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Miniaturized Solid Phase Extraction techniques for different kind of pollutants analysis: state of the art and future perspectives – PART 1

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Abstract

Solid Phase Extraction (SPE) has been practiced in a modern form for more than half a century. It was constantly developing, driven by the analysts needs. These needs are coming from the importance to select an appropriate analytical method, which should have satisfactory accuracy, precision and sensitivity. In the case of sorbent-based microextraction techniques, the choice of miniaturized variants that meet these requirements as well as the requirements of GAC is extremely wide. The increasing popularity of the technique has spurred the influx of many manufacturers into the commercial side of the technology, and many columns, cartridges and discs are comercially available. SPE-type techniques which can be connected with quantification techniques, are perfect to be applied for pollution analysis. The purpose of this article is to provide the reader with an updated, comprehensive overview of modern SPE techniques for different kind of pollutants analysis.

Keywords: Solid Phase Extraction Techniques; Sorbent-based Microextraction; Green Extraction Techniques; Miniaturization; Formats and Devices; Environmental Pollutions

1. Introduction

The rapidly growing number of the human population on Earth and the continuous development of civilization have a huge impact on the natural environment, which entails the increasing chemical contamination of soil, water and air. Reliable diagnosis and constant monitoring of the degree of contamination of natural resources, taking into account the plethora of potential pollutants and contaminants, requires the development of specialized research tools. Therefore, environmental analysis is one of the most important and most dynamically developing areas of contemporary instrumental analysis [1].

The highest acceptable concentrations of the most dangerous chemical compounds for humans and natural environment are often described in detail in various standards and legal regulations, which facilitate the development of appropriate analytical procedures addressed to specific substances. Nevertheless, a significant problem is the analysis of "Contaminants of Emerging Concern (CECs)", i.e. known chemical compounds, the presence of which in the natural environment should be expected, and which have not yet been included in the legal regulations.

There is no doubt that it is of paramount importance to select an appropriate analytical method, which should have satisfactory accuracy, precision, sensitivity, and a sufficiently low limit of detection and quantification (LOD and LOQ). It should be especially remembered that the harmful effects of many substances, e.g. xenobiotics and their metabolites released into the environment, are already achieved at a very low level of concentration [1]. In addition, the practical aspects of the method such as cost of analysis, analysis time, ease of use, and the degree of sophistication of the methodology are often pivotal. An equally important aspect is to ensure that the method remains in agreement with the idea of green chemistry [2]. Accordingly, it should be characterized by a relatively small amount of waste produced, low toxicity of the reagents used, low energy consumption, and safety for the operator. Indeed, an analytical method supposed to be a tool for ensuring the naturalness of the environment should set a good example by itself, be environmentally friendly, and thus be the best advertisement for the idea of sustainable development and pursue of naturalness.

It is assumed that even 80% of time can be routinely spent on proper collection, transport and preparation of samples for the analysis. These stages begin the entire analytical procedure, therefore, they directly determine the quality of results of the qualitative and quantitative analysis. Furthermore, they are often also associated with the greatest consumption of reagents, especially harmful solvents. In environmental analysis, one often deals with a fairly complex form of the matrix and the presence of analytes at low or even extremely low concentration levels [3]. This requires the application of various operations at the sample preparation stage: pre-concentration of the analyte, its isolation from the matrix or simplification of the matrix itself, and elimination of interferents and components that could hinder the implementation of the following steps of the procedure, e.g. substances that may lead to clogging of the chromatographic columns. Modern extraction techniques seem to be best suited for these tasks. In general, they can be divided into two types, differing in the state of the phase into which the extracted analytes are transferred: Liquid Phase Extraction (LPE) and Solid Phase Extraction (SPE).

It is impossible to clearly indicate which type of extraction is better for the analysis of environmental samples, it all depends on the specifics of a particular analytical problem and what resources a given laboratory has at its disposal. However, one can allow for some generalization (see Figure 1), that the selection of SPE is often associated with less solvent consumption, shorter extraction time, lower costs, and the entire procedure is usually simpler and more automated [3]. In recent years, there has been a rapid development of both LPE and SPE, and one of the main trends is striving for ever greater miniaturization in terms of the required sample amounts as well as the amounts of reagents and materials used. Hence, the peak of popularity is currently experienced by microextraction techniques, which are offered in many variants differing in their physicochemical basis, method of implementation, and the type of devices and materials used. In the case of SPE, the choice of miniaturized variants that meet the requirements of green analytical chemistry is extremely wide and hence not straightforward [3]. Although on the one hand this is a desirable situation, as it proves the high level of advancement of current technologies, on the other hand, it may impede choosing the optimal variant in the case of less experienced researchers.

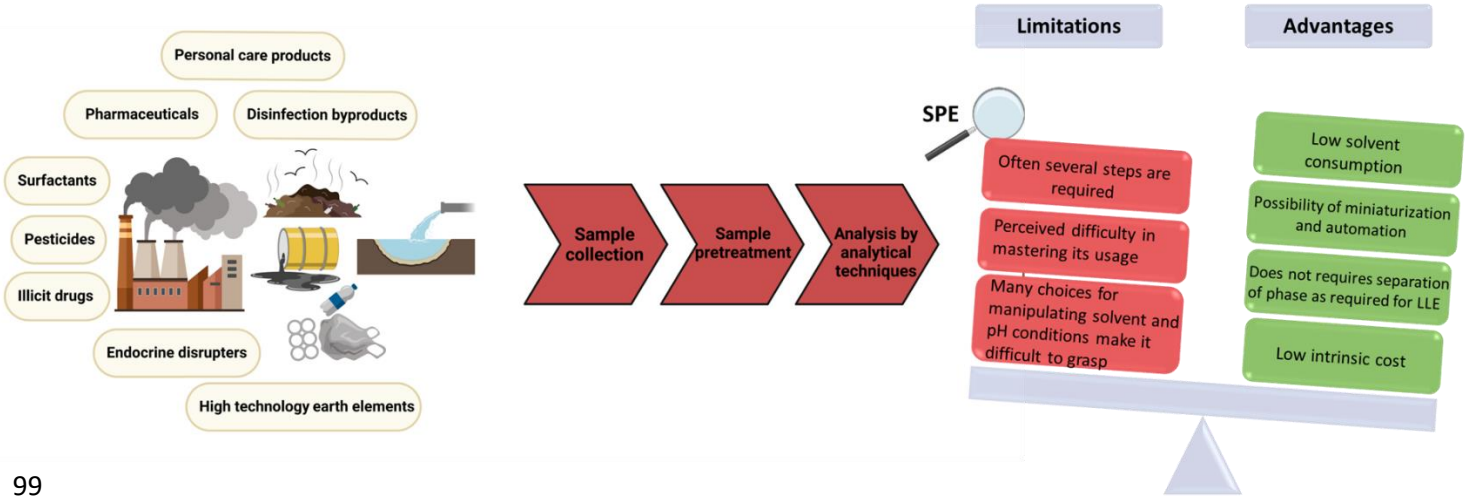

Figure 1. Application of SPE to environmental pollutant isolation and preconcentration with its advantages and drawbacks

The purpose of this article is to provide the reader with an updated and comprehensive overview of modern solid-based extraction techniques for different kind of pollutants analysis. The term sorbent-based microextraction is of paramount importance here since it covers both micro-solid extraction and solid-phase microextraction approaches which are covered in this article. In fact, it presents the current state of the art, along with the numerous references to the most important and representative original works describing specific analytical methods and pollutants. The main features of SPE are discussed, taking into account both strengths and weaknesses, different SPE formats, devices and trapping media. The main intention is to provide a reliable and useful source of information for the entire community of analytical and environmental chemists, and to facilitate the choice of the appropriate SPE variant, optimal with regard to planned application. We also outline the most promising directions for the development of the SPE technology in the near future, and the greatest challenges that will have to be faced. In sum, it need to be mentioned that on-site extraction techniques face two main challenges found in pollutant analysis, minimizing their effects on the analytical results. To be on-site applied, an extraction protocol should be miniaturized, portable, easy to handle, simple (low requirements of energy, reagents, and apparatus), rapid (when short-term information is required), and reproducible manufactured, and solid-based microextarction mostly fullfil these requirements [4].

2. Formats and devices used in solid phase extraction techniques

Without any doubt, the introduction of 12 principles of GAC contributed to rapid development in the range of new methodological and technological solutions in order to assure the quality of obtained results and at the same time, to improve the environmental character. Admittedly, SPE is not an exception, important progress in this technology has been noticed in case of miniaturization, simplification and automation of the primary concept. It is noticeable that the original SPE formats, proposed in 1951, consisted of granular activated carbon put into an iron cylinder, weighted up to 1.2-1.5 kg [5]. Not only the size of such formats has been changed, but also the range of new material classes used for adsorption process has been introduced. The aim was to increase the applicability of SPE for extracting various kinds of analytes from varied matrices, as well as to enhance the analytical performance by significant minimization of the aliquote of sorptive materials and use of solvent. The

schematic representation of the milestones in the progress of methodological solutions related to SPE formats is presented in Figure 2.

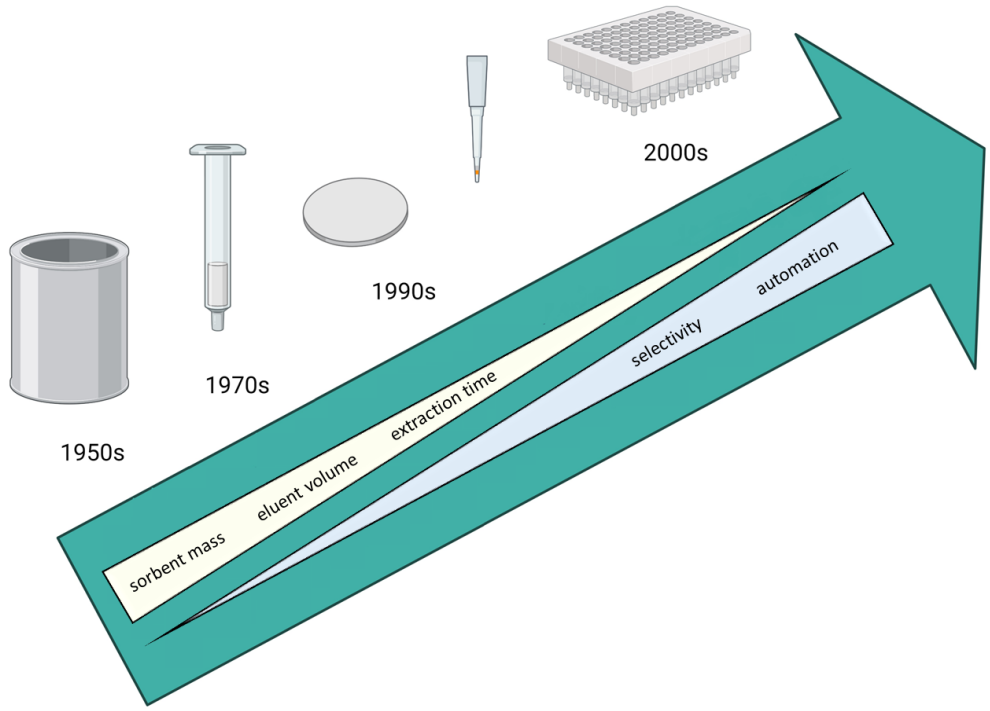

Figure 2. Schematic representation of the milestones in the progress of methodological solutions related to SPE formats used.

2.1. Formats of SPE techniques

2.1.1. Cartriges

Cartridges/columns or syringe-barrel are the most common used SPE setup. It comes with a wide range of stationary phases that can separate analytes based on their chemical characteristics. Analytical chemists prefer this format of SPE configuration in regular applications in quality control laboratories in the arena of food and environmental analysis for the separation and isolation of analytes in different samples [6].

SPE cartridges or tubes are small open-ended polypropylene or glass syringe barrels filled with several types of adsorptive media. In both of glass and plastic tubes, a layer of sorbent bed between polyethylene frits. The selection of a suitable stationary phase, which allows for the stopping of all analytes as well as the selection of the proper column volume, is significant to getting the best extraction efficiency. The liquid phase can be spread through SPE cartridges either by gravitational force or by dynamic method using positive pressure by aid of syringes, air or nitrogen lines, a vacuum flask or a centrifuge [3,7].

This format has a number of advantages, including the ability to create highly selective tools and the ability to combine many columns filled with the same or various types of sorbents in the laboratory. The combination of two distinct sorption materials improves the recovery rate and extraction efficiency of target analytes [8,9].

Despite of these advantages of cartridges there are some drawbacks especially in water analysis. Because the cross-sectional part is tiny, sample processing speeds are sluggish, the tolerance for particle and adsorbed matrix component obstruction is poor, low flow rate, plugging, and smaller breakthrough volume, and channeling limits the capacity to retain analytes [6].

The SPE extraction cartridge is especially appealing for application in pesticide residue analytical procedures in food samples and determining the total polycyclic aromatic compounds in contaminated soils because it often eliminates the need for costly and environmentally dangerous solvents. In particular, the current efforts focus on preparation of cartridges with the smallest feasible volume, holding specialized sorbents for analytes, and to reduce time-consuming laboratory activities as well as energy consumption per analytical cycle. High extraction efficiency, high cleanup, and low use of organic solvents during the conditioning, washing, and eluting phases are required in these situations. In this sense, by decreasing or eliminating the sorbent drying procedure, the total time necessary for the analysis can be reduced [1].

2.1.2. Disks

SPE disk or extraction disk or membrane extraction disk is another popular SPE format. It differs from cartridge in bed packing and the structure of particles [2,10]. The sorbent is embedded in a web of PTFE or glass fiber in these discs. Glass fiber discs are thicker and more robust than PTFE membranes, allowing for larger flow rates. The sorbent particles implanted in the discs are smaller (8 μm diameter quite than 40 μm diameter) than those established in the cartridges. Packaging of stationary phase of sorbent in SPE disks can be classified into immobilized sorbent in polymer or glass fiber, and packed sorbent between two glass fiber filters, the first type resembles filter paper which need special filtration apparatus [11]. Speedisk introduced by J. T Beker in 1998 to eliminate this drawback by fixation of slim layer of the sorption bed amid two layers of plastic grids and glass-fiber filters. They have large active surface and their design promote the recovery rate of the analytes by allowing high value of the sample flow. Instead, they increased the void volume [2]. Speedisk columns, combination of classical column and SPE disks, can overcome the large void volume. Additionally, use of shielding filters can eliminate the stage of sample filtration and reduce the clogging of the columns [12].

High flow rates (and hence shorter extraction times) are the principal advantages of disks, they reduce channelling and voiding effects, enable extremely efficient mass transfer, and eliminate clogging danger. Because of the smaller cross-sectional area of cartridges, the flow rate that can be passed through them is often lower than the flow rate used for disks. Nonetheless, disks are not as widely used as cartridges, and SPE cartridges continue to be the most popular. On the other hand, disks have experienced significant growth since their last survey was published [13]. Compared to traditional SPE cartridges, disks have two distinct benefits. Firstly, they can typically be run with smaller elution volumes and greater flow rates. The small particle size (8-12 μm) of the sorbent embedded in the politetrafluoroethylene (PTFE or Teflon) in the disc, compared to 40-80 μm in a traditional cartridge. Partitioning is aided by the decrease in void volume and enhance surface area associated with tiny particles. Second, the smaller particles give more density and consistency of packing, which lowers breakthrough and channeling and allows for higher flow rates and shorter extraction times [6].

Disks have the problem of only being commercially available for a restricted range of sorbent types, and none of them are selective enough to assist the analysis of complex samples and simplify data processing. Furthermore, compared to SPE cartridges, these devices are much more expensive. disks are only suggested when there is a great interaction between the analyte and the sorbent [13].

SPE disc and cartridge chromatographic procedures are extremely similar in application. Because of the huge cross-sectional areas of the disks and the ability to apply high flow rates, significant volumes of environmental water samples and suspensions may be analysed in fast time without the need for filtration. It's worth noting that filthy samples must be filtered before being extracted with cartridges [1].

2.1.3. Pipette tips

Pipette-tip or in-syringe SPE is a miniaturized style of traditional cartridge-based SPE, in which the sorbent is packed inside plastic micropipette tips or syringe needles. Using single-channel and multichannel pipettors or syringes, analytes are extracted by aspirating and desorbing the sample solution repeatedly [14]. Most of the analytical procedures consist of four main steps (sample collection, preparation, final analysis, and assessment of the results). Each phase has a distinct effect on environmental pollution; therefore, the analysts follow miniaturization of analytical procedures to render them greener.

Brewer patented the disposable pipette extraction (DPX) device in the early 2000s [15]. The DPX is yet another SPE alternative that combines effective and quick extraction with much lower solvent and time consumption. A C18 sorbent produced from chromatographic technology was used in the first commercial DPX. Currently, however, multiple phases are available. DPX is a dispersive μSPE technique that employments a expendable pipette tip with freely stuffed sorbent and upper and lower porous septa to keep it in put. DPX allows the sorbent to be combined with sample solutions [16].

SPE pipette tips have several advantages, including simplicity, reduced amount of absorbent material which contribute significally to very small sample and elution solvent volume, lower cost, the ability to treat several samples with a multichannel micropipette, a quicker extraction time, a high recovery factor, and ease of automation and the resultant eluents directly injected into a gas or liquid chromatography [17].

On the other hand, this format, has some drawbacks such as plugging, high fragility, a considerable amount of plastic waste, and reduced number of commercially available tips [18].

There is currently a large selection of tips available from various manufacturers, ranging in volume (from 1 to 200 μL) and volume of trapping material placed inside [19]. Because the SPE-TP was intended for micro-scale extraction and concentration, it was frequently employed for purification and concentration of proteases in genomic, proteomic, and metabolomic research for protein and peptide purification and isolation [20]. It has also become more popular recently in environmental analysis for the separation of drugs from food samples and biological fluids, as well as fungicides from grape juice and tap water [21–23].

Pipette tip micro solid-phase extraction is one of the most investigated solid-based sample preparation method. This procedure can use both synthetic and commercial sorbents, making them very useful for sample pretreatment of various formats of matrices with good selectivity. Furthermore, this approach is the most effective sorbent-based sample preparation method for downsizing of the traditional solid phase extraction method and minimising sample, material, and solvent consumption. As a result, is is referred to as solvent-free sample preparation procedure. It can also be viable in quantitative analysis of different analytes in various matrices with high extraction efficiencies and sample cleanup values [24,25].

2.1.4. Multi-well SPE plates

Multi-well SPE is a miniature and automated version of SPE that allows for the most precise control of sample and solvent manipulation. Standard microliter plates are utilised in this configuration. Small (0.65 mL or 2.5 mL) SPE cartridges packed with 3–200 mg of the sorbent are placed in each well. This format is available in 96, 384, and 1536 wells, the 96-well device is much more frequently selected by analytical researchers, allowing for the rapid and simultaneous processing of a huge number of samples in a brief period of time [14,26].

This format have many advantages of being economical by saving time and solvent, preparation of many samples can be done simultaneously, using of multi-channel pipettors facilitates liquid transfer steps, readily adaptable to all common automated handling systems, green method, increased precision and accuracy as compared with manual methods, and minimized dead volume [6].

The main disadvantages of this format are different from those of all microextraction methods. Respectively, a rigorous control of extraction conditions is required, including pH, ionic strength and temperature, to obtain best method precision. In addition, highly sensitive analytical instrumentation is required for detection to compensate for non-exhaustive analyte recovery, and in direct extraction mode, the analytical sensitivity of

this format is often lower than that of traditional methods. As a result, it is inappropriate for the development of methods that require exceptional sensitivity. Furthermore, due to evaporative losses, this approach is not suitable for volatile analytes due to the open-bed configuration[27].

Multi-well SPE plates have been employed in high-throughput clinical applications as well as in environmental monitoring of numerous types of xenobiotics in complicated matrices. The approach can be used to isolate pesticides from water samples and food, as well as to produce pharmaceuticals in human plasma, urine, and wastewater effluents, according to available data [28,29].

To date, high-throughput multi-well SPE plates have been successfully used in clinical, pharmacological, toxicological, food, and environmental analysis. Other applications, such as tissue analysis after homogenization or analysis of non-volatile components or pollutants in food commodities, have yet to be explored, offering numerous chances for future development. Metabolite profiling of plasma or blood, for example, might be easily moved to this high-throughput technology in the future to allow for the rapid preparation of huge numbers of samples [27].

2.1.5. Comparison of different formats used in SPE

Reduced bed masses, high-throughput capabilities, and greater technique development convenience are advantages of the new SPE formats. Small-bed-mass SPE devices enable faster technique development, lower solvent usage, and rapid overall sample preparation. Depending on the extraction goal, there are a variety of performance criteria for SPE devices and formats. These features, as well as their importance and determinants, were listed above. The sum of numerous properties of the SPE device and supporting systems are frequently used to derive a satisfactory performance To choose the appropriate format/device for a particular application, the same features are taking into account. In **Table 1**, different SPE formats and devices are compared and illustrated.

Table 1. Comparison of different formats and devices used in SPE.

Parameters	**Cartridges**	**Disks**	**Pipette tips**	**Multi-well plates**	**Dispersive SPE**
Mode	Moderately on-line	Moderately on-line	Mostly on-line	Mostly off-line	Mostly off-line
Level of automation	Moderate	Moderate	High	High	Low
Scale of extraction	Small scale: 1–3 mL (3–200 mg sorbent) Medium scale: 1–60 mL (3–200 mg sorbent) Large scale: 10–150 mL (3–200 mg sorbent)	Disks with diameter ranges from 4 mm to96 mm (3–200 mg sorbent)	Tips with volume of 1–200 μL	0.65 mL or 2.5 mL SPE cartridges (3–200 mg sorbent)	1–20 mg of sorbent
Mode of extraction	Extraction/ cleanup	Extraction	Extraction	Extraction	Extraction/ cleanup
Goal of extraction	Preconcentration/ remove matrix interference	Preconcentration	Preconcentration	Preconcentration	Preconcentration/ remove matrix interference
Time of extraction	Slow (minutes up to hours)	Moderate (minutes)	Fast (minutes)	Fast (minutes)	Fast (minutes)
Type of sorbent	Limited	Limited	Extensive	Limited	Extensive
Geometry of the sorbent material	Microparticles (˃40 μm)	Microparticles (˃8 μm)	Nanostructured materials	Microscale sorbent (˃40 μm)	Microparticles to nanostructured materials

Application	Environmental and food analysis	Environmental analysis (in particular large volume samples)	Biological research	Bioanalytical analysis	Environmental samples
Advantages	- Possibility of preparing in laboratory - Possibility of combining several columns filled with the same or different types of stationary phase - Low cost	- Small volume of elution solvents - Faster flow rates without channelling effect - Smaller void volume - Large surface area per unit bed mass - Possibility to skip the filtration step -Less-time consuming - Possibility of integrated sample-processing techniques, (in-vial desorption and on-disk derivatization) - Available in wide range of sizes	- Less time consuming and simplicity - Very small volume of sample and elution solvents - Ability to treat many samples by using a multichannel micropipette - Shorter extraction time - High recovery factor - Readily automated - Law cost - One extraction method for all analytes - Clean extract	- Rapid preparation of a large number of samples - Less labour and time consuming - Reduce handling errors - Small volume of elution solvents - Fast flow rates without channelling effect - Show excellent repeatability - Clean sample extracts minimizing the potential for ionization suppression	- Small volume of elution solvents and sorbent mass
Disadvantages	- Small cross-sectional area - Slow flow rate - Channelling - High void volume - Plugging	- Smaller breakthrough volume - More expensive than cartridges	- Plugging - Large amount of plastic waste	- Costly wells - Due to open-bed configuration, this technique is unsuitable for volatile analytes due to evaporative losses	- Effectiveness of extraction depends on choosing of appropriate sorbent

2.1.6. Application of selected solid-based extraction formats and devices

Since the development of the concept of sorbent-based extraction methods, significant progress has been made not only in their formats but also in methodology, including simplification, automation, and miniaturization of the original concept. In this sense, a high number of techniques collectively referred to as 'microextraction methods' have been developed based on the minimalization of the number of treatment steps (in order to reduce time and the possibility of contamination or losing analytes), the reduction/elimination of the use of organic solvents and reagents classified as rising environmental concerns or replacing them by non-toxic ones, the reduction of waste production and using smaller initial sample sizes [30,31].

Hence, the different miniaturized greener sorbent-based microextraction formats, such as solid-phase microextraction (SPME), micro stir-bar sorptive extraction (μ-SBSE), micro-solid-phase extraction (μ-SPE), microextraction in a packed syringe (MEPS), miniaturized matrix solid-phase dispersion (μ-MSPD), μ-QuEChERS ("micro-Quick, Easy, Cheap, Effective Rugged and Safe"), pipette-tip solid-phase extraction (PT-SPE), dispersive micro-solid phase extraction (μ-dSPE), have been introduced to analytical practice [30–32]. The pursuit to obtain precise and accurate measurements of analytes at trace or ultra-trace concentration level in complex matrices has led to rapid growth in the modification of microextraction approaches. In the literature, a huge number of new, often very complex names of novel micro-extraction approaches can be found [33–36]. As a result, deciphering the procedure used by researchers may be much more difficult. Moreover, the great variety of approaches available also makes the use of a single criterion to classify all of them problematic. Generally, taking into account the sorbent geometry in the extraction device and the number of operational steps, these approaches can be classified into two groups, micro-solid-phase extraction (μ-SPE) and solid-phase microextraction (SPME). The Figure 3 shows the classification of selected novel micro-extraction approaches most commonly used in environmental analysis in recent years.

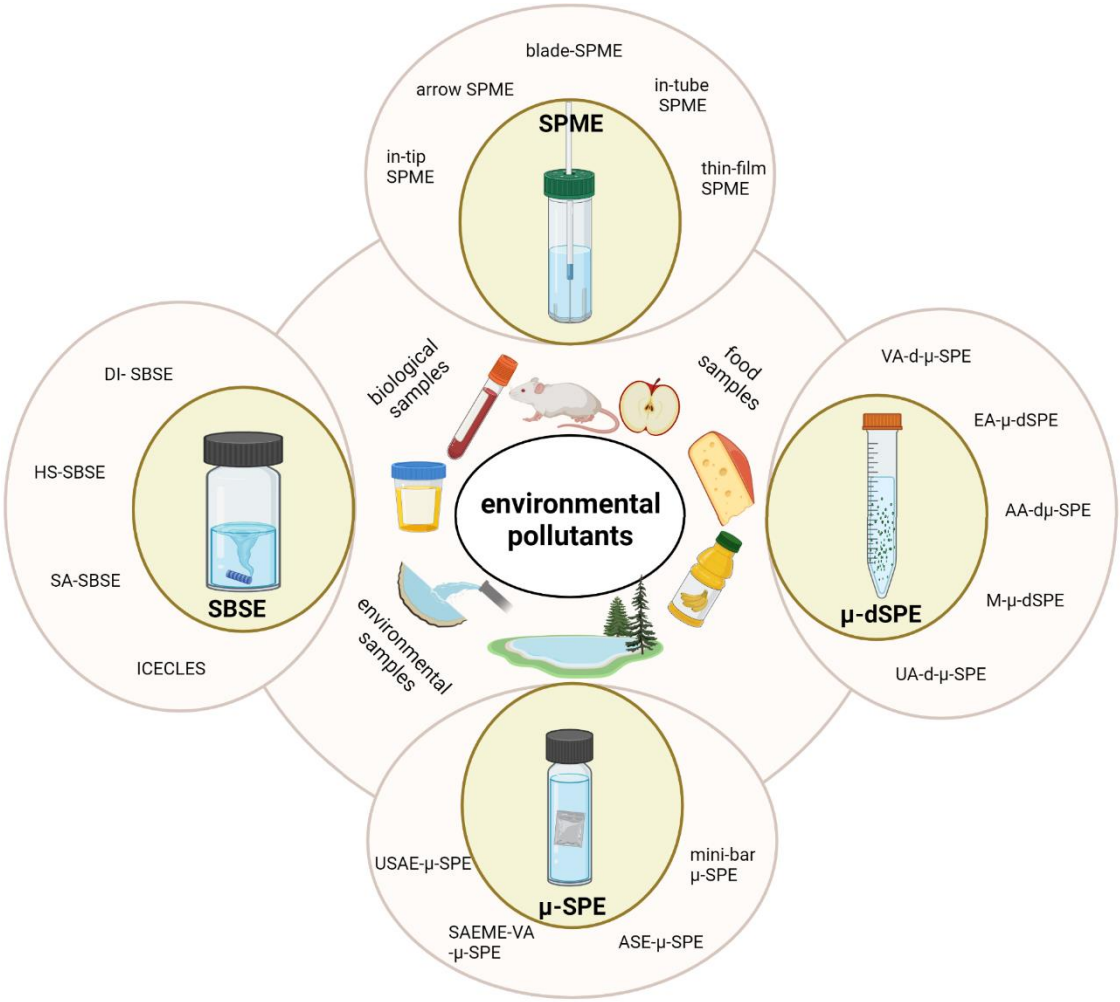

Figure 3. Different types of solid-based microextraction techniques applied to extraction of environmental pollutions from biological, food and environmental samples. Figure created using BioRender(https://biorender.com/).

The theoretical principles and modes of action of miniaturized solid-phase extraction techniques have been described in detail in our previous work [30] as well as in many others [31–33,37].
Therefore, this section focuses mainly on the review and discussion of the most important achievements and improvements in the miniaturized sorbent extraction methodologies used for environmental pollution analysis over the last years. Based on a review of scientific papers published recently, the following main strategies for greening the μSPE and improving effective isolation and enrichment analytes can be distinguished: (i) miniaturization of extraction device, (ii) application of assisted factors, (iv) combining with other extraction techniques (iii) automation, and (iv) utilization of flow injection techniques [38,39]. All of these modified forms have been successfully applied to isolate and enrich environmental pollutants from various types of samples.

2.1.6.1. μSPE

Since the introduction of the miniaturized SPE format into analytical practice in 2006, many modified forms have been developed. Starting with the type of membrane used, the shape of the μSPE device and the addition of a rotating element and ending with its combination with other techniques [34]. The ease of modification, the fact that they are simple to carry out and cost-effective, the high extraction efficiency and the protection of sorbent, preventing the absorption of interfering species, thereby reducing the matrix effect make this technique highly popular, in particular for the analysis of

complex samples, such as urine, blood, tissues, milk, sludge and food samples [40–44]. Generally, it is difficult to clearly indicate the area of application of this technique. The possibility of using various types of sorbents, both traditional, such as silica and bonded silica, polymeric and carbon-based materials, and modern ones, makes it suitable for the extraction of various types of compounds in environmental, food and biological samples [34]. For example, MIPs have been used in this mode for the extraction of aflatoxins from fish feed extract [45]. Metal-organic framework (UiO-66 (Zr)) has also been applied to isolate and enrich androgens and progestogen from water samples [46]. Additionally, for the determination of phthalates in milk, a natural sorbent such as the powder of *Moringa oleifera* seeds was used [47]. A review of articles published over the last 5 years indicates that the main field of μSPE application is the extraction of organic compounds from environmental, food and biological samples.

Porous membrane-protected micro-solid-phase extraction is also very versatile in terms of the sample type. It is applied in the preparation of both solid and liquid samples. In the case of liquid samples (beverages, environmental water, biofluids, liquid foods, etc.), the extraction device can be directly placed in the sample, while in the case of solid and semi-solid samples (e.g., sediment, biological fluids, food etc.) the digestion or dissolution of the sample in water or other solvent is required [45]. The main variations of this technique and applications are summarized in Table 2.

In the basic concept of porous membrane-protected SPE, to form the device, a small amount of sorbent is packed inside a sheet of porous polymer membrane. Polypropylene (PP) is the most widely used material because of its good thermal and chemical stability and the fact that it is easily heat-sealable [34]. However, due to its small pore size and low wettability, the extraction time is elongated. To overcome this limitation, other materials were used instead of PP. For example, cellulosic tea bag filter paper was used to prepare the μSPE device for isolation and preconcentration of BTEX from agricultural, well and rainwater samples [48]. Furthermore, polyamide organic membrane and polyether sulfone membrane were used in a study aiming to determine parabens in water samples and active ingredients of an herbal drug in rat plasma, respectively [49,50]. In order to increase the efficiency of the extraction process, the procedure can also be combined with other extraction techniques. To extract BPA from aqueous samples, ultrasound-assisted emulsification and micro-solid-phase extraction (USAE-μ-SPE) has been applied. The developed method provided high sensitivity, wide linear range and high recovery. Moreover, the mass of sorbent used and the LOD value was lower compared to another sample preparation procedures for BPA determination [51]. Similarly, this approach has been successfully applied to isolate estrogens from environmental water samples [52]. In another study, vortex-assisted dispersive liquid-liquid microextraction combined with the μSPE (DLLME–μ-SPE) procedure has been applied for the extraction of polycyclic aromatic hydrocarbons (PAHs) from ambient fine particulate matter. A comparative study on this combined procedure and conventional μ-SPE demonstrated higher efficiency of VA-DLLME–μ-SPE for most of the PAHs indicating that the vortex-assisted dispersive liquid-liquid microextraction step was significant as a first-stage enrichment process [53]. Furthermore, microwave-assisted (MAE-μ-SPE) [54], and accelerated solvent extraction (ASE-μ-SPE) [55], and accelerated solvent extraction (ASE-μ-SPE), as well as sonication-assisted emulsification microextraction combined with vortex-assisted μ-SPE (SAEME-VA-μ-SPE) have also been successfully applied to isolate various types of analytes [56,57].

While discussing the factors influencing the increase of the extraction efficiency, one cannot omit the modification based on the use of the rotating element.

Continuous motion and rotation of the device enhance the effective surface area of the sorbent exposed to sample solution and solve the previously faced problem of the traditional μSPE, connected with incomplete immerses of the device. To ensure rotation of the device, an approach based on placing a tiny metal rod along with the sorbent or inserting it into the outer bag, or (mini-bar μ-SPE) has been applied. The study focused on the comparison of extraction performance of antibacterial agents from wastewater samples using traditional μ-SPE and mini-bar μ-SPE showed more than double the increase of extraction recovery for triclosan and triclocarban, and about almost a third for methyl-triclosan. The authors attributed this fact to regular stirring patterns, resulting in better mixing and thus increasing the mass transfer of the analytes from the solution to the sorbent [58]. Mini-bar μ-SPE was also appreciated by other researchers and applied to extract i.a. pharmaceuticals and organochlorine pesticides from urine [59,60], polyaromatic hydrocarbons from wastewater [61] and non-steroidal anti-inflammatory drugs from wastewater and lake water samples [62].

2.1.6.2.SPME

Without any doubts, SPME is one of the most widely used sorption-based microextraction techniques nowadays. Since its initial introduction to analytical practice in 1989, it has been widely used in analysis of environmental, food, pharmaceutical, and biological samples. The search on Scopus database revealed that for 32 years, more than 17000 papers were published that are related to SPME. They include applications for the analysis of organic and inorganic compounds and the various modifications implemented to achieve the best extraction efficiency. The attractiveness of SPME is owed to its unique advantages, such as (i) simplicity, (ii) rapidity, (iii) high efficiency, (iv) compatibility with different separation (gas and liquid chromatography and capillary electrophoresis) and detection modes (MS, DAD, UV, FLD) (v) possibility of automation, (vi), no requirement for solvent or requirement of smaller solvent aliquots than other extraction methods, and (vii) low cost [36]. In addition, SPME enables the integration of several analytical workflow steps, such as sampling, extraction, preconcentration, and sample introduction into instrument, thus allowing for easy, quick, and accurate analysis [63]. Current trends in the SPME area are mainly focused on the development of novel sorbent coatings, novel geometrical configurations, operational modes, automation, and coupling with different analytical instruments [36].

To adjust the characteristics of a method to specific application and related requirements, different extraction configurations of SPME have been designed, including in-tube SPME, blade-SPME, thin-film SPME, arrow SPME, in-tip SPME, electromembrane-surrounded SPME and others. All these techniques have been described in detail in many articles [33,64,65].

Up to now, fiber SPME in which extraction phase is coated as a thin film on the surface of a needle, is still the most used configuration. There are two basic ways of SPME sampling: by direct immersion (DI-SPME), the fiber coated with an adsorbent is immersed into the sample matrix and via headspace, (HS-SPME) where the fiber is placed in the headspace of the sample. Then, the analytes trapped by the coating of the fiber can be thermally desorbed by subjecting the fiber to high temperatures in the inlet of a GC instrument or by its immersion in solvent. In a typical fiber-based SPME, the extraction performance mostly depends on the affinity and selectivity toward a target analyte of the extraction phase. Therefore, the selection of appropriate fiber coating is the most critical point in SPME [66]. Recently, many efforts have been made to develop novel fiber coatings for high extraction performance. In addition to the selection of an appropriate sorption material, the extraction efficiency is also influenced by the geometry of the fiber. It was stated that decreasing the device diameter results in an improved extraction rate due to radial diffusion [33]. Therefore, researchers' activities were oriented on the development of microscale devices. In 2016, Piri-Moghadam et al. introduced a miniaturized SPME fiber, named coated-tip SPME or minitips, which consist of acupuncture needles (150–500 μm length) that have been electrochemically coated in biocompatible N-vinylpyrrolidone-co-divinylbenzene (HLB). Application of conical shape tip favorably affected stability and handling, while preventing the device from bending during sampling [64]. The minitips have been used to extract diazepam, nordiazepam, oxazepam, and lorazepam from 1 μL of blood samples. In other work, minitips with biocompatible nanostructured conductive polymerpolypyrrole (PPy) were used to extract selected drugs from biological samples and quercetin from a single cell of onion [67]. Other researchers proposed using multiple fibers (MMF-SPME) consisting of four independent thin monolithic fibers with diameters of 500 μm and a gap of 200 mm between each individual fiber. The overall extraction efficiency of chlorophenols from tap, lake and river water samples obtained for this multiple-fiber device was higher than that of a single fiber of the equivalent area [68]. Due to the progress in miniaturized configurations and rapid development of biocompatible coatings materials, SPME is increasingly used in *in vivo* analysis (sampling directly performed on living organisms) in biochemical, clinical and environmental research. In the last five years, *in vivo* SPME was applied to the analysis of pharmaceuticals [69,70], tetrodotoxin [71], UV filters [72], fluoroquinolones [73], in living fishes, organophosphorus pesticides [74], insecticides [75], volatile organoselenium compounds [76] in plants as well as neurotransmitters and metabolites in different mammal tissues [77,78]. Undoubtedly, a strong point of *in vivo* techniques is a non-lethal sampling approach that provides more precise information of what is occurring in a complex living system.

In addition to the miniaturization, the activities of researchers were also focused on automation and combination with other analysis instruments that has been vastly documented in recent years [63,66,79]. All of these modifications resulted in the extension of the applicability of SPME for extracting analytes from different complex matrices and also influenced the increase in the effectiveness of the previously proposed applications. In this sense, many examples of the applications of SPME for determining environmental pollutants in liquid, gaseous and solid samples, including *in vivo* sampling, are available in the literature, and some recent relevant applications are summarized in Table 2.

2.1.6.3. Stir bar sorptive extraction

Stir bar sorptive extraction (SBSE) is an equilibrium-based microextraction technique such as SPME that utilizes a stir bar coated with a sorbent as an extraction phase. A typical SBSE device consists of a 1.5 cm long glass magnetic stirrer coated by a layer (typically 0.5–1 mm) of sorptive material. Depending on the matrix complexity and the analytes' properties, extraction can be carried out in two manners, either by direct immersion of stir bar (DI- SBSE) in the aqueous sample, or in the case of more volatile compounds analysis, by suspension of the stir bar in the headspace (HS-SBSE) above a sample by stainless-steel wire or by using magnets. Subsequently, the extracted analytes are desorbed using a thermal desorption unit coupled to gas chromatography. In the case of thermally labile analytes or when the separation is carried out using LC or CE, the analytes are desorbed by exposing the stir bar to a small volume of a suitable organic solvent [30,80].

Since the introduction of SBSE to analytical practice in 1999, it has become a powerful extraction and concentration method for solventless and miniaturized sample preparation in almost every field of analytical applications including food, flavour, environmental, and biomedical science (Table 2).

Although the majority of SBSE applications concerns the analytes extraction form aqueous matrices, information can also be found in literature on the applications of this technique to solid sample preparation. In those cases, the solid sample is either suspended in an aqueous solution and the stir-bar is dipped into the suspension, or solid-liquid extraction is performed before SBSE [81].

However, it should be noted that the field of application of SBSE is constantly increasing. This is due to the use of new sorbent materials and the introduction of numerous modifications to eliminate the limitations of the original device [82]. One of the major drawbacks of classical SBSE using PDMS was poor extraction of polar compounds. To overcome this limitation, two approaches, ice concentration liked with extractive stirrer (ICECLES) and solvent-assisted SBSE (SA-SBSE), have been proposed. ICECLES was first described by Maslamani et al. in 2016. This approach is based on the application of freezing during SBSE. During freezing, pure water of the sample is gradually frozen, while analytes are gradually concentrated in the remaining liquid part [83]. The results of the research aimed at the comparison of extraction efficiency of ICECLES to other microextraction sample preparation techniques for atrazine from drinking water demonstrated better response with respect to SBSE and SPME (almost twofold increase in comparison to SBSE and 7-fold increase in the extraction efficiency compared to SPME) [84]. This approach has also been successfully applied to the extraction of nitrosoamines [85] a and per- and polyfluoroalkyl substances [86] from drinking water and atrazine from soil [87]. Another interesting approach to extend the application of SBSE to more polar analytes was also developed this same year. Solvent-assisted SBSE (SA-SBSE) proposed by Ochiai at al. is based on the use of organic solvent (e.g., cyclohexane, iso-octane, ethyl acetate, acetone, acetonitrile, methanol) on a swollen PDMS stir bar. The solvent absorbed in the swollen PDMS phase acts as a modifier of the PDMS increasing the diffusion and also causing an increase in the volume of the extraction phase, resulting in enhanced recovery [88]. SA-SBSE is of interest in many application areas, especially when compounds with different polarity are analysed, e.g. flavour profiling and pesticide analysis [88–90].

Due to the stir bar being usually prepared by coating adsorbents directly on the surface of the device, the coating is vulnerable to damage by direct contact with the bottom of the container. Therefore, recently, different modifications were also carried out on the stir bar geometry. In 2020, Sukree and co-workers developed a new stainless steel mesh dumbbell SBSE device for the extraction of phthalate esters from instant noodle and rice soup samples. To fabricate the device, a piece of stainless-steel net was rolled into a tube. Subsequently, sorbent and a metal rod were inserted into the tube, the ends of the

tube were closed using Teflon caps. Through the use caps whose diameter was larger than that of the tube, the possibility of contact between the tube filled with sorbent with the bottom of the container was eliminated [91]. Another study by Mao et al. introduced a coated stir bar enclosed in a porous membrane. The membrane protected stir bar sorptive extraction (MPSBSE) was used on the water samples preparation step to determine non-steroidal anti-inflammatory drugs followed by HPLC-UV [62]. Moreover, to reduce the friction and increase the lifespan of the stir bar, some authors suggested to additionally use a porous alumina support [92], silicone wheels on two edges of a stir bar [93], and a dumbbell-shaped structure consisting of a p-naphtholbenzein modified porous PEEK (poly(ether ether ketone)) jacket and two lollipop-shaped stainless steel needles [94]. In 2020, another interesting modified device based on the use of 3D printing stirring cages for holding the nanofibers as adsorbent was proposed. The device was used for the extraction of eight bisphenols from river waters. The use of this approach made it possible to significantly shorten the extraction time compared to traditional SBSE [95].

In addition to developing new devices, researchers' efforts are also focused on increasing the degree of automation. However, so far, not many methods have been introduced. In 2016, Ghani and co-workers applied automated multi-syringe SBSE (MS-SBSE) to the extraction of four chlorophenols from environmental water samples. The MS-SBSE demonstrated high repeatability, high versatility of extraction conditions, and greatly simplified the human operation process. However, it should be emphasized that in this approach, only the extraction and desorption processes were automated, the concentration of the extract, and then the transfer sample to the HPLC system remained offline [96].

2.1.6.4.Dispersive μSPE

The next main sub-mode of miniaturized sorbent-based extraction methods is dispersive micro-solid-phase extraction (μ-dSPE), which is a scaled-down variant of dispersive solid-phase extraction (dSPE). This technique is also based on the dispersion of sorbent in the sample, but its amount is significantly reduced [31]. After extraction, the sorbent is separated from the sample and the analytes are desorbed either using a small amount of solvent, or thermally in a thermal desorption unit, and introduced into the detection system for the determination of the analyte. To separate the sorbent containing the trapped analytes from the remaining sample matrix, centrifugation is used most often. However, this step also can be performed by filtration (most often using a syringe filter) and by an external magnetic field when magnetic sorbent (M-μ-dSPE) is used. In this technique, high extraction efficiency can be obtained due to increased interaction between analytes and the sorbent. Therefore, the dispersion of the sorbent plays an essential role. To achieve adequate dispersion of the sorbent, two main approaches can be applied: the use of an external energy source or chemicals [30,97]. In the first approach, typically vortex (vortex-assisted dispersive micro-solid-phase extraction, VA-d-μ-SPE) or ultrasounds (ultrasound-assisted dispersive micro solid-phase extraction, UA-d-μ-SPE) is applied, which is very effective. However, it makes the overall procedure time-consuming and poses a risk of degradation of thermally labile analytes by temperature increase [98]. Therefore, recently, an alternative method to maximize the dispersion of the sorbent has been proposed. In 2016, Rajabi et al. introduced the so-called air-assisted dispersive micro-solid-phase extraction (AA-dμ-SPE) based on rapid aspiration and ejection of the sample and sorbent by means of a syringe (30 cycles) [99]. AA-dμ-SPE has been applied for the determination of tramadol in urine, saliva and plasma samples prior to GC–FID [100], PAHs in saliva and blood [99], and pesticides in fruit juice samples [101]. Another interesting development permitting an increase in dispersion is effervescence-assisted μ-dSPE (EA-μ-dSPE). This approach is based on the dispersion of sorbent assisted by effervescence. For that purpose, a tablet containing a proton donor compound, a source of CO_2 (usually sodium carbonate) and the solid sorbent is prepared and directly added to the sample. The tablet's dissolution generates carbon dioxide bubbles, which efficiently disperse the sorbent [37]. Depending on the sample volume, the tablets can be added to the beaker or placed in a syringe [102] or in pipette tip [103]. From a GAC point of view, it should be emphasized that the elimination of the need to use external energy sources in the EA-μ-dSPE and AA-dμ-SPE techniques enhanced their green character. Another way to meet the requirements of GAC is the automation of the process and direct coupling with instrumental techniques [38]. However, due to the necessity to carry out two stages of separation (isolation of the sorbent from the sample solution

after extraction, and separation of the eluent and the sorbent with analytes after elution), automation is not a simple task. Therefore, only a few automated approaches have been developed so far. In 2018, Vakh and colleagues proposed a new approach to the automation of magnetic dispersive micro-solid phase extraction based on the dispersion of the magnetic nanopraticles in a liquid sample phase by air-bubbling and collecting magnetic sorbent containing analytes in the fluidized reactor in a magnetic field. After the desorption of potassium hydroxide in methanol, the solution containing eluted analytes was, by means of a peristaltic pump, aspirated to a vial and then analyzed by HPLC-FLD. This automated approach was applied for the determination of fluoroquinolones in meat-based baby food samples. The overall process was completed in relatively shorter times compared to other methods reported for the determination of fluoroquinolones in food samples and required a smaller amount of sorbent [104]. Tang at al. developed an alternative fully automated approach using magnetic dissolvable Fe3O4-LDH core-shell microspheres as sorbent for the determination of acetylsalicylic acid, 2,5-dihydroxybenzoic acid, 2-phenylphenol and fenoprofen in aqueous samples followed by HPLC-PDA. An autosampler with a built-in agitator and a robotic arm with a micro-syringe was used to perform μ-dSPE in a fully automated mode. For the extraction, a vial containing the sorbent suspension and the sample (1 mL) was transferred to the agitator and then to an autosampler tray position in which a magnet was prepositioned. The sorbent was retained at the bottom of the vial and the robotic syringe aspirated the sample matrix. After desorption, 10 μL of the desorption solvent was collected and directly injected into the HPLC system. The developed method was rapid and straightforward, with very low solvent consumption and good reproducibility[105]

Due to the many advantages, such as simple operation and short time requirements, high extraction efficiency and capability of combination with different detection techniques, μ-dSPE is one of the extraction techniques with the highest number of analytical applications (e.g., environmental, clinical and food analysis) and different kinds of matrix, including wastewater, environmental water, biological fluids, soils and beverages [31,41,97,98,105–110]. Selected application of μ-dSPE -based methods in different fields of analytical chemistry are summarized in Table 2.

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Miniaturized extraction technique	Analyte	Matrix	Sorbent (mass)	Overall procedure time [min]	Extraction time [min]	Accelerate factor	Detection technique	Linear range	LOD	LOQ	Recovery [%]	Ref
Environmental samples												
µ-SPE	estrone, 17α-estradiol, 17α-ethynylestradiol, diethylstilbestrol	water	reduced graphene oxide (r-GO) (1 mg)	35	15	stirring	HPLC–UV	0.01–100 [µg/L]	0.24–0.52[ng/L]	0.80 – 1.51 [ng/L]	91-113	[105]
µ-SPE	testosterone , progesterone, testosterone propionate , medroxyprogesterone acetate	water	UiO-66(Zr) (10 mg)	70	40	stirring	HPLC–MS/MS	-	2-10 [ng/L]	7-20 [ng/L]	81.4-93.9	[46]
µ-SPE	benzene, toluene, ethylbenzene, xylenes	Water (10 mL)	β-CD (15 g)	50	30	stirring	GC-FID	0.5-500.0 [ng/mL]	0.15-0.60 [ng/mL]	0.5-2.0 [ng/mL]	64.5–101.3	[48]
USAE-µ-SPE	bispfenol A	Water (20 mL)	MIP (4 mg)	7	4	ultrasound	HPLC-DAD	0.5–700 [µg/L]	0.07 [µg/L]	0.23 [µg/L]	82.2–118.9	[51]
USAE-µ-SPE	17β-estradiol, estriol, 17α-ethynylestradiol	Water (10 mL)	MIL-101(Cr)	35	2	ultrasound	HPLC–MS/MS	5-50000 90-100000	0.954-2.43 [ng/L]	3.74-9.34 [ng/L]	85.4-120.8	[52]

								[ng/L]				
VA-DLLME–μ-SPE	PAHs (8 compounds)	air particular matter	reduced graphene oxide (1 mg)	30	7	stirring, ultrasound	GC-MS/MS	0.5–50 0.5–100 [μg/L]	0.013 –0.13 [μg/L]	0.042-0.45 [μg/L]	57-88	[53]
mini-bar μ-SPE	triclosan, triclocarban, methyl-triclosa	wastewater	graphen (20 mg)	135	120	stirring	HPLC-UV	0.2–1000 [μg/L]	0.04–0.07 [μg/L]	0.13-0.22 μg/L]	80.8-103	[58]
MMF-SPME	chlorophenols	environmental water	poly (vinylimidazole-ethylene dimethacrylate)	45	25	-	HPLC-DAD	1.0–200 [μg/L]	0.13-0.29 [μg/L]	0.44-0.98 [μg/L]	73.8–101	[68]
ICECLES	atrazine	Soil (10 g)	PDMS	315	240	stirring	HPLC-MS/MS	10-10 0 0 [ng/kg]	5 [ng/kg]	10 [ng/kg]	87-109	[87]
MS-SBSE	4-CP, 2,4-DCP, 2,4,6-TCP, PCP	environmental water (3 mL)	montmorillonite/epoxy composite	10	5	stirring	HPLC-DAD	0.2–200, 1–200, 1–500	0.02-0.34 [μg/L]	0.06-0.92 [μg/L]	88.5- 98.5	[96]
SBSE	BPA, BPAF, BPAP, BPC, BPBP, BPG, BPM, BPZ	river water	nPCL/μPCL	85	35	stirring	HPLC-DAD	0.5−200 7.0−200	0.1-2.1 [μg/L]	0.4−7.0 [μg/L]	87.1-106.5	[95]

SB-μ-SPE	PAHs (5 compounds)	wastewater	carbon foam (6 mg)	60	40	stirring	GC-MS	1–100, 25–100	0.29-8.4 [ng/mL]	-	91.8-102	[61]
μ-dSPE	Co (II), Ni (II), Mn (II) and Cd(II)	river, urban and industrial water (20 mL)	$ZnFe_2O_4$ nanotubes (20 mg)	-	0.83	ultrasound	ICP-MS	-	0.09-3.7 [pg/mL]	-	92.0–105.0	[106]
Food samples												
μ-SPE	Phthalates (13 compounds)	milk	powder of *M. oleifera* seeds (30 mg)	30	10	ultrasound	GC-MS	1-100 [μg/L]	0,01 – 1,2 [μg/L]	0,10 – 3,7 [μg/L]	78 ± 4 - 102 ± 4	[47]
μ-SPE	organochlorine pesticides (15 compounds)	Milk (10 mL)	zinc oxide incorporated carbon foam (15 mg)	40	30	stirring	GC-MS	1-250; 5-250 [ng/mL]	0.19-1.64 [ng/mL]	-	85.1-101.6	[44]
UAE-μ-SPE	aflatoxins B1, B2, G1, G2	fish feed (0,25 g)	MIP (50 mg)	35	10	ultrasound, stirring	HPLC-MS/MS	-	0,42-1,2 [μg/kg]	1,3-3,5 [μg/kg]	80.0-100.0	[45]
μ-SPE-D	formaldehyde, acetaldehyde, propanal,	fried food	NH2-β-CD-Poly(St-	20	5	stirring	HPLC-DAD	0.1-10	0.024-2.5	0.081-7.6	81.7–114.9	[107]

	butanal, pentanal, hexanal, heptanal		DVB-MAA (10 mg)					5-200 [µg/L]	[µg/L]	[µg/L]		
ASE-µ-SPE	tetracycline, deoxytetracycline,oxytetracycline	Meat (1 g)	copper(II) isonicotinate (10 mg)	60	20	-	HPLC-UV	0.005–10; 0.01–10 [µg/g]	7.4–16.3 [ng/g]	24.7–53.8 [ng/g]	92-105	[55]
in vivo SPME	Pharmaceuticals (12 compounds)	fish	PLCL	40	10	-	LC-MS/MS	2-50000; 20-50000 [ng/g]	0.16 - 5.35 [ng/g]	0.55-16.3 [ng/g]	-	[70]
in vivo SPME	acidic pharmaceuticals (10 compounds)	fish	C18@GO @PDDA	40	10	-	HPLC-MS/MS	1-50000 30-50000 [ng/g]	0.13-8.44 m[ng/g]	0.44-28.1 [ng/g]	-	[69]
in vivo SPME	UV filters (7 compounds)	fish	C_{18}	200	20	-	GC-MS	1-7 [µg/g]	2-25 [ng/g]	5-70 [ng/g]	-	[72]
in vivo SPME	hexachlorobenzene, fipronil, chlorfenapyr	garlic	MWCNTs/ PANI-PPy	50	25	-	GC-MS	1-150; 1-400 [ng/g]	0.38-2.28 [ng/g]	1.27–7.60 [ng/g]	-	[75]
ICECLES	per- and polyfluoroalkyl substances	drinking water	PDMS	125	120	stirring	HPLC-MS/MS	0.5-500 [ng/L]	0.05-0.3 [ng/L]	0.5-1.0 [ng/L]	73- 116	[86]

SA-SBSE	aroma compounds (28 compounds)	beer	PDMS	160	60	stirring	GC-MS/MS	1-40, 200-4000, 1000-10000 [ng/mL]	-	-	-	[88]
SBSE	DEP, DBP, DEHP	instant food	XAD-2 (60 mg)	48	45	stirring	GC-ECD	10-1000 [µg/L]	3.30–9.37 [µg/L]	11.01-19.1 [µg/L]	81.89 ± 0.17 - 109.5 ± 2.0	[91]
AA-dµ-SPE	diazinon, metalaxyl	fruit juices	SUPRAS and CLDH(Zn-Fe)@Fe3O4 (10 mg)	18	5	air-assisted dispersion	GC-FID	0.6–2000, 2–2000 [µg/L]	0.2-0.8 [µg/L]	0.6-2 [µg/L]	85–96.6	[101]
M- dµ-SPE	norfloxacin, fleroxacin, ofloxacin	baby food	Zr-Fe-CMNPs	-	5	magnetic dispersion	HPLC-FLD	5-1000, 10-1000 [µg/L]	1.5-3.0 [µg/L]	5.0-10.0 [µg/L]	75±4 –80 ±3	[104]
Biological samples												
µ-SPE	cocaine and its metabloites	plasma	MIP (50 mg)	28	10	shaking	HPLC-MS/MS	-	0.061-0.87 [mg/mL]	0.20-2.9 [mg/mL]	97–105	[111]

µ-SPE	perfluorinated carboxylic acids	plasma	CTAB-MCM-41 (15 mg)	-	25	shaking	LC-MS/MS	100-5000 [ng/L]	21.23-65.07 [ng/L]	70.77-216.91 [ng/L]	89.52-101.10	[42]
MAE-µ-SPE	methyl paraben ethyl paraben propyl paraben butyl paraben	ovarian cancer tissues (5g)	HayeSepA (25 mg)	40	20	microwave	HPLC-UV	5-200 [ng/g]	0.005-0.0244 [ng/g]	-	82-100	[43]
mini-bar µ-SPE	metformin, buformin, phenformin, propranolol	Urine (20 mL)	Graphen (20 mg)	97	60	stirring	HPLC-UV	17–1000 [µg/L]	4.03-17.0 [µg/L]	12.2-51.6 [µg/L]	75.1-116	[59]
mini-bar µ-SPE	organochlorine pesticides	Urine (10 mL)	LDH-G (20 mg)	43	35	stirring	GC-MS	1-200; 5-200 [ng/mL]	0.22-1.38 [ng/mL]	-	84.2-102	[60]
minitips SPME	diazepam, nordiazepam, oxazepam, lorazepam	blood (1 µL)	HLB	6.10	5	-	LC-HRMS	0.5-500 25-425 [ng/mL]	0.1-2.5 [ng/mL]	0.5-25 [ng/mL]	-	[67]
SPME	Chlorophenol (8 compounds)	urine, serum	MWCNT/PES	7	5	-	GC-ECD	0.005-1000 [µg/L]	0.3–30 [ng/L]	-	91.6–102.5	[108]
SB-µ-SPE	organochlorine pesticides (15 compounds)	Urine (10 mL)	LDH-G	40	25	stirring	GC-MS	1–200, 5–200 [ng/mL]	0.22-1.38	-	84.2-100.2	[60]

									[ng/mL]			
AA-dμ-SPE	PAHs (5 compounds)	Saliva (10 mL), blood	C_3N_4/Fe_3O_4 (15 mg)	-	-	air-assisted dispersion	GC-FID	1.0–100 [ng/mL]	0.30–0.60 [ng/mL]	1.0-2.0 [ng/mL]	94.94-98.36	[99]
μ-dSPE	estrogens and glucocorticoids (8 compounds)	Urine (8 mL)	MIL-53(Al) (8 mg)	60	30	stirring	UPLC-MS/MS	0.005025–368.6 [μg/L]	0.0015 - 1.0 [μg/L]	0.005-1.8 [μg/L]	88.4–93.2	[109]
VA-M-d-μSPE	celecoxib	urine, plasma, breast milk (10 mL)	MChNP (2 mg)	4.3	2.3	stirring	HPLC-DAD	5-500, 10-500 [μg/L]	1.8-3.2 [μg/L]	5.94-10.56 [μg/L]	96.75-99.00	[110]

4-CP- 4-Chlorophenol; 2,4-DCP- 2,4-dichlorophenol; 2,4,6-TCP- 2,4,6-trichlorophenol; BPA-bisphenol A; BPAF- bisphenol AF, BPAP- bisphenol AP; BPBP- bisphenol BPBP; BPC- bisphenol C; BPG- bisphenol G; BPM- bisphenol M; BPZ- bisphenol Z; DAD- Diode Array Detector DEHP- diethylhexyl-phthalate; DBP-dibutyl phthalate; DEP-diethyl phthalate; EDC- Electron Capture Detector; FID- Flame Ionization Detector; FLD- Fluorescence Detector; Fr-SBSE- fractionated SBSE; GC- gas chromatography; GO-graphen oxide; LC- liquid chromatography; LDH-G- layered double hydroxide/graphene, MChNP- Magnetic chitosan nanoparticles; MIP- Molecularly Imprinted Polymers MWCNTs/PANI-PPy - multiwalled carbon nanotubes/polyaniline-polypyrrole@polydimethylsiloxane; MWCNT/PES-multi-walled carbon nanotubes-polyethersulfone; PAHs- polycyclic aromatic hydrocarbons; PCP- pentachlorophenol; PDMS- polydimethylsiloxane; MS- mass spectrometry; PLCL- Poly(lactic acid-co-caprolactone; nPCL/μPCL - polycaprolactone nano- and microfibers; SUPRAS- supramolecular solvents; UV-ultraviolet.

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3. Summary and future chalenges

The greenness of analytical methods, although nowadays seems to be an important criterion that is considered with a similar attention as analytical validation criteria, is often treated too narrowly. In addition to the amount and toxicity of the solvents used and the energy consumption of research devices, in the case of sorbent-based microextraction, it is extremely important to take into account the production process of materials used as sorbents. Efforts to improve all of the above-mentioned criteria are crucial for achieving an even better match of the available extraction methods to the contemporary challenges of environmental analysis. In addition, the future investigation in the area of natural sorbents (chitosan, zeolite-, cellulose-, hydroxyapatite-based sorbents, etc.) is of high impornatce as they are promising materials that are already being used in SPE techniques with satisfactory results.

It is also worth emphasizing the need for continuous support for basic and applied research by institutions financing science, as well as for tightening cooperation between the academic and industrial sectors. The energy transformation taking place before our eyes and the departure from fossil fuels is indeed an excellent opportunity to establish cooperation with industrial entities which, even for purely marketing reasons, could be interested in supporting work on new methods of controlling chemical contamination of the environment.

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