; TCP, Trichlorophenol; VOCs, Volatile organic compounds

Table 6.

Application of MSPE-based methods in different fields of analytical chemistry

Analytes	Application	Magnetic material coating	Eluent	Final Determination	Remarks	Ref.
Environmental water samples						
Sulfonylurea herbicides	Tap, reservoir, river and rice field water samples	SiO_2/ DODMAC	Acetonitrile, 1.5 mL	HPLC – DAD	LOD: 0.078–0.1 µg/L R: 80.4–107.1 %	[102]
Carbamate pesticides	Reservoir, river and pool water samples	G	Acetone, 0.5 mL	HPLC – DAD	LOD: 0.02–0.04 ng/mL R: 87.0–97.3 %	[103]
PAHs	Tap water samples	SiO_2/C_{18}	n-Hexane, 1.5 mL	GC – MS	LOD: 0.8–36 µg/L R: 35–99 %	[104]
Cr(III), Cu(II), Pb(II)	River and lake water samples	SiO_2/ *Bizmutiol* II	HNO_3, 1 mL	ICP – OES	LOD: 0.043–0.085 ng/mL R: 90–104 %	[105]
Endocrine disrupting chemicals	Sewage influents, tap and sea water samples	Poly(DVB-co-MAA)	Methanol, 1 mL	LC – MS/MS	LOD: 1–36 pg/mL R: 56–111 %	[106]
Biological samples						
PAHs	Urine samples	$SiO_2/(C_6H_5)_2$	Hexane, 0.6 mL	GC – MS	LOD: 0.04–0.39 ng/L R: 88–97 %	[107]
Estrogens	Plasma samples of pregnant women	SiO_2/MIPs	Toluene/acetonitrile (9:1, v/v), 1 mL	HPLC – UV	LOD: 0.30–0.40 ng/mL R: 86.6–96.2 %	[108]
Phthalate monoesters	Human urine samples	MWCNTs	Isopropanol, 5 mL	GC – MS	LOD: 0.025–0.050 ng/mL R: 92.6–98.8 %	[109]
Cr(III), Cu(II), Pb(II), Zn(II)	Human hair samples	SiO_2/H_2Dz	HNO_3, 1 mL	ICP – OES	LOD: 0.01–006 µg/L R: 85.0–104.5 %	[110]
Food samples						
Melamine	Milk samples	MIPs	Methanol with 5.0% acetic acid, 5 mL	LC – MS/MS	LOD: 2.6 ng/mL R: 88.0–95.8%	[111]
Acetanilide herbicides	Green tea samples	G	Acetone, 1 mL	GC – FID	LOD: 0.01–0.03 µg/L R: 80.2–93.2 %	[112]
Cd, Cu, Hg, Pb	Milk powder samples	SiO_2/ γ-MPTMS	HCl and 2% thiourea, 0.5 mL	ICP – MS	LOD: 0.02–0.11 ng/L R: 96–104 %	[113]
Ochratoxin A	Rice, wheat and corn samples	MSPT/ EGBMA	Thiourea, 2 mL	HPLC – FLD	LOD: 0.3–2.6 ng/mL R: 84–96 %	[114]
Benzimidazole drugs (BZDs)	Swine muscle and swine liver samples	SiO_2/ P(MAA-co-EGDMA)	MeCN/TFA (100:0.5, v/v), 1 mL	FASS – CZE	LOD: 1.05–12.61 ng/g R: 81.1–105.4 %	[115]

C, Carbon; CPBr, Cetylpyridinium bromide; CZE, Capillary-zone electrophoresis; DAD, Diode-array detector; DODMAC, Dioctadecyl dimethyl ammonium chloride; DVB, Divinylbenzene; EGBMA, Ethylene glycol bis-mercaptoacetate; EGDMA, Ethylene glycol dimethacrylate; ETAAS, Electrothermal atomic absorption spectrometry; FID, Flame-ionization detector; FLD, Fluorescence detector; G, Graphene; GC, Gas chromatography; HPLC, High-performance liquid chromatography; ICP, Inductively-coupled plasma; LC, Liquid chromatography; MAA, Methacrylic acid; MIP, Molecularly-imprinted polymer; MS, Mass spectrometry; MS/MS, Tandem mass spectrometry; MSPT, 3-trimethoxysilyl-1-propanethiol; MWCNT, Multi-walled carbon nanotube; OES, Optical-emission spectrometry; OPA, N-octadecylphosphonic acid; PAH, Polycyclic aromatic hydrocarbon; UV, Ultraviolet spectrometry; VIS, Visible spectroscopy; V-Pic, N-(pyridin-2-ylmethyl)ethenamine; γ-MPTMS, γ-Mercaptopropyltrimethoxysilane.

Table 7.
Application of immunoextraction in SPE in different fields

Analyte	Sample Type	Immunosorbent	Analytical method	Ref.
Endomorphin 1 Endomorphin 2	Human plasma	Silica based sorbent with polyclonal antibody against Endomorphin 1 and Endomorphin 2	CE-MS	[119]
Estrone, 17α-estradiol , estrone 3-sulfate	Human plasma	Agarose gel solid support with antibodies against each analyte	LC-MS/MS	[120]
Daidzein, Genistein, Biochanin A	Orange fruits	Agarose gel with polyclonal rabbit antisera against selected isoflavonoid	HPLC–ESI-MS	[121]
epitestosterone	Human urine	CNB reactivated Sepharose 4B with immobilized anti-epitestosterone monoclonal antibodies	HPLC/MS/MS	[122]
α-lactoglobulin, β-lactalbumin	Milk sample	Magnetic beads functionalized with antibodies against for α-lactoglobulin, β-lactalbumin	EC-UV EC-MALDI-MS	[123]
LCD	Human hair, urine, plasma	ImmunElute resin contains immobilized monoclonal antibodies to LSD	HPLC-FD	[124]

CE-MS, Capillary electrophoresis-mass spectrometry; HPLC/MS/MS, *High-performance* liquid chromatography-tandem mass spectrometry; LC-MS/MS, Liquid chromatography-tandem mass spectrometry,;HPLC–ESI-MS, *High-performance* liquid chromatography-*electrospray*-ionization mass spectrometry; CE-MALDI-MS , Capillary electrophoresis–matrix-assisted laser desorption/ionization-mass spectrometry , HPLC-FD, *High-performance* liquid chromatography coupled with fluorescence detection; LIF, Laser-induced fluorescence; LSD, Lysergic acid diethylamide

Table 8.
Comparison of sample volume and extraction time required for using different SPE-based sample preparation techniques

Method	Sample volume (mL)	Extraction time (min)
SPE	≤1	10–15
SPME	0.5–20	10–20
SBSE	1–100	10–60
MEPS	0.01–1	1–4

Table 9.
Characteristics of imprinting techniques used for the preparation of MIP particles for SPE [134]

	Description	Advantages	Drawbacks
Imprinting techniques			
Non-covalent imprinting	The complex of template and functional monomer is formed *in situ* by non-covalent interactions, such as	Easy preparation of the template/ monomer complex. Easy removal of the	To maximize the formation of the labile complex of template and monomer, the polymerization conditions

	electrostatic forces, hydrogen bonding, van der Waals forces, or hydrophobic interactions. The rebinding of template molecules with MIPs is also carried out by the same non-covalent interactions.	templates from the polymers. Fast binding of templates to MIPs. Its potential application to a wide range of target molecules.	must be carefully chosen to minimize non-specific binding sites.
Covalent imprinting	The complex is formed by covalent-linkage of a functional monomer and template prior to polymerization. The MIPs obtained rebind template molecules via the same covalent interactions.	The monomer/ template complexes are stable and stoichiometric. Wide variety of polymerization conditions can be employed.	The troublesome and less economical synthesis of monomer/template complexes. The slow release and binding of templates limit its application.
Semi-covalent imprinting	The polymers are prepared like those in covalent imprinting, while the guest binding employs non-covalent interactions.	The stable and stoichiometric complex. The fast guest binding.	It requires careful design of the sacrificial spacer that links the template and the functional monomer. It often requires custom synthesis that can only be carried out by experienced researches.
Polymerization methods			
Bulk polymerization	The most widely used method for the preparation of MIPs. The reaction mixture of template, functional monomers, cross-linker, initiator, and solvent are added to a test tube, the mixture is purged with nitrogen to remove oxygen, and the test tube is sealed under vacuum. After polymerization under appropriate conditions, the MIP particles can be obtained by grinding, sieving, and repeated flotation in sequence.	The apparatus acquired for synthesis is relatively simple. The reaction conditions can be easily controlled.	The chromatographic performance of these particles is usually unsatisfactory due to their irregular size and shape. The tedious and time consuming process and low yield of MIPs prevent their industrial production and acceptance in analytical laboratories.
Suspension polymerization	This technique involves suspension in either water or perfluorocarbon. This method can produce MIP beads in the 5- to 50-μm size range.	The simplest and most common approaches for the production of MIP. High-quality MIP beads.	Water is incompatible with most non-covalent imprinting procedures. Liquid fluorocarbons are somewhat expensive.
Two-step or multistep swelling polymerization	These methods can produce spherical MIPs of uniform size within the range of 5–100 μm. The spherical particles obtained have separating abilities comparable with those prepared by bulk polymerization.	Much better column efficiencies and peak shapes than MIP beads prepared by bulk polymerization.	Chromatographic performance is still unsatisfactory, despite the highly uniform packing.
Precipitation polymerization	The one-step preparation of monodisperse and spherical MIP particles, about 5 μm in diameter which can be applied to HPLC and SPE separation. s	It requires no surfactant and only minimal optimization of polymerization conditions, while producing high-quality products in good yield in one step.	In the MIP beads prepared by the above methods the binding sites are inside their network, causing a slow mass transfer of target molecule.
Surface-initiated polymerization	Method developed for the preparation of an MIP film grafted on the surface of beads. The process is carried out by initially grafting the initiator to	Controllable film thickness. Relatively fast mass transfer. Regular size.	Research is still necessary.

	the surface of spherical particles, and then carrying out the polymerization reaction of monomers on the surface of the supports, causing the formation of grafted MIP films.	MIP film grafted on the surface of beads will draw much attention in MISPE.	
In situ polymerization	The reaction mixture containing the template molecules, functional monomers, cross-linking agents, porogenic agents and initiators are poured into a stainless-steel tube, sealed at one end, and degassed ultrasonically. Then the other end is sealed and the reaction is allowed to process by heating polymerization.	Very simple and easy method. It does not require any subsequent treatment of the resultant material, except washing to extract the template, and can be used directly in their applications.	It can be carried out by experienced researches.

Table 10.
Applications of MISPE methods in different fields of analytical chemistry

Analyte	Application	Template	MIP synthesis	MISPE mode	Analytical system	Ref.
Environmental samples						
Bisphenol A	Spiked tap water, Spiked lake water	Bisphenol A	Non-covalent, Precipitation	On-line	MISPE/UV	[137]
Triazines	Water samples	Cyanazine	Non-covalent, bulk	Off-line	Fluorescent measurement	[138]
Organophos-phorus pesticides	Water and soil	Monocroto-phos	Non-covalent, bulk	Off-line	GC/NPD	[139]
Pirimicarb	Tap water, spring water, river water, sea water	Pirimicarb	Non-covalent, bulk	On-line	MISPE/Voltammetric detection	[140]
Biological samples						
Adrenergic drugs	Urine	Dopamine hydrochloride	Non-covalent, bulk	Off-line	LC/fluorescence detection	[141]
Bisphenol A	Serum	Bisphenol A-d_{16}	Non-covalent, multi-step swelling	On-line	MISPE/LC/MS	[142]
Cotinine	Urine	Cotinine	Non-covalent, bulk	Off-line	LC/UV	[143]
Tramadol	Plasma	Tramadol	Non-covalent, bulk	On-line	MISPE/LC/UV	[144]
Food samples						
Caffeine	Beverages, spiked human plasma	Caffeine	Non-covalent, bulk	Off-line	LC/UV	[145]
Sulfamethazine	Milk	Sulfamethazine	Non-covalent, bulk	On-line	MISPE/SWV	[146]
Ochratoxin A	Wheat extracts	Ochratoxin A	Non-covalent, bulk	On-line	MISPE/PE/fluorescence	[147]
Nerve agent degradation products	Rice	Pinacolyl methylphos-phonic acid	Non-covalent, bulk	Off-line	CE	[148]

Drug samples						
Ceramides	Yeast lipid extracts	Ceramide III	Non-covalent, *in situ*	On-line	MISPE/light scattering detector	[149]
Paracetamol	Drug (Endophy)	Paracetamol	Non-covalent, bulk	Off-line	LC/DAD	[150]
(−)-Ephedrine	Herbal ephedra	(−)-Ephedrine	Non-covalent, bulk	Off-line	LC/UV	[151]
Harmaline and harmine	*Peganum nigellastrum*	Harmine	Non-covalent, bulk	On-line	MISPE/MS	[152]

Table 11.
Applications of DMSPE methods in different fields of analytical chemistry

Analyte	Sample type	Sorbent	Analytical system	LOD	Recovery [%]	Ref.
Pb(II), Cd(II)	Water samples	MWCNTs	TXRF	Pb(II): 2.1 ng/mL Cd(II): 1.0 ng/mL	100	[153]
DIC, DPH	Biological fluids and waste water	CTAB-coated Fe_3O_4@decanoic acid	HPLC-UV	DPH: 1.8–3.0 g/L DIC: 1.5–3.5 g/L	DPH: 47.3 – 60 DIC: 64 – 76.7	[154]
Estrogenic compounds	Mineral water, tap water waste water	Core-shell Fe_3O_4@poly(dopamine) MNPs	HPLC-EI-MS	0.01-0.34 µg/L	70-119	[155]
LRZ, NRZ	Biological fluids	Fe_3O_4/PANI–p-TSA	HPLC-UV	NRZ: 0.5–1.8 mg/L LRZ: 0.2–2.0 mg/L	NRZ: 84–99 LRZ: 90– 99	[156]
PAHs	Water	MNPs-nylon 6 composites	UPLC-PDAD	0.05- 0.58 µg/L	80-111	[157]
Phenolic compounds	Chrysanthemum tea, chrysanthemum beverage	CS-MWCNTs	UHPLC-TOF-MS-MS	0.22–16.19 ng/mL	89-106	[158]

CTAB-coated Fe_3O_4@decanoic acid, Cetyltrimethyl ammonium bromide-coated Fe_3O_4@decanoic-acid nanoparticles; CS-MWCNTs, Trace-chitosan-wrapped multi-walled carbon nanotubes; DIC, Sodium diclofenac; DPH, Diphenhydramine hydrochloride; IS solution, Internal standard solution; LRZ, Lorazepam; MWCNTs, Multi-walled carbon nanotubes; NRZ, Nitrazepam; PANI–p-TSA, Polyaniline-p-toluene sulfonic acid; PAHs, Polycyclic aromatic hydrocarbons; PDAD, Photodiode-array detector; TOF-MS-MS, Time-of-flight tandem mass spectrometry; TXRF, Total-reflection X-ray fluorescence spectrometry; UPLC, Ultra-performance liquid chromatography

Table 12.
Advantages and drawbacks of green solid phase-based extraction techniques

Technique	Advantages	Disadvantages
Solid-phase microextraction (SPME)	- eliminates the need for solvents - speed, simplicity and sensitivity - possibility of using for polar and non-polar analytes in a wide range of matrices - compatibility with different systems for analyte separation and detection - small in size - headspace and immersion modes	- batch-to-batch variation of fiber coatings - robustness of fiber coatings - limited range of stationary phase
In-tube SPME	- high sorption capacity - no bleeding from thick-film coatings	- limited range of stationary phases
Solid-phase dynamic extraction (SPDE)	- higher sensitivity than SPME - high concentration factor	- limited range of stationary phases - more complicated analytical process

	- shorter extraction time and smaller sample size than SPME - high mechanical and thermal resistance of sorptive element - relatively low cost	- possibility of analytes remaining on the inner wall of the needle after thermal desorption
Micro-SPE (μSPE)	- minimized usage of solvent - higher enrichment factor than SPME - very high selectivity and sensitivity, easy to use and less time consuming - relatively low cost - compatibility with different systems of analyte separation and detection - headspace and immersion modes	- limited range of stationary phases - possibility of analyte carryover - fiber fragility
Adsorptive microextraction (AμE)	- higher recovery factor than SBSE - easy to use and cost effective - easy preparation of most suitable sorbent for each specific type of application - compatibility with different systems of analyte separation and detection	- only for polar analytes - need for tight control of extraction conditions
Stir-cake sorptive extraction (SCSE)	- higher recovery and reproducibility than SPME - very simple and high extraction capacity - low detection limit and wide linear range - easy to prepare the most suitable sorbent for each specific type of application - excellent longevity of extractive medium - very versatile approach, broad applicability	- longer time needed to reach extraction equilibrium
Rotating-disc sorbent extraction (RDSE)	- higher analyte recovery, better repeatability and more prolonged use of extractive material than traditional SBSE - direct evaluation of analytes using solid-phase spectrophotometry - reusable discs - compatibility with chromatographic and spectrophotometric techniques	- need for tight control of extraction conditions - strong matrix effects
Stir-rod sorptive extraction (SRSE)	- good extraction capacity - easy to prepare the most suitable sorbent for each specific type of application - easy to use and cost effective - excellent longevity of extractive medium - compatibility with different systems of analyte separation and detection	- research is still necessary - strong matrix effects - need for tight control of extraction conditions
Solid-phase nanoextraction (SPNE)	- very small volume of samples - good extraction factor - simplicity, short time of analysis, relatively low cost - short extraction and desorption time - possibility of full automation - direct link-up with a GC - possibility of *in-situ* and *in-vivo* sampling	- robustness of fiber coatings - limited range of stationary phase
Stir Bar Sorptive Extraction (SBSE)	- higher enrichment factor than SPME - lower detection limit than SPME - possibility of selecting the most convenient sorbent coating for each particular type of target compound - compatibility with different systems of analyte separation and detection - high thermal and chemical stability of stir-bar coatings - headspace and immersion modes	- limited range of stationary phases - high enrichment factor only for non-polar analytes - relatively high cost of sorption element - need for tight control of extraction conditions - strong matrix effects
Immunoaffinity solid-phase extraction	- very high affinity to target analytes - high selectivity and sensitivity - compatibility with different systems of analyte separation and detection	- quantification in very low dynamic range

Aptamer SPME	- very high affinity, specificity, selectivity and stability - easy to prepare and to modify at low cost - simple regeneration	- porosity of the coatings can negatively impact on the performance by retaining unwanted species from the sample matrix