Chemia Naissensis, Vol 1, Issue 1, 93-123

Recent developments in sorbent based water samples treatments prior GC-MS analysis of polycyclic aromatic hydrocarbons

Slobodan A. Ćirić[1*], Violeta D. Mitić[1], Jelena S. Nikolić[1], Marija D. Ilić[1], Marija V. Dimitrijević[1], Strahinja R. Simonović[2], Vesna P. Stankov Jovanović[1]

1- *University of Niš, Faculty of Science and Mathematics, Department of Chemistry, Višegradska 33, 18000 Niš, Serbia*

2- *University of Priština (with contemporary seat at Kosovska Mitrovica), Faculty of Science and Mathematics, Department of Chemistry, Lole Ribara 29, 38220 Kosovska Mitrovica, Kosovo, Serbia*

[*]Corresponding author: Slobodan A. Ćirić- slobodan.ciric@pmf.edu.rs, University of Niš, Faculty of Science and Mathematics, Department of Chemistry, Višegradska 33, 18000 Niš, Serbia

ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are omnipresent contaminants of the environment, with evidenced harmful effects to human health. Especially endangered are waters, which may affect biota directly or by enabling transport through all environmental compartments. Therefore, constant monitoring of PAHs content in waters is of essential importance. Before most of the analysis, sample preparation is compulsory. Conventional extraction techniques are often time and reagents consuming and not following the rules of "green analytical chemistry". Thus, miniaturization of classic extraction methods is of high importance to reduce solvent volumes, waste, time of treatment and cost. Recent sample preparation techniques, such as solid phase extraction (SPE), microextraction by packed sorbent (MEPS), solid phase microextraction (SPME), stir bar sorptive extraction (SBSE), dispersive solid phase extraction (dSPE) and dispersive micro-solid phase extraction (D-µ-SPE) were proven as suitable for the extraction of polycyclic aromatic hydrocarbons (PAHs) from water samples and their determination by gas chromatography-mass spectrometry. These sample pretreatments are following "green chemistry" principles, offering the simplicity of operation, reducing costs and time of preparation, without compromising the general analytical parameters of the applied analytical method.

***Keywords**: PAHs, water samples, sample preparation, sorbents, GC-MS*

Introduction

Analytical procedures typically consist of several equally important steps - sampling, sample treatment, isolation of the target compounds, identification, quantification, and data handling. All operations carried out with samples before the instrumental determination of target compounds are considered to be part of the sample preparation step. Sample preparation includes sampling, labeling, mechanical processing and homogenization of the studied matrix. Also, any gravimetric or volumetric determination in order to characterize the matrix structure could be considered as a sample preparation step. Fractionation, isolation, and enrichment of the target compounds from potential interferences are crucial in every analysis. Nevertheless, the term sample preparation has typically been associated with the latter group of chemical operations, all earlier mechanical and basic treatments being named as sample pre-treatment (Koning et al., 2009). Also, sample preparation is the most important procedure to remove the matrix interferences and enrich the analytes, especially for environmental water analysis. Furthermore, sampling and sample preparation procedures are the most crucial steps in all analytical techniques applied for the analysis of heterogeneous materials.

Nowadays, sample preparation procedures are more than ever linked with the protection of the environment following the philosophy of Green Analytical Chemistry (GAC). GAC was introduced in 2000 in order to reduce or to remove the side-effects of analytical practices on operators and the environment. Even though it is a 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 (Armenta et., al 2008). GAC is focused on developments in instrumentation and methodologies that generate less hazardous waste and therefore are more secure for utilization and more environmentally friendly, enabling analytical laboratories to be sustainable regarding costs and energy. Despite the concept of GAC providing ideology, it also poses many 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 (Gałuszka et al., 2013).

There are different ways to make sample preparation "green" (Płotka et al., 2013). First, it is necessary to eliminate, or at least 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 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. There are many review papers focused on different aspects of "green" sample preparation for chromatographic analysis (Armenta et al., 2008; Pawliszyn et al., 2010; Welch et al., 2010).

Pollutants analysis is a challenge for researchers because their concentrations in samples are usually very low. Also, the extreme complexity of environmental samples requires instate and delicate procedures. Besides, many structural isomers are often present in environmental samples (Poster et al., 2006). Because of that, it is necessary to establish extraction and clean up technique that meets the requirements that analytical method must satisfy in term of accuracy and precision, but also simplicity and cost.

PAHs in water

Polycyclic aromatic hydrocarbons (PAHs) represent a very significant group of environmental pollutants due to their potentially harmful effects on health exerting carcenous, mutagenous and teratogenous actions (EPA, 1987). Because of the listed characteristics, but also of their conspicuous to degradation in nature, they have been listed by the US-EPA as priority pollutants, but also by the European Environment Agency (ATSDR, 2006).

The definition of PAHs implied numerous groups of organic compounds containing two or more fused rings, of aromatic character and made up of carbon and hydrogen atoms. They can be produced naturally or by anthropogenic activities, and high amounts of PAHs are emitted from incomplete combustion or high-temperature pyrolytic processes involving fossil fuels, forest fires, volcanoes or hydrothermal processes, usage of coal and from motor vehicle exhaust (Poster et al., 2006; Wenzl et al., 2006). Due to a large number of sources PAHs have been registered in water, air, soil, agricultural products and nearly everywhere in the environment (Khalili – Fard et al., 2012). The possible sources of PAHs in water may be through atmospheric deposition (*via* wet and dry particle deposition and gross gas absorption), wastewater treatment plant discharges, tributaries, stormwater runoff, oil spills, groundwater discharges from underground water and runoff of PAHs from contaminated sites. (Rodenburg et al., 2010)

Long-term data on POPs in water provide important information that can be used to appraise the powerfulness of actions taken to diminish emissions. Concentrations of POPs (including PAHs) in surface water are directly linked to their bioaccumulation in the food chain (Hu et al., 2007).

Trends in sample preparation as a most critical step in PAH analysis, are aimed to avoid disadvantages of existing techniques. Conventional techniques, such as liquid-liquid extraction (LLE), solid-liquid extraction (SLE) and Soxhlet extraction, are still widely accepted and used for routine applications and/or reference purposes. However, in recent years, some of these techniques have been revisited, and upgraded versions in which their most pressing shortcomings have been solved, are now available. The studies in this field have also led to the development of new faster and more powerful and/or versatile extraction and preconcentration techniques (Dean, 2009).

As an alternative to LLE, solid-phase extraction (SPE) has become more popular than LLE for analyte preconcentration and matrix removal, due to its simplicity and economy regarding time and solvent save. SPE has gained wide acceptance because of the inherent disadvantages of LLE, whose drawbacks include (Picó et al., 2007):

- inability to extract polar compounds;
- being laborious and time-consuming;
- expense;
- the tendency to form emulsions;
- need for evaporation of large volumes of solvents; and,

- disposal of toxic or flammable chemicals.

Due to increasing demand for simple, rapid, and accurate sample preparation procedures new techniques have been developed. The following sections provide an overview of sorbent-based sample pretreatment techniques such as SPE, microextraction by packed sorbent (MEPS), solid phase microextraction (SPME), stir bar sorptive extraction (SBSE), dispersive solid phase extraction (dSPE) and dispersive micro solid phase extraction (D-µ-SPE) with mention of their general application in various contaminants analysis and the analysis of PAHs in water.

Sorbent based sample pretreatment techniques

Many techniques currently used for pretreatment of gaseous, fluid or liquid samples are based on trapping the investigated analytes on or in a suitable sorbent. Preconcentrated target compounds are subsequently desorbed, in a selective fashion, by elution with a relatively small amount of solvent either in a vial or in an appropriate interface; or by thermal desorption, typically in the injection port of the instrument selected for the final determination. The latter approach avoids dilution but is limited to (semi-)volatile thermally stable compounds. In general, techniques based on sorption extraction can nowadays be considered well established and accepted. As expected for sophisticated techniques, in most instances no significant conceptual changes have been introduced during the last decade, and as with other techniques, instrumental developments have mainly been orientated to increase automation and integration of the techniques with final instrumental analysis (a field where miniaturization has again played a relevant role). Thereby, the most active research topics concerning these techniques have been the synthesis of new sorbent phases that solved the remaining practical problems in this research field and the development of novel application studies (Ramos, 2012).

Solid phase extraction (SPE)

SPE as a physical extraction process was first introduced in the mid-1970s (Chen et al., 2010) and today is the most popular technique for environmental and food samples. The SPE procedure, due to its high versatility is used for many purposes (purification, trace enrichment, desalting, derivatization, and class fractionation) (Andrade-Eiroa et al., 2015). The principles of SPE and liquid-liquid extraction are similar. The problems associated with LLE (incomplete phase separations (emulsion); use of expensive, breakable specialty glassware; less-than-quantitative recoveries; disposal of large quantities of organic solvents), can be overcome using SPE procedure. SPE procedure consists of 1) loading a sample on a cartridge containing sorbent that binds target compounds, 2) washing undesirable compounds, and 3) eluting target compounds.

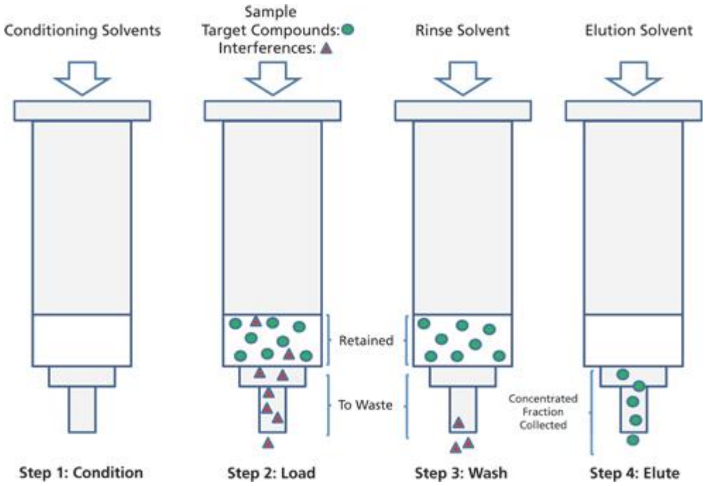

Figure 1. Illustration of solid-phase extraction (SPE) procedure (Zdravkovic, 2017)

Also, SPE has proved more efficient than LLE because of higher recovery, it is easy to perform, rapid, and can be automated (Gilar et al., 2001; Titato and Lanças, 2005).

To get optimal SPE extraction conditions, the choice of sorbent is a crucial factor because it can control parameters of primary importance (selectivity, sensitivity, affinity, and capacity) (Nováková and Vlcková, 2009). The choice of sorbent depends on the nature of the analytes and their physical and chemical properties, which define the interaction with the chosen sorbent. The selectivity of the sorbent depends on the attractive forces between the analytes and the functional groups on the surface of the sorbent. The interactions with analytes can be achieved by hydrophobic, hydrophilic, cationic-anionic and selective antigen-antibody contacts.

The sorbents widely used for SPE packing can be classified into (Lucci et al., 2012):

- polar phases (normal phase), (underivatized silica material (SPE-Si), magnesium silicate (SPE- Florisil) and aluminum oxide materials (SPE-alumina)
- non-polar phases (reversed phase), (alkyl or aryl silica and polymer-based materials - cyano (SPE-CN), octyl (SPE-8), octadecyl (SPE-18) and phenyl (SPE-Ph), copolymers of styrene-divinylbenzene (SPE-PSDVB))
- ion exchange is based on positively or negatively charged groups that are bonded to the silica surface
- immunoaffinity adsorbents (antibody materials bonded onto silica gel support).

A large variety of sorbents commercially available makes this technique suitable for the determination of analytes with divergent chemical structures and polarities. Current research is focused mainly on the development of novel sorbents allowing higher loading capacities, increased retention efficiency of vastly polar analytes from water samples. Application of molecularly imprinted polymers (MIPs) and selective immuno-sorbents (ISPEs) enables improved selectivity during the retention process and so contributing to the simplification of the subsequent clean-up and/or detection steps (Fontanals et al., 2007). In a little while back published paper, five ionic liquid-modified porous polymers with different imidazolium-based functional groups were obtained, and a new molecular imprinting technique was introduced to form the ordered functional groups in the porous structure (Tian et al., 2011).

The progress in sorbent materials synthesis has enabled pure sorbents with small particles. These small particles (ca. 40 μm) provided higher retention capacities than conventional-size ones, and promoted the use of smaller SPE cartridges, without a significant loss of retention efficiency. Reducing the size of the conventional 1–6 mL SPE syringe barrels to the 10 mm × 1–2 mm i.d. of the Prospeckt type cartridges used in the hyphenated systems led to a reduction of sample volumes from 0.5–1.0 L to less than 50–100 mL. Quite often, even 5–10 mL suffices to obtain similar LODs of 0.01–0.1 µg L^{-1} with SPE-LC and 1000-fold lower with SPE-GC that previously required 100- fold larger volumes. More importantly, quantitative elution of the analytes can be achieved with 50–100µL of the appropriate solvent, *i.e.*, with a volume small enough to allow complete transfer to the instrument selected for final determination. This fact promoted the development of hyphenated and automated systems for unattended, green and fast (ca. up to 20 min) treatment of aqueous samples with the minimal sample and solvent consumption and significant reduction of waste generation (Bagheri et al., 1993).

Graphene has also been used as the sorbent in the sample preparation because of its ultra-high specific surface area, superior chemical stability, and excellent thermal stability (Liu et al., 2011; Liu et al., 2012; Wang et al., 2013).

Besides the development of new sorbents, a number of modifications based on miniaturization and automation resulted in the development of new extraction techniques - solid-phase dynamic extraction (SPDE), microextraction by packed sorbent (MEPs), matrix solid-phase dispersion (MSPD), stir-bar sorptive extraction (SBSE), solid-phase microextraction (SPME), automated headspace dynamic solid-phase extraction, and dispersive solid-phase extraction (d-SPE) (Andrade-Eiroa et al., 2015).

Due to the usual low levels of PAHs in water samples, a pre-concentration step before analysis is required and owing to the trend for decreasing the use of organic solvents in the laboratory. Solid-phase extraction (SPE) is preferred over liquid-liquid extraction (LLE), where classical extraction sorbents used for the extraction of PAHs from water are C8, C18 or polymers of styrene-divinylbenzene (Marce´ and Borrull, 2000; Martinez et al., 2004), where sorbents are packed in cartridges or disks. Solid-phase extraction (SPE) is a conventional extraction and preconcentration method for PAHs from aqueous samples (Li and Lee, 2001; Bruzzoniti et al., 2010). The main drawbacks of the SPE technique are its high organic solvent consumption and sample consumption.

Sargenti et al. (1998) compared four different extraction techniques (solid-phase extraction, supercritical fluid extraction (SFE), solid-phase extraction followed by supercritical fluid extraction (SPE/SFE) and liquid-liquid extraction (LLE)) for the extraction of 16 PAHs from drinking water. The results showed that recoveries were good for SPE and SPE/SFE for all compounds, recoveries for SFE were worse than SPE/SFE, and LLE had the worst recovery and reproducibility.

Microextraction by packed sorbent (MEPS)

New novelty in the area of sample preparation is microextraction by packed sorbent (MEPS) originally designed and patented by Astra Zeneca, Sweden (Abdel-Rehim, 2003; Abdel-Rehim, 2004). MEPS is a miniaturized SPE technique in which sorbent packing material (ca. 1 mg) is placed at the top of the syringe needle (Moein et al., 2015). MEPS can be fully automated, the sample preparation procedure is performed online using the same syringe, and the whole extract is injected into a chromatographic system (Abdel-Rehim, 2010). The difference between MEPS and SPE is that, in SPE, the solution flow is in one direction (up to down) but in MEPS it is in two directions (up and down) (Yang et al., 2017).

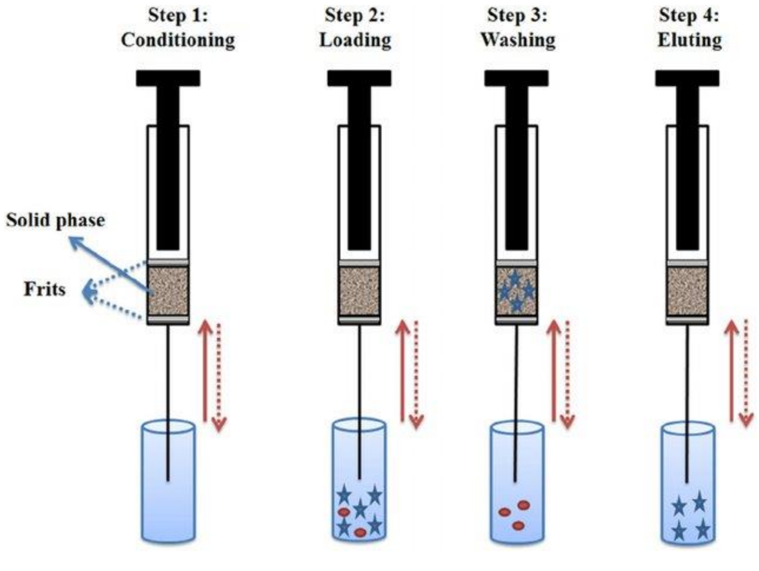

Figure 2. Illustration of microextraction by packed sorbent (MEPS) (Moein et al., 2015)

For extraction, 10-250 µL of an aqueous sample is successively withdrawn and ejected, allowing preconcentration of the analytes on the selected sorbent. Commercially available MEPS uses the same sorbents as regular SPE columns. Analytes elution is typically accomplished with 20–50 µL of an appropriate solvent, which can directly be transferred to the GC/LC (gas chromatography or liquid chromatography) port. Compared to other sample preparation techniques, MEPS provides significantly shorter extraction times and significantly less sample capacity and solvent use (about 10 µL) than classical SPE (Fu et al., 2012).

MEPS applications include the determination of PAHs in water (El-Beaqqali et al., 2006; Fu et al., 2012). MEPS procedure reported by Fu et al. (2012) for PAH analysis is performed with a MEPS system containing a syringe equipped with C18 sorbent incorporated in the needle. Before each sample extraction, MEPS sorbent was conditioned using 80 µL of methanol and 100 µL of ultrapure water. Both methanol and water were discarded into waste vials. The water sample (50 µL each) was pulled/pushed through the syringe 40 times at a speed of 5 µL s^{-1} by the autosampler. Then sorbent was washed using 100 µL pure water to reduce interference absorption and was dried by ten cycles of drawing and pressing air. Finally, analytes were eluted with 50 µL methanol directly into the GC large volume injector. To get rid of any carryover effect, eight 80 µL portions of methanol were used to clean the sorbent after the extraction/elution step. MEPS showed similar recovery results compared to the SPE method. However, a better sensitivity was obtained using the proposed MEPS method. Furthermore, MEPS minimized the volume of organic solvent used for the elution, as well as sample volumes. The proposed MEPS–GC–MS method could be used as a screening method for monitoring PAHs in environmental waters (Fu et al., 2012).

Solid phase microextraction (SPME)

The research of solid-phase microextraction processes (SPME) started 30 years ago (Arthur and Pawliszyn, 1990; Pawliszyn, 1997). This method was adopted as an alternative, to the until then applied sample preparation techniques, but nowadays it has diverse applications with the purpose to extract various analytes. SPME represent fast and cost-effective sample preparation method for GC and LC that does not require any solvent. SPME is composed of two basic steps: (1) partitioning of analytes between the extraction phase and the sample matrix and (2) desorption of concentrated extracts into an analytical instrument.

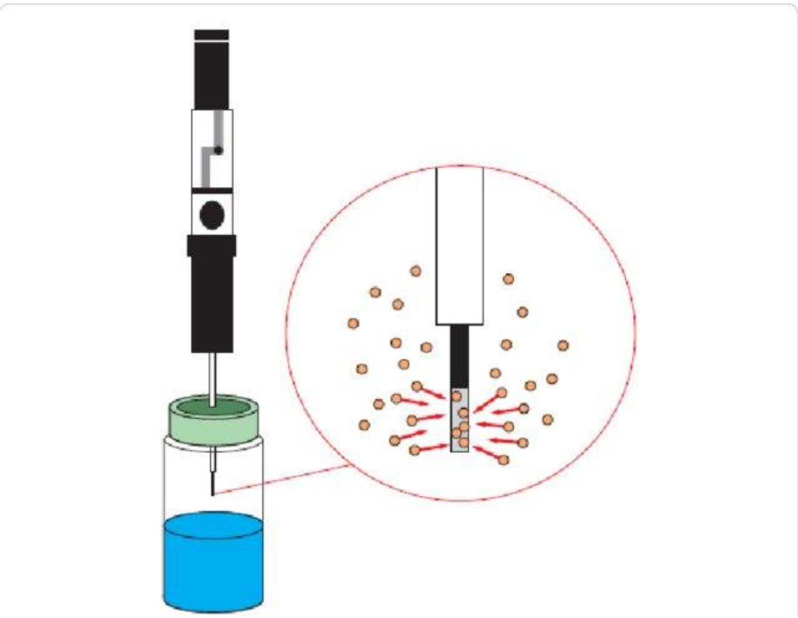

Figure 3. Illustration of solid phase microextraction (SPME) (Schmidt and Podmore, 2015)

A few factors, such as temperature, pH, stirring, and concentration of salt may affect the time of equilibration and the equilibrium constant (Pawliszyn, 1997). By changing pH, the neutrality of the target compound can be achieved. Basic pH promotes recoveries of basic analytes, while acidic analytes are recovered in greater extent at acidic pH. Recovery may be equally improved by salt addition, *e.g.*, NaCl, which provokes evident ionic effects. Many of the target analytes are polar and firmly bound to the matrix. To make these analytes inclinable to thermal desorption from SPME fiber, during GC analysis, derivatization may be required. Proper few derivatization techniques have been employed and reported in previous papers (Pan and Pawliszyn, 1997). The process of derivatization implies the addition of appropriate reagents to the sample matrix and extraction/derivatization on the fiber. The high potential for derivatization exists in SPME, allowing enhanced analysis, but unfortunately, this potential has not been studied enough. Notwithstanding several studies of SPME deal with drugs and their metabolites in body fluids (plasma and urine), (Fritz, 1999), only minority of them treat SPME optimization for analysis of drugs in plasma. In the majority of uses, SPME is coupled on-line with GC/MS, while LC/MS is applied rarely.

There are two configurations of SPME: fiber SPME and in-tube SPME (Kataoka, 2003; Hinshaw, 2003). The theories behind fiber and in-tube SPME methods are similar. With fiber SPME, analytes are adsorbed on the outer surface of the fiber from an agitated sample solution; while with in-tube SPME, they are adsorbed on the inner surface of the capillary column from a flowing sample solution. Therefore, with in-tube SPME, it is necessary to prevent plugging of the capillary column and flow lines by filtering the sample solution before an extraction. On the other hand, the fiber SPME should be handled carefully during insertion and agitation because the fiber is fragile and may break easily (Pawliszyn, 1997; Lord and Pawliszyn, 2000). However, a fiber SPME is generally limited to the analysis of volatile and thermally stable compounds. It tends to encounter complexity in coupling with LC. Thus, a fiber SPME associated with LC was usually introduced to analyze weakly volatile and thermally labile compounds not amenable to GC (Lord and Pawliszyn, 2000; Zambonin, 2003).

The volume of the sorbent is very small (< 0.7 µl) in SPME, and this limits the amount of extracted analyte and hampers the usefulness of the technique for ultra-trace analysis (Baltussen et al., 1999). Besides, the extraction efficiency is low, even in cases of analytes with fairly high partition coefficient between the gas and liquid phases, and this makes quantification vulnerable to matrix effects. Because of these reasons, quantitative analysis by SPME is not straightforward, but the simplicity and easiness of the use make the technique very suitable as a screening tool (Baltussen et al., 1998; Mol et al., 1995). Differences between SPE, MEPS, and SPME are presented in Table 1 (Abdel –Rehim, 2011).

Table 1. Overview of SPE, MEPS and SPME characteristics

	SPE	**MEPS**	**SPME**
Sorbent amount	50 – 2000 mg	2 – 4 mg	thickness 150 µm
Time	15 min	1 min	20 – 40 min
Recovery	good	good	low
Sensitivity	good	good	low
Cartridge re-use	1 extraction	100 extractions	50 extractions

In SPME procedure for PAHs analysis in water, the polydimethylsiloxane (PDMS) fibers (100 µm film thickness) were put in the injection port of the instrument for 3 h, at 270 °C. The volume of water sample (8 mL), was placed in a vial and capped with PTFE coated septa (10 mL). The fibers are submerged in water samples with agitation at 250 rpm for 60 minutes; afterward, the fiber was thermally desorbed for 10 min into the injection system (Rami et al., 2012). Various experiments have been performed to define the optimal conditions for SPME application in PAHs analysis in water such as temperature, equilibration time, salinity and compound concentration (King et al., 2003). Report of Chen (2004) showed that under optimized conditions, SPME demonstrates to be a very simple, rapid, sensitive and accurate technique for the extraction of polycyclic aromatic hydrocarbons from water samples where high recovery and good reproducibility were obtained by using PDMS fiber.

Stir bar sorptive extraction (SBSE)

SBSE was introduced in 1999 by Baltussen et al. This technique was developed to extract organic analytes from liquid samples and is based on the sorption of analytes onto a thick film of polydimethylsiloxane (PDMS) coated on an iron stir bar (Popp et al., 2001). It consists of two steps: (1) extraction of an analyte from sample to the PDMS polymer and (2) desorption of analyte from sorbent to chromatographic system.

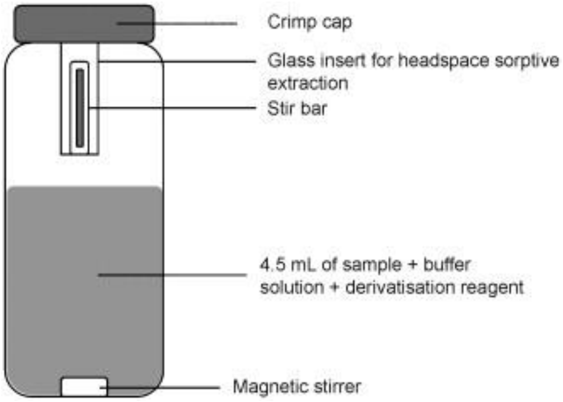

Figure 4. Illustration of stir bar sorptive extraction (SBSE) (Prieto et al., 2008)

The liquid sample is stirred with a stir bar, and after extraction, the stir-bar is removed and dried with soft tissue. The analytes are desorbed either thermally (for GC analysis) or with liquid (mainly for LC analysis). In contrast to SPME, a particular interface is required for thermal desorption. The desorption process is relatively slow, owing to a large amount of coating. Typical desorption times are 10 min, which means that the desorbed analytes must be re-concentrated before the GC separation. This procedure is usually done in a programmed temperature vaporizer (PTV) with cryogenic cooling. For semi-volatile analytes with boiling points above 200 °C, ambient temperature is sufficient for focusing, while for volatile analytes temperatures as low as - 150 °C can be used with liquid nitrogen cooling (Kawaguchi et al., 2006).

Several studies have demonstrated the practicability of SBSE where this technique has been applied for the extraction of different types of organic compounds in aqueous solutions (Kolahgar et al., 2002) and wine (Sandra et al., 2001). However, the technique has not been as widely accepted as could be anticipated, probably due to the limited number of coatings materials commercially available and the difficulty of full automation. At present, efforts in this field focuses on the development of dual phase/ hybrid twisters, in which the conventional PDMS phase is combined with another sorbent to increase the selectivity and/or efficiency of the extraction process (Ibrahim et al., 2011), as well as in the development of alternative new coating materials with improved analytical features (Faraji et al., 2011). Matrix effect is one of the major limitations of SBSE. Samples with high organic matter or suspended solid components, such as environmental samples, biological fluids or foods, are very tough to extract with SBSE. Taking into account that stir-bars are expensive and must be reused for several extractions as long as the coating is in appropriate conditions, SBSE has not the best precisions when compared to other extraction techniques such as SPE. Therefore, SBSE may be the best choice for ultra-trace analysis, but probably not the best technique for small sample volumes or when high precision is required. (Camino-Sánchez et al., 2014).

SBSE has been successfully applied to preconcentrate trace amounts of volatile organic compounds, organochlorine compounds, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl (PCBs), pesticides, hormones, alkylphenol, and bisphenol A (Rykowska and Wasiak, 2013).

The SBSE method exerted an enormous capability to extract PAHs from water (Popp et al., 2001; Hauser et al., 2002). Procedure for SBSE of PAHs from water described by Popp et al. (2001) consists of using new or used stir bars which were conditioned as follows: the stir bars were placed into a vial containing 1 mL of a 1:1 mixture of methylene chloride and methanol, and treated for 5 min with sonication. Then the solvent mixture was rejected, and the procedure was repeated three times. The twister was dried in a desiccator at room temperature and heated for 90 minutes at 280 °C with a nitrogen stream of about 100 mL min^{-1}. To enrich the PAHs, a 10 mL water sample was placed in a 10 mL glass vial and then extracted for 60 min at a stirring speed of 1000 rpm. After extraction, the stir bar was removed with clean tweezers and dried with a lint-free tissue. Then the stir bar was placed into the insert (250 μL glass flat bottom) of a 2 mL vial. The insert was filled with 150 μL acetonitrile (ACN) or with an ACN-water mixture (4:1). Desorption of the PAHs was performed with an ultrasonic device for 10 min. After desorption, the stir bar was removed by a magnetic rod, and the vial with the 250 μL insert was placed into the autosampler of the LC instrument used. Time of extraction and time od desorption was optimized, and ACN was chosen as the solvent in order to enable sensitive determination of PAHs in water samples.

Dispersive solid-phase extraction (dSPE)

Most likely, the most powerful method introduced lately in the field of SPE has been the method known as QuEChERS. The acronym applies for Quick, Easy, Cheap, Rugged, Effective and Safe; they are the most important properties of the analytical method used for the determination of pesticides in vegetables and fruits (Anastassiades et al., 2003). The method is a multi-step procedure based on solvent extraction of the target compound and extracts clean up using dispersive solid-phase extraction (d-SPE). Instead of adding sample extract to packed sorbent materials, like in SPE, the extract is added to a tube containing powder form of sorbent.

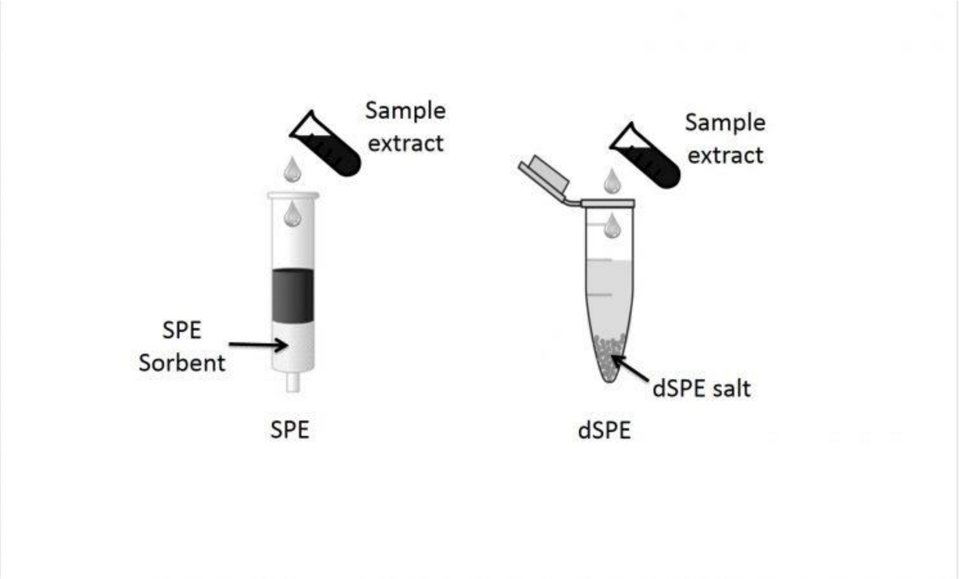

Figure 5. The difference between SPE and dSPE procedure (Lam, 2016)

The procedure starts with the addition of magnesium sulfate to secure water removal from an organic solvent, continuing with primary secondary amine (PSA) sorbent addition, to eliminate polar compounds, (mostly organic acids, sugars, and polar pigments). In some other procedures, graphitized carbon black is added to the sample to eliminate sterols and pigments like chlorophyll. The usefulness of dSPE was established after being recognized by the Association of Official Analytical Chemists (AOAC) as an international method for multiclass pesticide determination in fruits and vegetables (Lehotay, 2007). The primary objective of the sorbent is the retention of the matrix components while the analytes remain in the liquid phase. This balance between selectivity and sensitivity is achieved by adding low amounts of sorbent. More than 50 sorbents were tested for dSPE, but four types of sorbents are commonly employed in dSPE, namely: primary–secondary amine (PSA), graphitized carbon black (GCB), RP-C18 and alumina (Anastassiades, 2006). The sorbent selection is usually carried out taking into account the nature of the interferences to be eliminated. Thus, PSA is used for polar organic acids, sugars, pigments, and fatty acids while GCB is more appropriate to retain aromatic and polar compounds; RP-C18 is more convenient for starch, sugars, and lipophilic compounds, alumina retains vitamins, glycosides and plant sterols (Lagana et al., 2002; Lagarda et al., 2006). PSA in combination with GCB gives excellent results for samples with high contents of carotenoids or chlorophyll (Anastassiades, 2006).

QuEChERS technique including dSPE was used for PAH analysis in various matrices. Some publications describe analysis if 16 priority PAH (Cvetkovic et al., 2016; Kao et al., 2014; Madureira et al., 2014; Ramalhosa et al., 2009), while some describe analysis only of some of them (Sadowska-Rociek et al., 2014; Surma et al., 2014; Yoo et al., 2014).

Dispersive micro-solid phase extraction (D-µ-SPE)

D-µ-SPE is a very efficient procedure to increase the selectivity of analytical processes. It is a sample preparation technique where the solid sorbent in the µg range is dispersed in the solution being analyzed (Kocot et al., 2013a). 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 before analysis of the organic extract. After elution of adsorbed analytes, they are thermally desorbed or directly determined by a suitable technique (Khezeli and Daneshfar, 2017).

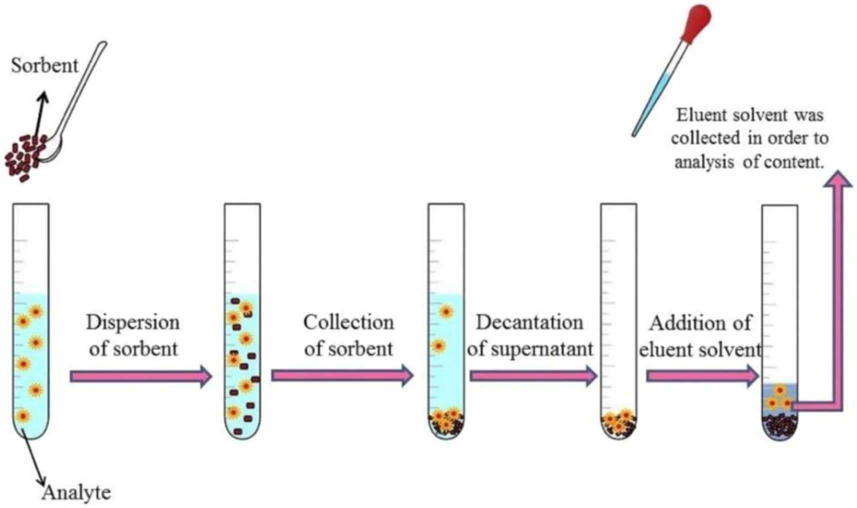

Figure 6. Illustration of dispersive micro-solid phase extraction (D-µ-SPE) (Khezeli and Daneshfar, 2017)

Due to the immediate reaction between analytes of interest and the sorbent, sample-preparation time is shortened (Kocot et al., 2013b). Moreover, because the contact between the target analytes and the support is higher 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 D-µ-SPE 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 (Kocot et al., 2013c).

The advantages of D-µ-SPE over conventional methods are that D-µ-SPE allows the direct contact between the analytes/interferes with the adsorbent thank to the homogeneous dispersion of the solid in the liquid matrix sample. Although it was initially proposed to increase the method selectivity, it can also be used to increase the sensitivity by retaining the target analytes on the appropriate sorbent material (Alcudia-León et al., 2008), uses smaller quantities of sorbents and solvents. Furthermore, it is simple and uses inexpensive equipment. For PAHs analysis in water samples there are variety of sorbents applicated in D-µ-SPE, for example, magnetic nanoparticles-nylon 6 composites (Reyes-Gallardo et al., 2014), magnetic graphitic carbon nitride (g-C_3N_4/Fe_3O_4) (Rajabi et al., 2016), biocompatible calcium carbonate vateritic polymorph was recrystallized from eggshell waste (Nuhu et al., 2012).

The main differences between SPE and D-µ-SPE as extraction methods are:

a) Sorbent type - there are several types of sorbents for SPE (normal-phase, reversed-phase, ionic and other special sorbents). In contrast, the number of solid sorbents in D-µ-SPE is much more in progress, and an increased interest in the development of synthetic new sorbents is present. However, in SPE method due to the unsatisfactory selectivity of traditional sorbents, they usually can´t separate analytes efficiently in complex biological or environmental samples (He et al., 2007);

b) The difference in extraction procedure - in SPE liquid sample is passed through a column containing sorbent that retains the target analytes. Sample loading step for cartridge SPE requires a relatively long period. In the case of D-µ-SPE, a small amount of a solid sorbent (µg or mg range) is dispersed in the sample solution to extract the target analytes.

c) Extraction time -SPE as a well-known method of separation and pre-concentration has been developed and widely used in different fields, but it is a time-consuming method. In D-µ-SPE, extraction is not carried out in the SPE cartridge, but it is performed in the bulk solution. Compared with SPE, D-μ-SPE enables the analytes to interact equally with all of the dispersed sorbent particles, to achieve higher capacity per amount of sorbent and to avoid common problems of conventional SPE method such as channeling or blocking of cartridges or discs. D-μ-SPE has the following advantages: less organic solvent and sorbent consumption, high extraction efficiency and short time requirement.

d) Applicability of nano-materials - Application of the nano-materials packed into a cartridge of SPE can be hampered because these materials can cause high back pressure and long sample loading time (Asgharinezhad et al., 2015). Nano-materials possess large surface area and short diffusion route, which may result in high extraction efficiency and rapid extraction dynamics of D-μ-SPE. As previously reported by Jeannot and Cantwell (1996) the extraction rate constant is a function of the mass-transfer coefficient of analytes, interface area between the aqueous phase and extraction phase. Therefore, compared to the traditional micrometer-sized sorbents used in SPE, nano-materials offer a significantly larger surface area and a shorter diffusion route causing the rapid extraction dynamics and high extraction capacity in D-μ-SPE (Huang et al., 2013).

Conclusion

Industrial or naturally produced PAHs can accumulate in the environment, in surface and ground water, soil, food, and food products. They are usually present at ultra-trace amounts and in matrices of high complexity. Sample preparation is a crucial step in the development of an analytical method for environmental and food analysis. Determination of analytes present in complex samples at a very low concentration level usually requires analytical procedures that include isolation and/or enrichment of target analytes before their quantification. SPE offers an excellent alternative to classical LLE. Miniaturization based on the classic SPE method is of high importance in order to reduce solvent volumes, wasted material, time and cost. Recent sample preparation techniques presented here, such as SPE, MEPS, SPME, SBSE, dSPE, and D-μ-SPE are suitable for determination of various contaminants in the environment. A vast number of extraction methods have been used for PAHs extraction from water samples, and this review suggests sorbent based sample pretreatment techniques, which offer green extraction options, the simplicity of operation, relatively low costs of instrumentation, easy coupling to chromatographic systems and shortening the time of extraction.

Conflict of interest

Declarations of interest: none.

Acknowledgment

The Ministry of Education, Science and Technological Development of the Republic of Serbia [Project Grant Numbers OI172051 and OI172047] supported the research.

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