

1 Miniaturized Solid Phase Extraction techniques for different kind of pollutants analysis: state of 2 the art and future perspectives – PART 1

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25

26 Abstract

27

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

40

41

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

44

45 1. Introduction

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

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

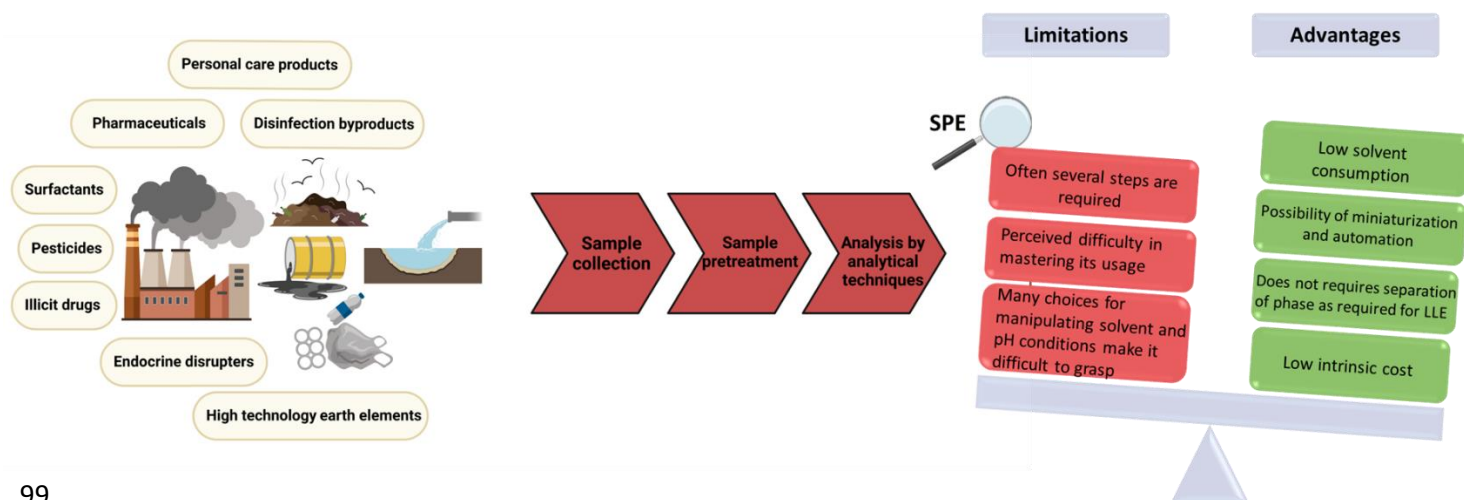
59 There is no doubt that it is of paramount importance to select an appropriate analytical method, which
60 should have satisfactory accuracy, precision, sensitivity, and a sufficiently low limit of detection and
61 quantification (LOD and LOQ). It should be especially remembered that the harmful effects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

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

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

97





99

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

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

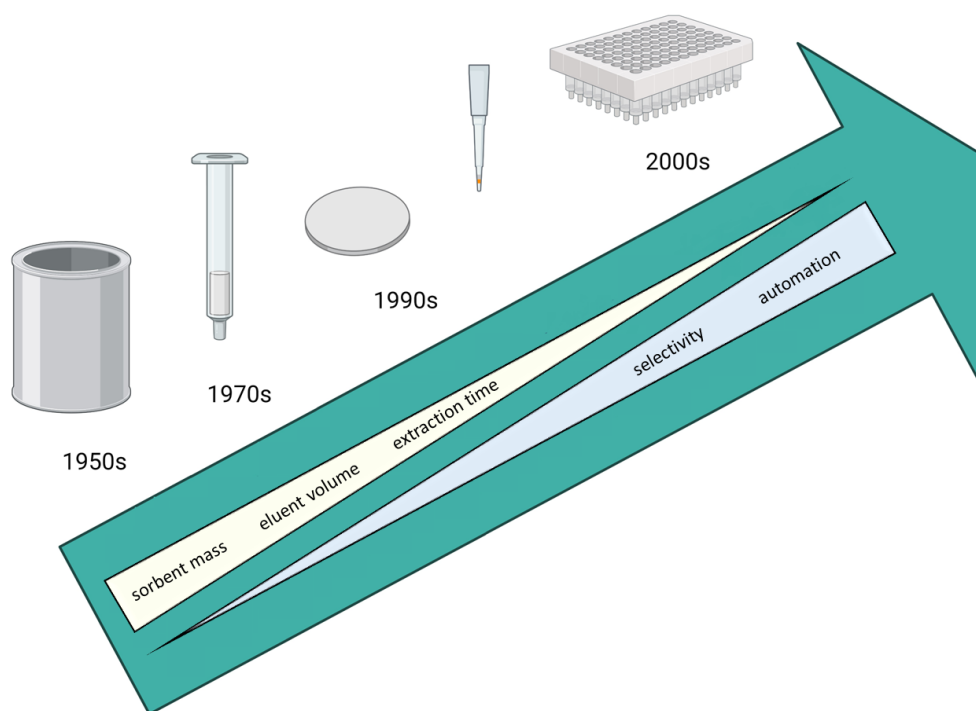
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119 2. Formats and devices used in solid phase extraction techniques

120

121 Without any doubt, the introduction of 12 principles of GAC contributed to rapid development in the
 122 range of new methodological and technological solutions in order to assure the quality of obtained
 123 results and at the same time, to improve the environmental character. Admittedly, SPE is not an
 124 exception, important progress in this technology has been noticed in case of miniaturization,
 125 simplification and automation of the primary concept. It is noticeable that the original SPE formats,
 126 proposed in 1951, consisted of granular activated carbon put into an iron cylinder, weighted up to 1.2-
 127 1.5 kg [5]. Not only the size of such formats has been changed, but also the range of new material classes
 128 used for adsorption process has been introduced. The aim was to increase the applicability of SPE for
 129 extracting various kinds of analytes from varied matrices, as well as to enhance the analytical
 130 performance by significant minimization of the aliquote of sorptive materials and use of solvent. The

131 schematic representation of the milestones in the progress of methodological solutions related to SPE
132 formats is presented in Figure 2.
133



134
135
136
137 Figure 2. Schematic representation of the milestones in the progress of methodological solutions related
138 to SPE formats used.
139

140 141 **2.1. Formats of SPE techniques**

142 143 **2.1.1. Cartridges**

144
145 Cartridges/columns or syringe-barrel are the most common used SPE setup. It comes with a wide range of
146 stationary phases that can separate analytes based on their chemical characteristics. Analytical chemists prefer
147 this format of SPE configuration in regular applications in quality control laboratories in the arena of food and
148 environmental analysis for the separation and isolation of analytes in different samples [6].
149

150 SPE cartridges or tubes are small open-ended polypropylene or glass syringe barrels filled with several types
151 of adsorptive media. In both of glass and plastic tubes, a layer of sorbent bed between polyethylene frits. The
152 selection of a suitable stationary phase, which allows for the stopping of all analytes as well as the selection
153 of the proper column volume, is significant to getting the best extraction efficiency. The liquid phase can be
154 spread through SPE cartridges either by gravitational force or by dynamic method using positive pressure by
155 aid of syringes, air or nitrogen lines, a vacuum flask or a centrifuge [3,7].
156

157 This format has a number of advantages, including the ability to create highly selective tools and the ability to
158 combine many columns filled with the same or various types of sorbents in the laboratory. The combination
159 of two distinct sorption materials improves the recovery rate and extraction efficiency of target analytes [8,9].
160

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

165
166 The SPE extraction cartridge is especially appealing for application in pesticide residue analytical
167 procedures in food samples and determining the total polycyclic aromatic compounds in contaminated soils
168 because it often eliminates the need for costly and environmentally dangerous solvents. In particular, the
169 current efforts focus on preparation of cartridges with the smallest feasible volume, holding specialized
170 sorbents for analytes, and to reduce time-consuming laboratory activities as well as energy consumption per
171 analytical cycle. High extraction efficiency, high cleanup, and low use of organic solvents during the
172 conditioning, washing, and eluting phases are required in these situations. In this sense, by decreasing or
173 eliminating the sorbent drying procedure, the total time necessary for the analysis can be reduced [1].

174 175 2.1.2. Disks

176
177 SPE disk or extraction disk or membrane extraction disk is another popular SPE format. It differs from
178 cartridge in bed packing and the structure of particles [2,10]. The sorbent is embedded in a web of PTFE or
179 glass fiber in these discs. Glass fiber discs are thicker and more robust than PTFE membranes, allowing for
180 larger flow rates. The sorbent particles implanted in the discs are smaller (8 μm diameter quite than 40 μm
181 diameter) than those established in the cartridges. Packaging of stationary phase of sorbent in SPE disks can
182 be classified into immobilized sorbent in polymer or glass fiber, and packed sorbent between two glass fiber
183 filters, the first type resembles filter paper which need special filtration apparatus [11]. Speedisk introduced
184 by J. T Beker in 1998 to eliminate this drawback by fixation of slim layer of the sorption bed amid two
185 layers of plastic grids and glass-fiber filters. They have large active surface and their design promote the
186 recovery rate of the analytes by allowing high value of the sample flow. Instead, they increased the void
187 volume [2]. Speedisk columns, combination of classical column and SPE disks, can overcome the large void
188 volume. Additionally, use of shielding filters can eliminate the stage of sample filtration and reduce the
189 clogging of the columns [12].

190
191 High flow rates (and hence shorter extraction times) are the principal advantages of disks, they reduce
192 channelling and voiding effects, enable extremely efficient mass transfer, and eliminate clogging danger.
193 Because of the smaller cross-sectional area of cartridges, the flow rate that can be passed through them is often
194 lower than the flow rate used for disks. Nonetheless, disks are not as widely used as cartridges, and SPE
195 cartridges continue to be the most popular. On the other hand, disks have experienced significant growth since
196 their last survey was published [13]. Compared to traditional SPE cartridges, disks have two distinct benefits.
197 Firstly, they can typically be run with smaller elution volumes and greater flow rates. The small particle size
198 (8-12 μm) of the sorbent embedded in the polytetrafluoroethylene (PTFE or Teflon) in the disc, compared to
199 40-80 μm in a traditional cartridge. Partitioning is aided by the decrease in void volume and enhance surface
200 area associated with tiny particles. Second, the smaller particles give more density and consistency of packing,
201 which lowers breakthrough and channeling and allows for higher flow rates and shorter extraction times [6].

202
203 Disks have the problem of only being commercially available for a restricted range of sorbent types, and none
204 of them are selective enough to assist the analysis of complex samples and simplify data processing.
205 Furthermore, compared to SPE cartridges, these devices are much more expensive. disks are only suggested
206 when there is a great interaction between the analyte and the sorbent [13].

207
208 SPE disc and cartridge chromatographic procedures are extremely similar in application. Because of the huge
209 cross-sectional areas of the disks and the ability to apply high flow rates, significant volumes of environmental
210 water samples and suspensions may be analysed in fast time without the need for filtration. It's worth noting
211 that filthy samples must be filtered before being extracted with cartridges [1].

212 213 2.1.3. Pipette tips

214

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

221
222 Brewer patented the disposable pipette extraction (DPX) device in the early 2000s [15]. The DPX is yet
223 another SPE alternative that combines effective and quick extraction with much lower solvent and time
224 consumption. A C18 sorbent produced from chromatographic technology was used in the first commercial
225 DPX. Currently, however, multiple phases are available. DPX is a dispersive μ SPE technique that
226 employs a expendable pipette tip with freely stuffed sorbent and upper and lower porous septa to keep it
227 in put. DPX allows the sorbent to be combined with sample solutions [16].

228
229 SPE pipette tips have several advantages, including simplicity, reduced amount of absorbent material which
230 contribute significantly to very small sample and elution solvent volume, lower cost, the ability to treat several
231 samples with a multichannel micropipette, a quicker extraction time, a high recovery factor, and ease of
232 automation and the resultant eluents directly injected into a gas or liquid chromatography [17].

233
234 On the other hand, this format, has some drawbacks such as plugging, high fragility, a considerable amount
235 of plastic waste, and reduced number of commercially available tips [18].

236
237 There is currently a large selection of tips available from various manufacturers, ranging in volume (from 1 to
238 200 μ L) and volume of trapping material placed inside [19]. Because the SPE-TP was intended for micro-
239 scale extraction and concentration, it was frequently employed for purification and concentration of proteases
240 in genomic, proteomic, and metabolomic research for protein and peptide purification and isolation [20]. It
241 has also become more popular recently in environmental analysis for the separation of drugs from food
242 samples and biological fluids, as well as fungicides from grape juice and tap water [21–23].

243
244 Pipette tip micro solid-phase extraction is one of the most investigated solid-based sample preparation method.
245 This procedure can use both synthetic and commercial sorbents, making them very useful for sample
246 pretreatment of various formats of matrices with good selectivity. Furthermore, this approach is the most
247 effective sorbent-based sample preparation method for downsizing of the traditional solid phase extraction
248 method and minimising sample, material, and solvent consumption. As a result, is is referred to as solvent-
249 free sample preparation procedure. It can also be viable in quantitative analysis of different analytes in various
250 matrices with high extraction efficiencies and sample cleanup values [24,25].

251 252 *2.1.4. Multi-well SPE plates*

253
254 Multi-well SPE is a miniature and automated version of SPE that allows for the most precise control of sample
255 and solvent manipulation. Standard microliter plates are utilised in this configuration. Small (0.65 mL or 2.5
256 mL) SPE cartridges packed with 3–200 mg of the sorbent are placed in each well. This format is available in
257 96, 384, and 1536 wells, the 96-well device is much more frequently selected by analytical researchers,
258 allowing for the rapid and simultaneous processing of a huge number of samples in a brief period of time
259 [14,26].

260
261 This format have many advantages of being economical by saving time and solvent, preparation of many
262 samples can be done simultaneously, using of multi-channel pipettors facilitates liquid transfer steps, readily
263 adaptable to all common automated handling systems, green method, increased precision and accuracy as
264 compared with manual methods, and minimized dead volume [6].

265
266 The main disadvantages of this format are different from those of all microextraction methods. Respectively,
267 a rigorous control of extraction conditions is required, including pH, ionic strength and temperature, to obtain
268 best method precision. In addition, highly sensitive analytical instrumentation is required for detection to
269 compensate for non-exhaustive analyte recovery, and in direct extraction mode, the analytical sensitivity of

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

273
274 Multi-well SPE plates have been employed in high-throughput clinical applications as well as in environmental
275 monitoring of numerous types of xenobiotics in complicated matrices. The approach can be used to isolate
276 pesticides from water samples and food, as well as to produce pharmaceuticals in human plasma, urine, and
277 wastewater effluents, according to available data [28,29].

278
279 To date, high-throughput multi-well SPE plates have been successfully used in clinical, pharmacological,
280 toxicological, food, and environmental analysis. Other applications, such as tissue analysis after
281 homogenization or analysis of non-volatile components or pollutants in food commodities, have yet to be
282 explored, offering numerous chances for future development. Metabolite profiling of plasma or blood, for
283 example, might be easily moved to this high-throughput technology in the future to allow for the rapid
284 preparation of huge numbers of samples [27].

285
286 *2.1.5. Comparison of different formats used in SPE*

287
288 Reduced bed masses, high-throughput capabilities, and greater technique development convenience are
289 advantages of the new SPE formats. Small-bed-mass SPE devices enable faster technique development,
290 lower solvent usage, and rapid overall sample preparation. Depending on the extraction goal, there are
291 a variety of performance criteria for SPE devices and formats. These features, as well as their importance
292 and determinants, were listed above. The sum of numerous properties of the SPE device and supporting
293 systems are frequently used to derive a satisfactory performance. To choose the appropriate
294 format/device for a particular application, the same features are taken into account. In **Table 1**, different
295 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	<u>Small scale:</u> 1–3 mL (3–200 mg sorbent) <u>Medium scale:</u> 1–60 mL (3–200 mg sorbent) <u>Large scale:</u> 10–150 mL (3–200 mg sorbent)	Disks with diameter ranges from 4 mm to 96 mm (3–200 mg sorbent)	Tips with volume of 1–200 μ L	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 (\sim 40 μ m)	Microparticles (\sim 8 μ m)	Nanostructured materials	Microscale sorbent (\sim 40 μ m)	Microparticles to nanostructured materials

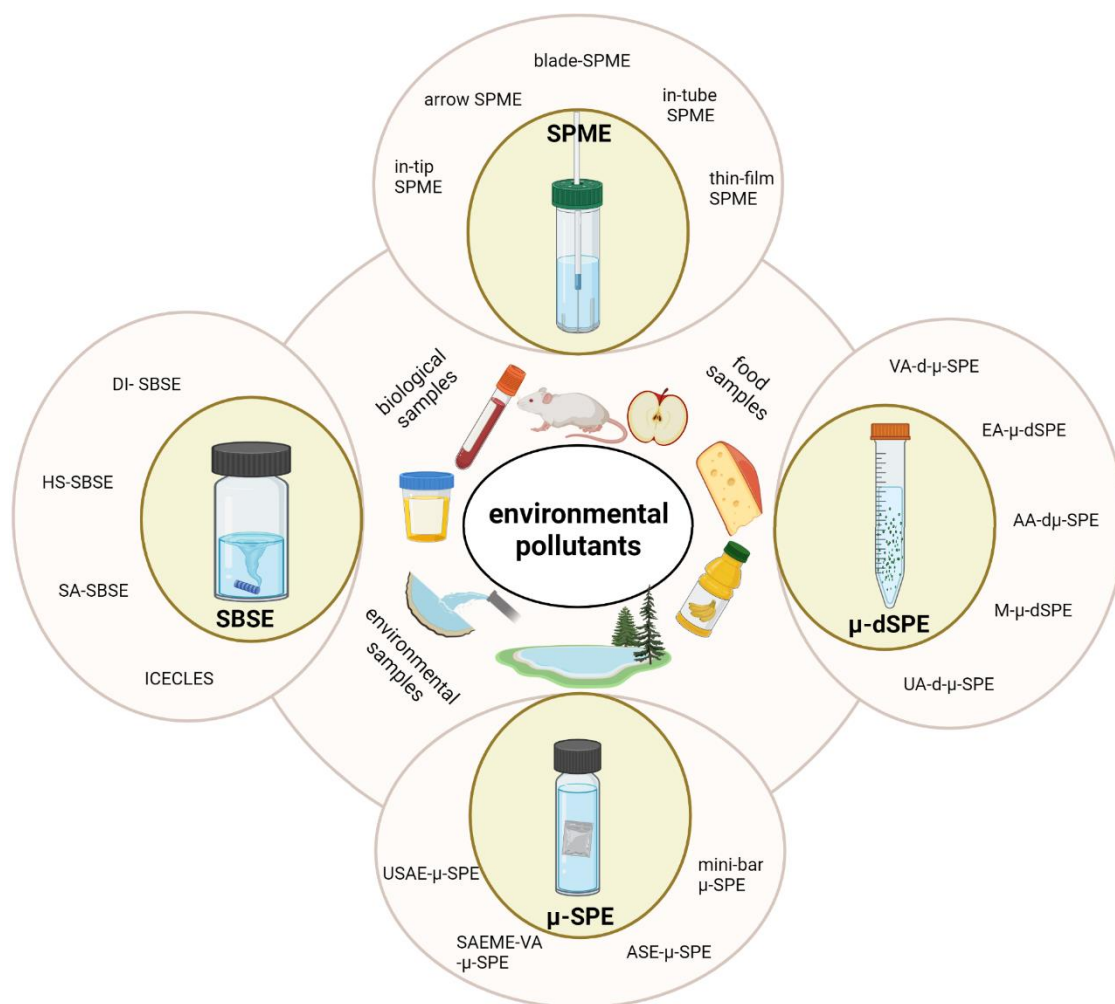


Application	Environmental and food analysis	Environmental analysis (in particular large volume samples)	Biological research	Bioanalytical analysis	Environmental samples
Advantages	<ul style="list-style-type: none"> - Possibility of preparing in laboratory - Possibility of combining several columns filled with the same or different types of stationary phase - Low cost 	<ul style="list-style-type: none"> - 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 	<ul style="list-style-type: none"> - 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 - Low cost - One extraction method for all analytes - Clean extract 	<ul style="list-style-type: none"> - 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 	<ul style="list-style-type: none"> - Small volume of elution solvents and sorbent mass
Disadvantages	<ul style="list-style-type: none"> - Small cross-sectional area - Slow flow rate - Channelling - High void volume - Plugging 	<ul style="list-style-type: none"> - Smaller breakthrough volume - More expensive than cartridges 	<ul style="list-style-type: none"> - Plugging - Large amount of plastic waste 	<ul style="list-style-type: none"> - Costly wells - Due to open-bed configuration, this technique is unsuitable for volatile analytes due to evaporative losses 	<ul style="list-style-type: none"> - Effectiveness of extraction depends on choosing of appropriate sorbent

294 2.1.6. *Application of selected solid-based extraction formats and devices*

295
296 Since the development of the concept of sorbent-based extraction methods, significant progress
297 has been made not only in their formats but also in methodology, including simplification, automation,
298 and miniaturization of the original concept. In this sense, a high number of techniques collectively
299 referred to as ‘microextraction methods’ have been developed based on the minimalization of the
300 number of treatment steps (in order to reduce time and the possibility of contamination or losing
301 analytes), the reduction/elimination of the use of organic solvents and reagents classified as rising
302 environmental concerns or replacing them by non-toxic ones, the reduction of waste production and
303 using smaller initial sample sizes [30,31].

304
305 Hence, the different miniaturized greener sorbent-based microextraction formats, such as solid-phase
306 microextraction (SPME), micro stir-bar sorptive extraction (μ -SBSE), micro-solid-phase extraction (μ -
307 SPE), microextraction in a packed syringe (MEPS), miniaturized matrix solid-phase dispersion (μ -
308 MSPD), μ -QuEChERS (“micro-Quick, Easy, Cheap, Effective Rugged and Safe”), pipette-tip solid-
309 phase extraction (PT-SPE), dispersive micro-solid phase extraction (μ -dSPE), have been introduced to
310 analytical practice [30–32]. The pursuit to obtain precise and accurate measurements of analytes at trace
311 or ultra-trace concentration level in complex matrices has led to rapid growth in the modification of
312 microextraction approaches. In the literature, a huge number of new, often very complex names of novel
313 micro-extraction approaches can be found [33–36]. As a result, deciphering the procedure used by
314 researchers may be much more difficult. Moreover, the great variety of approaches available also makes
315 the use of a single criterion to classify all of them problematic. Generally, taking into account the sorbent
316 geometry in the extraction device and the number of operational steps, these approaches can be classified
317 into two groups, micro-solid-phase extraction (μ -SPE) and solid-phase microextraction (SPME). The
318 Figure 3 shows the classification of selected novel micro-extraction approaches most commonly used
319 in environmental analysis in recent years.



320
 321
 322 **Figure 3.** Different types of solid-based microextraction techniques applied to extraction of
 323 environmental pollutions from biological, food and environmental samples. Figure created using
 324 BioRender(<https://biorender.com/>).
 325

326 The theoretical principles and modes of action of miniaturized solid-phase extraction techniques have
 327 been described in detail in our previous work [30] as well as in many others [31–33,37].
 328 Therefore, this section focuses mainly on the review and discussion of the most important achievements
 329 and improvements in the miniaturized sorbent extraction methodologies used for environmental
 330 pollution analysis over the last years. Based on a review of scientific papers published recently, the
 331 following main strategies for greening the μ SPE and improving effective isolation and enrichment
 332 analytes can be distinguished: (i) miniaturization of extraction device, (ii) application of assisted factors,
 333 (iv) combining with other extraction techniques (iii) automation, and (iv) utilization of flow injection
 334 techniques [38,39]. All of these modified forms have been successfully applied to isolate and enrich
 335 environmental pollutants from various types of samples.
 336
 337

338 2.1.6.1. μ SPE

339
 340 Since the introduction of the miniaturized SPE format into analytical practice in 2006, many
 341 modified forms have been developed. Starting with the type of membrane used, the shape of the μ SPE
 342 device and the addition of a rotating element and ending with its combination with other techniques
 343 [34]. The ease of modification, the fact that they are simple to carry out and cost-effective, the high
 344 extraction efficiency and the protection of sorbent, preventing the absorption of interfering species,
 345 thereby reducing the matrix effect make this technique highly popular, in particular for the analysis of

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

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

363 In the basic concept of porous membrane-protected SPE, to form the device, a small amount of
364 sorbent is packed inside a sheet of porous polymer membrane. Polypropylene (PP) is the most widely
365 used material because of its good thermal and chemical stability and the fact that it is easily heat-sealable
366 [34]. However, due to its small pore size and low wettability, the extraction time is elongated. To
367 overcome this limitation, other materials were used instead of PP. For example, cellulosic tea bag filter
368 paper was used to prepare the μ SPE device for isolation and preconcentration of BTEX from
369 agricultural, well and rainwater samples [48]. Furthermore, polyamide organic membrane and polyether
370 sulfone membrane were used in a study aiming to determine parabens in water samples and active
371 ingredients of an herbal drug in rat plasma, respectively [49,50]. In order to increase the efficiency of
372 the extraction process, the procedure can also be combined with other extraction techniques. To extract
373 BPA from aqueous samples, ultrasound-assisted emulsification and micro-solid-phase extraction
374 (USAE- μ -SPE) has been applied. The developed method provided high sensitivity, wide linear range
375 and high recovery. Moreover, the mass of sorbent used and the LOD value was lower compared to
376 another sample preparation procedures for BPA determination [51]. Similarly, this approach has been
377 successfully applied to isolate estrogens from environmental water samples [52]. In another study,
378 vortex-assisted dispersive liquid-liquid microextraction combined with the μ SPE (DLLME- μ -SPE)
379 procedure has been applied for the extraction of polycyclic aromatic hydrocarbons (PAHs) from ambient
380 fine particulate matter. A comparative study on this combined procedure and conventional μ -SPE
381 demonstrated higher efficiency of VA-DLLME- μ -SPE for most of the PAHs indicating that the vortex-
382 assisted dispersive liquid-liquid microextraction step was significant as a first-stage enrichment process
383 [53]. Furthermore, microwave-assisted (MAE- μ -SPE) [54], and accelerated solvent extraction (ASE- μ -
384 SPE) [55], and accelerated solvent extraction (ASE- μ -SPE), as well as sonication-assisted
385 emulsification microextraction combined with vortex-assisted μ -SPE (SAEME-VA- μ -SPE) have also
386 been successfully applied to isolate various types of analytes [56,57].

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

389 Continuous motion and rotation of the device enhance the effective surface area of the sorbent exposed
390 to sample solution and solve the previously faced problem of the traditional μ SPE, connected with
391 incomplete immerses of the device. To ensure rotation of the device, an approach based on placing a
392 tiny metal rod along with the sorbent or inserting it into the outer bag, or (mini-bar μ -SPE) has been
393 applied. The study focused on the comparison of extraction performance of antibacterial agents from
394 wastewater samples using traditional μ -SPE and mini-bar μ -SPE showed more than double the increase
395 of extraction recovery for triclosan and triclocarban, and about almost a third for methyl-triclosan. The
396 authors attributed this fact to regular stirring patterns, resulting in better mixing and thus increasing the
397 mass transfer of the analytes from the solution to the sorbent [58]. Mini-bar μ -SPE was also appreciated
398 by other researchers and applied to extract i.a. pharmaceuticals and organochlorine pesticides from urine
399 [59,60], polyaromatic hydrocarbons from wastewater [61] and non-steroidal anti-inflammatory drugs
400 from wastewater and lake water samples [62].

401
402 2.1.6.2.SPME

403
404 Without any doubts, SPME is one of the most widely used sorption-based microextraction
405 techniques nowadays. Since its initial introduction to analytical practice in 1989, it has been widely used
406 in analysis of environmental, food, pharmaceutical, and biological samples. The search on Scopus
407 database revealed that for 32 years, more than 17000 papers were published that are related to SPME.
408 They include applications for the analysis of organic and inorganic compounds and the various
409 modifications implemented to achieve the best extraction efficiency. The attractiveness of SPME is
410 owed to its unique advantages, such as (i) simplicity, (ii) rapidity, (iii) high efficiency, (iv) compatibility
411 with different separation (gas and liquid chromatography and capillary electrophoresis) and detection
412 modes (MS, DAD, UV, FLD) (v) possibility of automation, (vi), no requirement for solvent or
413 requirement of smaller solvent aliquots than other extraction methods, and (vii) low cost [36]. In
414 addition, SPME enables the integration of several analytical workflow steps, such as sampling,
415 extraction, preconcentration, and sample introduction into instrument, thus allowing for easy, quick, and
416 accurate analysis [63]. Current trends in the SPME area are mainly focused on the development of novel
417 sorbent coatings, novel geometrical configurations, operational modes, automation, and coupling with
418 different analytical instruments [36].

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

423 Up to now, fiber SPME in which extraction phase is coated as a thin film on the surface of a
424 needle, is still the most used configuration. There are two basic ways of SPME sampling: by direct
425 immersion (DI-SPME), the fiber coated with an adsorbent is immersed into the sample matrix and via
426 headspace, (HS-SPME) where the fiber is placed in the headspace of the sample. Then, the analytes
427 trapped by the coating of the fiber can be thermally desorbed by subjecting the fiber to high temperatures
428 in the inlet of a GC instrument or by its immersion in solvent. In a typical fiber-based SPME, the
429 extraction performance mostly depends on the affinity and selectivity toward a target analyte of the
430 extraction phase. Therefore, the selection of appropriate fiber coating is the most critical point in SPME
431 [66]. Recently, many efforts have been made to develop novel fiber coatings for high extraction
432 performance. In addition to the selection of an appropriate sorption material, the extraction efficiency is
433 also influenced by the geometry of the fiber. It was stated that decreasing the device diameter results in
434 an improved extraction rate due to radial diffusion [33]. Therefore, researchers' activities were oriented
435 on the development of microscale devices. In 2016, Piri-Moghadam et al. introduced a miniaturized
436 SPME fiber, named coated-tip SPME or minitips, which consist of acupuncture needles (150–500 μm
437 length) that have been electrochemically coated in biocompatible N-vinylpyrrolidone-co-
438 divinylbenzene (HLB). Application of conical shape tip favorably affected stability and handling, while
439 preventing the device from bending during sampling [64]. The minitips have been used to extract
440 diazepam, nordiazepam, oxazepam, and lorazepam from 1 μL of blood samples. In other work, minitips
441 with biocompatible nanostructured conductive polymer polypyrrole (PPy) were used to extract selected
442 drugs from biological samples and quercetin from a single cell of onion [67]. Other researchers proposed
443 using multiple fibers (MMF-SPME) consisting of four independent thin monolithic fibers with
444 diameters of 500 μm and a gap of 200 μm between each individual fiber. The overall extraction
445 efficiency of chlorophenols from tap, lake and river water samples obtained for this multiple-fiber device
446 was higher than that of a single fiber of the equivalent area [68]. Due to the progress in miniaturized
447 configurations and rapid development of biocompatible coatings materials, SPME is increasingly used
448 in *in vivo* analysis (sampling directly performed on living organisms) in biochemical, clinical and
449 environmental research. In the last five years, *in vivo* SPME was applied to the analysis of
450 pharmaceuticals [69,70], tetrodotoxin [71], UV filters [72], fluoroquinolones [73], in living fishes,
451 organophosphorus pesticides [74], insecticides [75], volatile organoselenium compounds [76] in plants
452 as well as neurotransmitters and metabolites in different mammal tissues [77,78]. Undoubtedly, a strong
453 point of *in vivo* techniques is a non-lethal sampling approach that provides more precise information of
454 what is occurring in a complex living system.

455 In addition to the miniaturization, the activities of researchers were also focused on automation
456 and combination with other analysis instruments that has been vastly documented in recent years
457 [63,66,79]. All of these modifications resulted in the extension of the applicability of SPME for
458 extracting analytes from different complex matrices and also influenced the increase in the effectiveness
459 of the previously proposed applications. In this sense, many examples of the applications of SPME for
460 determining environmental pollutants in liquid, gaseous and solid samples, including *in vivo* sampling,
461 are available in the literature, and some recent relevant applications are summarized in Table 2.

464 2.1.6.3. Stir bar sorptive extraction

465
466 Stir bar sorptive extraction (SBSE) is an equilibrium-based microextraction technique such as
467 SPME that utilizes a stir bar coated with a sorbent as an extraction phase. A typical SBSE device consists
468 of a 1.5 cm long glass magnetic stirrer coated by a layer (typically 0.5–1 mm) of sorptive material.
469 Depending on the matrix complexity and the analytes' properties, extraction can be carried out in two
470 manners, either by direct immersion of stir bar (DI-SBSE) in the aqueous sample, or in the case of more
471 volatile compounds analysis, by suspension of the stir bar in the headspace (HS-SBSE) above a sample
472 by stainless-steel wire or by using magnets. Subsequently, the extracted analytes are desorbed using a
473 thermal desorption unit coupled to gas chromatography. In the case of thermally labile analytes or when
474 the separation is carried out using LC or CE, the analytes are desorbed by exposing the stir bar to a small
475 volume of a suitable organic solvent [30,80].

476 Since the introduction of SBSE to analytical practice in 1999, it has become a powerful
477 extraction and concentration method for solventless and miniaturized sample preparation in almost every
478 field of analytical applications including food, flavour, environmental, and biomedical science (Table
479 2).

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

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

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

510 tube were closed using Teflon caps. Through the use caps whose diameter was larger than that of the
511 tube, the possibility of contact between the tube filled with sorbent with the bottom of the container was
512 eliminated [91]. Another study by Mao et al. introduced a coated stir bar enclosed in a porous membrane.
513 The membrane protected stir bar sorptive extraction (MPSBSE) was used on the water samples
514 preparation step to determine non-steroidal anti-inflammatory drugs followed by HPLC-UV [62].
515 Moreover, to reduce the friction and increase the lifespan of the stir bar, some authors suggested to
516 additionally use a porous alumina support [92], silicone wheels on two edges of a stir bar [93], and a
517 dumbbell-shaped structure consisting of a p-naphtholbenzein modified porous PEEK (poly(ether ether
518 ketone)) jacket and two lollipop-shaped stainless steel needles [94]. In 2020, another interesting
519 modified device based on the use of 3D printing stirring cages for holding the nanofibers as adsorbent
520 was proposed. The device was used for the extraction of eight bisphenols from river waters. The use of
521 this approach made it possible to significantly shorten the extraction time compared to traditional SBSE
522 [95].

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

530

531

532 2.1.6.4. Dispersive μ SPE

533

534 The next main sub-mode of miniaturized sorbent-based extraction methods is dispersive micro-
535 solid-phase extraction (μ -dSPE), which is a scaled-down variant of dispersive solid-phase extraction
536 (dSPE). This technique is also based on the dispersion of sorbent in the sample, but its amount is
537 significantly reduced [31]. After extraction, the sorbent is separated from the sample and the analytes
538 are desorbed either using a small amount of solvent, or thermally in a thermal desorption unit, and
539 introduced into the detection system for the determination of the analyte. To separate the sorbent
540 containing the trapped analytes from the remaining sample matrix, centrifugation is used most often.
541 However, this step also can be performed by filtration (most often using a syringe filter) and by an
542 external magnetic field when magnetic sorbent (M- μ -dSPE) is used. In this technique, high extraction
543 efficiency can be obtained due to increased interaction between analytes and the sorbent. Therefore, the
544 dispersion of the sorbent plays an essential role. To achieve adequate dispersion of the sorbent, two main
545 approaches can be applied: the use of an external energy source or chemicals [30,97]. In the first
546 approach, typically vortex (vortex-assisted dispersive micro-solid-phase extraction, VA-d- μ -SPE) or
547 ultrasounds (ultrasound-assisted dispersive micro solid-phase extraction, UA-d- μ -SPE) is applied,
548 which is very effective. However, it makes the overall procedure time-consuming and poses a risk of
549 degradation of thermally labile analytes by temperature increase [98]. Therefore, recently, an alternative
550 method to maximize the dispersion of the sorbent has been proposed. In 2016, Rajabi et al. introduced
551 the so-called air-assisted dispersive micro-solid-phase extraction (AA-d- μ -SPE) based on rapid
552 aspiration and ejection of the sample and sorbent by means of a syringe (30 cycles) [99]. AA-d- μ -SPE
553 has been applied for the determination of tramadol in urine, saliva and plasma samples prior to GC-FID
554 [100], PAHs in saliva and blood [99], and pesticides in fruit juice samples [101]. Another interesting
555 development permitting an increase in dispersion is effervescence-assisted μ -dSPE (EA- μ -dSPE). This
556 approach is based on the dispersion of sorbent assisted by effervescence. For that purpose, a tablet
557 containing a proton donor compound, a source of CO₂ (usually sodium carbonate) and the solid sorbent
558 is prepared and directly added to the sample. The tablet's dissolution generates carbon dioxide bubbles,
559 which efficiently disperse the sorbent [37]. Depending on the sample volume, the tablets can be added
560 to the beaker or placed in a syringe [102] or in pipette tip [103]. From a GAC point of view, it should
561 be emphasized that the elimination of the need to use external energy sources in the EA- μ -dSPE and
562 AA-d- μ -SPE techniques enhanced their green character. Another way to meet the requirements of GAC
563 is the automation of the process and direct coupling with instrumental techniques [38]. However, due to
564 the necessity to carry out two stages of separation (isolation of the sorbent from the sample solution

565 after extraction, and separation of the eluent and the sorbent with analytes after elution), automation is
566 not a simple task. Therefore, only a few automated approaches have been developed so far. In 2018,
567 Vakh and colleagues proposed a new approach to the automation of magnetic dispersive micro-solid
568 phase extraction based on the dispersion of the magnetic nanoparticles in a liquid sample phase by air-
569 bubbling and collecting magnetic sorbent containing analytes in the fluidized reactor in a magnetic field.
570 After the desorption of potassium hydroxide in methanol, the solution containing eluted analytes was,
571 by means of a peristaltic pump, aspirated to a vial and then analyzed by HPLC-FLD. This automated
572 approach was applied for the determination of fluoroquinolones in meat-based baby food samples. The
573 overall process was completed in relatively shorter times compared to other methods reported for the
574 determination of fluoroquinolones in food samples and required a smaller amount of sorbent [104]. Tang
575 et al. developed an alternative fully automated approach using magnetic dissolvable Fe₃O₄-LDH core-
576 shell microspheres as sorbent for the determination of acetylsalicylic acid, 2,5-dihydroxybenzoic acid,
577 2-phenylphenol and fenoprofen in aqueous samples followed by HPLC-PDA. An autosampler with a
578 built-in agitator and a robotic arm with a micro-syringe was used to perform μ -dSPE in a fully automated
579 mode. For the extraction, a vial containing the sorbent suspension and the sample (1 mL) was transferred
580 to the agitator and then to an autosampler tray position in which a magnet was prepositioned. The sorbent
581 was retained at the bottom of the vial and the robotic syringe aspirated the sample matrix. After
582 desorption, 10 μ L of the desorption solvent was collected and directly injected into the HPLC system.
583 The developed method was rapid and straightforward, with very low solvent consumption and good
584 reproducibility[105]
585 Due to the many advantages, such as simple operation and short time requirements, high extraction
586 efficiency and capability of combination with different detection techniques, μ -dSPE is one of the
587 extraction techniques with the highest number of analytical applications (e.g., environmental, clinical
588 and food analysis) and different kinds of matrix, including wastewater, environmental water, biological
589 fluids, soils and beverages [31,41,97,98,105–110]. Selected application of μ -dSPE -based methods in
590 different fields of analytical chemistry are summarized in Table 2.
591

592 Table 2. Selected application of μ -dSPE -based methods in different fields of analytical chemistry

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, 17 α -estradiol, 17 α -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	bisphenol 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	17 β -estradiol, estriol, 17 α -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 [μ g/L]	0.013 –0.13 [μ g/L]	0.042– 0.45 [μ g/L]	57-88	[53]
mini-bar μ -SPE	triclosan, triclocarban, methyl-triclosan	wastewater	graphen (20 mg)	135	120	stirring	HPLC-UV	0.2– 1000 [μ g/L]	0.04– 0.07 [μ g/L]	0.13– 0.22 μ g/L]	80.8-103	[58]
MMF-SPME	chlorophenols	environmental water	poly (vinylimidazole-ethylene dimethacrylate)	45	25	-	HPLC-DAD	1.0–200 [μ g/L]	0.13– 0.29 [μ g/L]	0.44– 0.98 [μ g/L]	73.8–101	[68]
ICECLES	atrazine	Soil (10 g)	PDMS	315	240	stirring	HPLC-MS/MS	10-100 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 [μ g/L]	0.06– 0.92 [μ g/L]	88.5- 98.5	[96]
SBSE	BPA, BPAF, BPAP, BPC, BPBP, BPG, BPM, BPZ	river water	nPCL/ μ PC L	85	35	stirring	HPLC-DAD	0.5–200 7.0–200	0.1-2.1 [μ g/L]	0.4–7.0 [μ g/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 ₂ O 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 <i>M. oleifera</i> 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	NH ₂ - 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)@Fe ₃ O ₄ (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 metabolites	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 [μ g/L]	4.03-17.0 [μ g/L]	12.2-51.6 [μ g/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 μ L)	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 [μ g/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-d μ -SPE	PAHs (5 compounds)	Saliva (10 mL), blood	C ₃ N ₄ /Fe ₃ O 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(AI) (8 mg)	60	30	stirring	UPLC-MS/MS	0.00502–5–368.6 [μg/L]	0.0015–1.0 [μg/L]	0.005-1.8 [μg/L]	88.4–93.2	[109]
VA-M-d- μ SPE	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/ μ PCL - polycaprolactone nano- and microfibers; SUPRAS- supramolecular solvents; UV-ultraviolet.

594 3. Summary and future challenges

595
596 The greenness of analytical methods, although nowadays seems to be an important criterion that is
597 considered with a similar attention as analytical validation criteria, is often treated too narrowly. In
598 addition to the amount and toxicity of the solvents used and the energy consumption of research devices,
599 in the case of sorbent-based microextraction, it is extremely important to take into account the
600 production process of materials used as sorbents. Efforts to improve all of the above-mentioned criteria
601 are crucial for achieving an even better match of the available extraction methods to the contemporary
602 challenges of environmental analysis. In addition, the future investigation in the area of natural sorbents
603 (chitosan, zeolite-, cellulose-, hydroxyapatite-based sorbents, etc.) is of high importance as they are
604 promising materials that are already being used in SPE techniques with satisfactory results.
605

606 It is also worth emphasizing the need for continuous support for basic and applied research by
607 institutions financing science, as well as for tightening cooperation between the academic and industrial
608 sectors. The energy transformation taking place before our eyes and the departure from fossil fuels is
609 indeed an excellent opportunity to establish cooperation with industrial entities which, even for purely
610 marketing reasons, could be interested in supporting work on new methods of controlling chemical
611 contamination of the environment.
612

613

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