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Review Article

# Miniaturized solid-phase extraction techniques in sample preparation applied to food matrices: A review

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ABSTRACT

Sample preparation is a critical step in analytical workflows, especially in food analysis, where complex matrices require efficient and reliable extraction techniques. Traditionally, methods such as liquid–liquid extraction have been widely used. However, the growing need for greener and more sustainable approaches has shifted the focus toward solid-phase extraction (SPE). In recent years, miniaturized SPE techniques have emerged as a powerful alternative, offering reduced sample and solvent consumption, simplified workflows, and compatibility with modern analytical platforms. This review explores the development and application of miniaturized SPE methods in food analysis, discussing key advances, advantages over traditional techniques, and remaining challenges. The solid-phase miniaturized techniques covered include solid-phase microextraction, stir-bar sorptive extraction, magnetic solid-phase extraction, immunoaffinity solid-phase extraction, microextraction by packed sorbent, molecularly imprinted solid-phase extraction, and dispersive micro-solid-phase extraction. By summarizing the literature and providing a critical overview of these approaches, this work highlights the potential of miniaturized SPE as a cornerstone for innovative and sustainable food analysis.

## 1. Introduction

Historically, sample preparation has often been an overlooked aspect of analytical workflows, with advances in separation techniques receiving the most attention [1]. However, as these methods reached higher levels of maturity, it became increasingly clear that sample preparation remains crucial, dictating the success and reliability of any analytical procedure, regardless of the sophistication of the instrumentation [2]. The sample preparation process, particularly the extraction step, plays a fundamental role in determining the accuracy and reliability of the analysis of target compounds. This stage is essential for removing matrix interferences, isolating, and concentrating analytes, ensuring high-quality measurements [3–5]. Traditional methods like solid-phase extraction (SPE) and liquid–liquid extraction (LLE) were initially developed to address these challenges. However, these techniques are resource-intensive, requiring significant volumes of solvents and samples while generating substantial waste, practices that conflict with the goals of green analytical chemistry (GAC) [6]. To mitigate these

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*Abbreviations:* μECD, micro electron capture detector; AA-d-D-μSPE, air-assisted dispersive micro-solid-phase extraction; AμE, adsorptive microextraction; CAR, carboxen; CE, capillary electrophoresis; CW, Carbowax; D-μSPE, dispersive micro-solid-phase extraction; D-SPE, dispersive solid-phase extraction; DAD, diode array detector; DI, direct immersion; DVB, divinylbenzene; ELISA, enzyme-linked immunosorbent assay; FID, flame ionization detector; FLD, fluorescence detector; GAC, green analytical chemistry; GAPI, green analytical procedure index; GC, gas chromatography; GC–MS/MS, gas chromatography-tandem mass spectrometry; HF-LPME, hollow-fiber liquid-phase microextraction; HF-SPME, hollow-fiber solid-phase microextraction; HPLC, high-performance liquid chromatography; HS, head-space adsorption; IASPE, immunoaffinity solid-phase extraction; ILs, ionic liquids; ISs, immunosorbents; IT, in-tube; IT-SPME, in-tube solid-phase microextraction; LOD, limit of detection; LC, liquid chromatography; LLE, liquid–liquid extraction; MALDI, matrix-assisted laser desorption/ionization; MEPS, microextraction by packed sorbent; MISPE, molecularly imprinted solid-phase extraction; MIPs, molecularly imprinted polymers; M-m-dSPE, magnetic micro solid-phase extraction; MP-DI-SPME, membrane-protected direct immersion solid-phase microextraction; MS, mass spectrometry; MSPE, magnetic solid-phase extraction; PAHs, polycyclic aromatic hydrocarbons; PDMS, polydimethylsiloxane; PEG, polyethylene glycol; PILs, polymeric ionic liquids; PP-HF, polypropylene hollow fiber; PT-SPE, pipette tip solid-phase extraction; PV, polystyrene; RDSE, rotating-disc sorbent extraction; SBSDME, stir-bar sorptive dispersive microextraction; SBSE, stir-bar sorptive extraction; SCSE, stir-cake sorptive extraction; SPDE, solid-phase dynamic extraction; SPE, solid-phase extraction; SPME, solid-phase microextraction; SPME-Arrow, solid-phase microextraction Arrow; SRSE, stir-rod sorptive extraction; UA-D-μSPE, ultrasound-assisted dispersive micro-solid-phase extraction; UV, ultraviolet; VA-d-D-μSPE, vortex-assisted dispersive micro-solid-phase extraction.

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issues, modern sample preparation methods have been developed, focusing on miniaturization and automation [7]. These contemporary approaches prioritize environmental sustainability by minimizing solvent and sample usage, reducing the number of procedural steps, and shortening analysis times among others, thus creating faster, more efficient, and streamlined workflows [8,9].

In particular, SPE-derived methods have gained remarkable popularity due to their versatility and adaptability to an extended range of sample matrices. SPE-based methods offer flexible configurations that can be tailored to specific analytical needs, making them suitable for isolating and preconcentrating analytes with diverse molecular structures. Their widespread application is further supported by their efficiency in removing matrix interferences, enhancing sensitivity, and improving overall analytical performance [10,11]. This adaptability, combined with their recent alignment with green chemistry principles through reduced solvent usage and miniaturized formats, has increased the use of these techniques in modern sample preparation workflows. Some of these techniques are solid-phase microextraction (SPME), hollow-fiber SPME (HF-SPME), solid-phase microextraction Arrow (SPME-Arrow), pipette tip solid-phase extraction (PT-SPE), in-tube SPME (IT-SPME), solid-phase dynamic extraction (SPDE), micro solid-phase extraction (μSPE), adsorptive microextraction (AμE), stir-cake sorptive extraction (SCSE), rotating-disc sorbent extraction (RDSE), stir-rod sorptive extraction (SRSE), stir-bar sorptive extraction (SBSE), magnetic solid-phase extraction (MSPE), immunoaffinity solid-phase extraction (IASPE), microextraction by packed sorbent (MEPS), molecularly imprinted solid-phase extraction (MISPE), and dispersive micro-solid-phase extraction (D-μSPE) [3,12].

When dealing with complex matrices such as foodstuffs, reproducibility often depends heavily on their specific characteristics [13]. As a result, achieving optimal analytical performance may require combining multiple techniques to effectively eliminate interfering compounds while minimizing the number of steps involved [14]. Conventional extraction methods continue to be extensively employed for processing such intricate matrices due to their robustness and reliability. However, significant advancements in analytical chemistry have led to develop numerous miniaturized works exploring innovative approaches to improve the treatment of complex food samples [15].

This review provides an updated perspective on the advances and future directions of solid-phase-based sample preparation methods. Unlike previous works that address microextraction techniques in a broader analytical context or focus on other applications, this review is, to the best of our knowledge, the first to focus exclusively on food sample analysis.

## 2. Methodology of literature review

This review discusses the trends that have followed the study of miniaturized SPE sample preparation techniques applied to food matrices. Scopus, Web of Science, Science Direct and Google Scholar were used as databases to search for references using the following keyword combinations: “miniaturization” OR “miniaturized” AND “sample preparation” OR “sample treatment” OR “sample pretreatment” AND “food”, followed by the name of each of the miniaturized techniques considered in the current study. This review exclusively considers scientific research published in English to evaluate their relevance to the topic of this review. All articles between 2010 and 2025 were read and their pertinence to the subject was confirmed. The number of published articles focusing on food analysis using miniaturized SPE-based techniques has been the first issue considered (see Fig. 1A). Initially, this value was relatively low. However, in the following years, there was a consistent increase indicating a growing interest in this area, likely driven by the demand for greener, more efficient sample preparation methods, as well as advances in sorbent materials and analytical instrumentation [8]. This upward trend continued until 2019, which marked the peak with 35 publications. After said year, the number of articles showed a slight decline, yet the trend remained relatively high through to 2022, with 25 publications recorded that year. This gradual

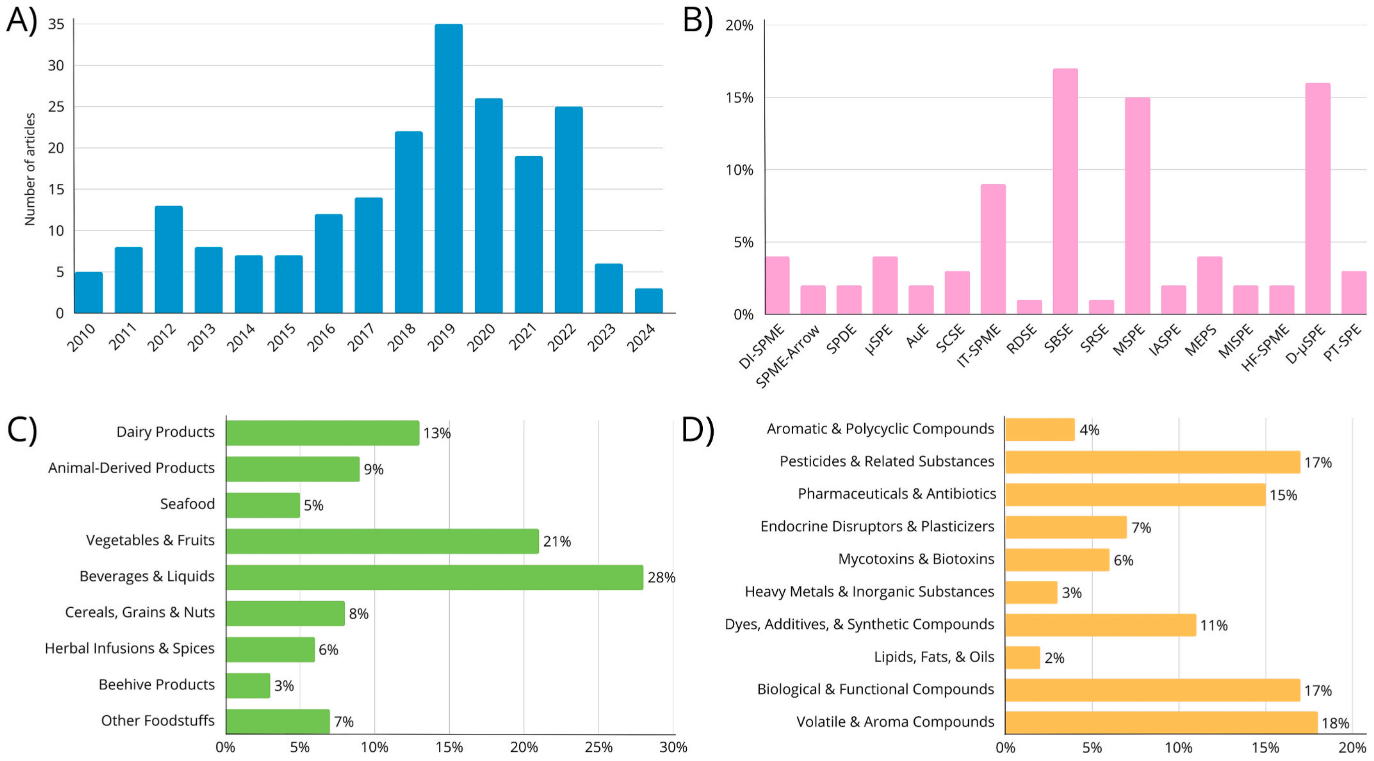

**Fig. 1.** A) Time trend of SPE-based microextraction techniques applied to analysis of food matrices. B) Distribution of miniaturized SPE-based sample preparation methods. C) Frequency of analysis by miniaturized SPE-based sample preparation methods in food matrices. D) Frequency of analyte families determined by miniaturized SPE-based sample preparation methods in food matrices.

decrease from the 2019 peak may be attributed to the establishment of robust methodologies and a shift in research focus toward novel materials, alternative techniques, and applications beyond food analysis. Among the microextraction sample preparation techniques examined (see Fig. 1B), SBSE emerged as the most commonly used, accounting for 17 % of the published articles during this period. D-μSPE follows closely with 16 %, while MSPE (15 %) and headspace adsorption SPME (HS-SPME) (11 %) also represent significant portions. SRSE, and RDSE are less broadly applied, likely due to their recent development and the established effectiveness of other more studied techniques, such as SBSE. Techniques such as SBSE, D-μSPE, and MSPE are likely more used today due to their greater development and previous applications. These methods offer several advantages, as outlined in Table 1 which contribute to their popularity in food analysis. For instance, SBSE is highly versatile, as it can be applied to gases, liquids, and solids, making it suitable for a broad range of matrices. MSPE stands out for its reusability and the minimal amounts of reagents required, which are both cost-effective and eco-friendly. Lastly, D-μSPE is particularly advantageous in terms of extraction time and extraction efficiency because of the large surface area it offers.

When considering the food matrices analysed, beverages and liquids like wine, vinegar, drinking water, and soft drinks account for the largest portion, representing 28 % of all the articles included in this study (see Fig. 1C). Vegetables and fruits follow with 21 %, likely due to the broad range of food items encompassed by this category. Dairy products rank third, comprising 13 % of the studies, while other matrices show a relatively even distribution of publications (3–9 %). Regarding the analytes, the most commonly determined ones (see Fig. 1D) are volatile and aroma-related compounds (18 %), likely due to the widespread use of headspace techniques, as shown in Fig. 1B. Pesticides and biological compounds, each representing 17 %, followed by antibiotics and pharmaceuticals (15 %), are also frequently studied due to the broad range of products within these categories and their importance in food safety. The remaining compounds fall near or below 10 %.

Lastly, in sample preparation, the selection of solvents plays a critical role in ensuring analytical efficiency while minimizing environmental and operator hazards [16]. The use of solvents, particularly in large volumes, raises concerns regarding their impact on human health and the environment. GAC principles advocate for either eliminating solvents altogether [17,18], or utilizing minimal amounts of safer alternatives, such as microliters of environmentally friendly ones [19,20]. The greenness of the solvents employed in the selected studies was reviewed according to CHEM21 solvent guide [21], and is summarized in Table 2. Among these, the top three most commonly used solvents were methanol (37.0 %), acetonitrile (28.1 %), and acetic acid (8.1 %). Methanol, which is considered a recommended solvent in the aforementioned guide, is not only the most frequently used but also used alone or in high percentages in mixtures for different techniques [22,23]. Acetonitrile, applied in similar ways [24,25], is more problematic in terms of greenness but ranks second in usage. Acetic acid is less commonly employed, and is typically mixed with water, acetonitrile or methanol, but often at low percentages—close to 1 % [26,27]—though some cases report concentrations up to 30 % [28]. Despite the trend toward greener solvents shown, the review identified instances of highly hazardous solvent use. Examples include diethyl ether, employed in volumes ranging from 25 to 250 mL [29,30], and chloroform, used in quantities as high as 20 mL [31]. These findings highlight the need for continued efforts to shift toward greener solvents, reducing both volume and hazard potential.

## 3. Description of miniaturized solid-phase extraction techniques in sample preparation applied to food matrices

As previously mentioned, various miniaturized sample preparation techniques have been applied to food matrices, offering significant advances in analytical performance, efficiency, and sustainability. While

**Table 1**
Advantages and disadvantages of the studied solid-phase miniaturized techniques.

| Technique | Advantages | Disadvantages |
|---|---|---|
| SPME | - Can be applied to gas, liquid and solid samples.<br>- Allows for simultaneous extraction, concentration, and determination.<br>- Great sensitivity.<br>- Minimal sample volume.<br>- Can be reused.<br>- Portability when needed.<br>- Compatibility with instrumental techniques. | - Potential contamination of the SPME needle.<br>- Low robustness of fiber coatings.<br>- Limited range of stationary phases. |
| HF-SPME | - PP-HF is affordable, robust and reusable. | - PP-HF offers low selectivity.<br>- Limited surface area for absorption. |
| SPME-Arrow | - Gentle penetration of silicon septa in vials and injectors.<br>- Less fragile than SPME fibers.<br>- Better protection from contamination and mechanical damage.<br>- Fully automatable with autosamplers. | - Need to widen the injection port before use. |
| PT-SPE | - Low sample, sorbent and elution solvent quantities.<br>- Can process multiple samples simultaneously.<br>- Short extraction time.<br>- High recovery efficiency.<br>- Compatibility with instrumental techniques.<br>- Ease of automation. | - High fragility.<br>- Risk of clogging.<br>- Significant plastic waste (pipette tips).<br>- Limited number of commercial tips. |
| IT-SPME | - Can improve sensitivity with longer tubes and larger quantities of sorbent material | - Risk of clogging.<br>- Limited range of stationary phases. |
| SPDE | - Enhanced interphase contact.<br>- Short extraction time.<br>- Low sample capacity.<br>- Superior mechanical resistance than classical SPME. | - Complex retention and elution processes.<br>- Carry-over. |
| μSPE | - Can be applied to semisolid, solid, or suspension matrices.<br>- Less sorbent contamination, matrix effects and blockages.<br>- High preconcentration factors.<br>- Minimal amounts of organic solvent.<br>- Can be reused.<br>- Less time-consuming than conventional SPME. | - Carry-over.<br>- Limited range of stationary phases. |
| AμE | - Compatibility with instrumental techniques.<br>- Higher recovery factors than SBSE. | - Can only be used for polar analytes. |
| SCSE | - Can be reused.<br>- High extraction capacity. | - More time consuming than SBSE. |
| RDSE | - Can be reused.<br>- Disk design can be produced in a laboratory setting.<br>- Provides a larger active surface area than SBSE. | - Strong matrix effects. |
| SRSE | - Prevents loss of the coating.<br>- Can be reused.<br>- Easy to use. | - Strong matrix effects.<br>- Not widely used. |
| SBSE | - Can be applied to gas, liquid and solid matrices.<br>- Potential for automation.<br>- Ability to achieve high preconcentration factors.<br>- Possible elimination of solvents. | - Narrow range of polarities can be extracted with the available stationary phases.<br>- Strong matrix effects. |
| MSPE | - Low amount of sorbent material.<br>- Can be reused.<br>- Short extraction time. | - Requires stirring. |

(continued on next page)

**Table 1** (*continued*)

| Technique | Advantages | Disadvantages |
|---|---|---|
| IASPE | - Specificity and selectivity in complex sample matrices. | - Mostly applied to biological compounds. |
| MEPS | - Extensive range of analytes and matrices.<br>- Minimal sample, sorbent and solvent volumes.<br>- Can be reused.<br>- Two-directional flow facilitates sample loading, sorbent conditioning, and analyte elution. | - Sorbent clogging.<br>- Not suitable for high sample volumes.<br>- Carry-over. |
| MISPE | - Exceptional chemical and mechanical stability.<br>- Great recognition capabilities for specific molecules. | - Time-consuming nature of MIP preparation and use. |
| D-μSPE | - Larger surface area than conventional SPE methods.<br>- Better extraction efficiency.<br>- Short extraction time. | - Some derived techniques risk degrading thermally sensitive analytes. |

**AμE** – adsorptive microextraction; **D-μSPE** – dispersive micro-solid-phase extraction; **HF-SPME** – hollow-fiber SPME.; **IASPE** – immunoaffinity solid-phase extraction; **IT-SPME** – in-tube **SPME.**; **MEPS** – microextraction by packed sorbent.; **MISPE** – molecularly imprinted solid-phase extraction; **MSPE** – magnetic solid-phase extraction; **PT-SPE** – pipette tip solid-phase extraction; **RDSE** – rotating-disc sorbent extraction; **SBSE** – stir-bar sorptive extraction; **SCSE** – stir-cake sorptive extraction; **SPDE** – solid-phase dynamic extraction; **SPME** – solid-phase microextraction; **SPME-Arrow** – solid-phase microextraction Arrow; **SRSE** – stir-rod sorptive extraction; **μSPE** – micro solid-phase extraction.

**Table 2**
Most frequently used solvents for the different SPE-based microextraction techniques in food matrices.

| Solvent | Safety score[a] | Frequency[b] (%) |
|---|---|---|
| Acetic acid | P | 8.1 |
| Acetone | R | 4.5 |
| Acetonitrile | P | 28.1 |
| Chloroform | HH | 0.4 |
| Dichloromethane | H | 1.6 |
| Diethyl ether | HH | 1.2 |
| Dimethylformamide | H | 0.4 |
| Ethanol | R | 5.7 |
| Ethyl acetate | R | 0.4 |
| Formic acid | P | 4.1 |
| Hexane | H | 4.5 |
| Isopropanol | R | 1.2 |
| Lactic acid | P | 0.4 |
| Methanol | R | 37.0 |
| Pyridine | H | 0.4 |
| Tetrahydrofuran | P | 0.4 |
| Toluene | P | 1.6 |

[a] Classification performed according to CHEM21 solvent guide [21].

[b] Frequency was based on how often each solvent was used in the reviewed articles. R: recommended; P: problematic; H: hazardous; HH: highly hazardous.

most of these techniques are classified as "green" due to their reduced solvent consumption and lower environmental impact, each method presents distinct advantages and limitations. Understanding these trade-offs is crucial for selecting the most suitable approach for a given analytical challenge. A comparative overview of their benefits and drawbacks is provided in Table 1. Regarding the green assessment, only a few studies have employed recent metrics to evaluate the greenness of the analytical method [32–37]. Some of the reviewed papers assessed the greenness of their sorbent synthesis using the analytical eco-scale that operates on a scale from 0 to 100, where scores below 50 indicate inadequate green analysis, values between 50 and 75 reflect an acceptable green analysis, and scores above 75 are considered of excellent green analysis. They obtained scores of 65 [33], 71 [34], 79 [37], and 84 [35]out of 100, indicating generally acceptable to excellent green characteristics. Though it must be mentioned that the first one only applied it to the synthesis of the sorbent, not the whole methodology of the extraction. Moreover, another study employed the green analytical procedure index (GAPI) [32], which does not provide a numerical score, but stated that multiple parts of the proposed methods are green, mainly due to solvent-free sample preparation techniques that eliminate the need for organic solvents. Finally, one paper applied the HEXAGON tool [36], which uses a scale from 0 to 4, considering the lowest the score as the greenest. This was used in order to compare different methods and reported values ranging from 1 to 2.71.

### 3.1. Solid-phase microextraction (SPME)

Conventional SPE techniques often involve slow extraction processes, significant waste production, complex and costly equipment and an excessive use of samples, sorbent materials, reagents and solvents, while offering limited sensitivity [38]. On the contrary, SPME has emerged as an effective method for separation and preconcentration of organic and inorganic compounds, addressing and overcoming many of these limitations, while presenting numerous advantages since its initial introduction to analytical practice in 1989 [11]. SPME operates by extracting one or more analytes from the sample phase through adsorption or absorption onto a solid phase coated onto a silica fiber or metallic support. The analytes retained on the solid phase are then desorbed using an appropriate solvent or thermal treatment before analysis. This technique is highly versatile, as it can be applied to samples in various physical states, such as gases, liquids and solids, making it suitable for a broad range of applications [10]. It also allows for simultaneous extraction, concentration, and analyte determination, which reduces analysis time. SPME offers great sensitivity as well, since it can detect substances at ppt levels, while requiring only minimal sample volumes, making it ideal for limited or valuable samples. The method is straightforward and fast, as it does not rely on complex equipment, intricate procedures, or specialized tools, in addition to being cost-effective by eliminating the need for expensive and toxic organic solvents and enabling fiber reuse. The compact size of SPME fibers ensures portability for *in-situ* sample collection when needed, and compatibility with automation, enhancing overall efficiency [38]. SPME also integrates seamlessly with other instrumental techniques, such as gas chromatography (GC), liquid chromatography (LC), high-performance liquid chromatography (HPLC), and capillary electrophoresis (CE), in both off-line and on-line modes, as well as several detectors, such as mass spectrometry (MS), diode array detector (DAD), ultraviolet (UV) and fluorescence (FLD). The effectiveness of SPME for analyte separation and preconcentration is influenced by various factors, including the extraction mode, the fiber attributes, the characteristics of the sample matrix (including volume and pH), its temperature and the duration of sorbent-sample contact [12]. Considering the previously stated points, it is clear that selecting the appropriate stationary phase is a critical step. Currently, an ample variety of commercial stationary phases are available, including divinylbenzene (DVB), polyethylene glycol (PEG), polydimethylsiloxane (PDMS), carboxen (CAR), and carbowax (CW) [10]. To extract analytes that differ significantly in polarity or solubility, composite stationary phases have been developed, combining both polar and nonpolar materials. Examples include PDMS/DVB, PDMS/CAR and CW/DVB [3]. Additionally, new sorbents have been developed in modern SPME approaches, which include carbon-based materials, molecularly imprinted polymers (MIPs) [9], metal nanoparticles, ionic liquids (ILs), mesoporous and nanoporous silicates, polymeric ionic liquids (PILs), aniline-silica nanocomposites, conductive polymers, metal complex-imprinted polymers, immunosorbents (ISs), and materials synthesized using the sol–gel method [3].

The SPME can be applied in two different ways, depending on the interaction between the fiber coated with the solid phase and the sample: direct immersion (DI) and HS [38]. In the DI-SPME method, the stationary phase, which is immobilized on the fiber, is immersed in the sample solution, allowing direct interaction with the analytes (see Fig. 2B). To avoid damage, it could be further protected by a membrane (membrane-protected direct immersion solid-phase microextraction, MP-DI-SPME) [10]. As shown in Table S1, the food matrices analysed with this mode include wine [35], tea [39], milk [40], and flour [41]. The analytes studied are quite diverse, such as pesticides [24], lipids [40], and tetracyclines [42]. The most commonly used analytical techniques are GC and LC coupled with MS or UV detectors, though GC coupled to micro electron capture detector (μECD) has also been reported [24]. Sample amounts range from as little as 100 mg [22] to as much as 7 g [43]. However, in the latter case, no organic solvents were used during the sample preparation procedure, which represents an improvement in terms of greenness. Regarding organic solvents, volumes as low as 100 μL of isopropanol [40]—a recommended solvent according to the CHEM21 solvent guide [21] (see Table 2)—were used. Some of these use MIPs as the sorbent in the fiber, showing that new materials can be applied to microextraction techniques [39,41,42]. Matrix effect is also a critical aspect to consider, however, it has only been evaluated in a few of the reviewed studies. Darvishnejad et al. [44] did this by comparing peak area ratios of selected analytes in tomato and cucumber matrices to those in a neat solution at two different concentration levels. The reported matrix effect percentages (ME%) ranged from 92.8 % to 96.7 % suggesting minimal interference, and so, the calibration curves could be prepared in water. In another study [35], sample dilution was employed as a strategy to reduce the matrix effect, while others used matrix-matched calibration, to compensate for matrix-related interferences [22,24].

In HS-SPME, the analytes do not come into direct contact with the fiber (see Fig. 2A). Instead, they are transferred from the sample matrix into the gas phase, which is in contact with both the sample and the fiber placed in the headspace. This separation ensures that the fiber coating remains unaffected and undamaged by non-volatile impurities from the matrix or solvents. In this case, the transfer of analytes to the fiber coating occurs more rapidly because diffusion in the gas phase is faster than in the liquid phase, leading to a quicker attainment of thermodynamic equilibrium [1]. Due to the requirement for compounds to be in gaseous phase in the vial, volatile and aroma compounds have been extensively studied using this technique (see Table S1). However, essential oils [45] and polychlorinated biphenyls [46] have also been detected. Various matrices have been analysed, including fruits such as passion fruit [47], melon [48], and mango [49], beverages like brewing malt [17] and orange juice [50], and complex matrices like fish [51]. Sample amounts typically range between 0.5 and 5 g, with no solvents used, as the sample is placed directly in the vial and sometimes heated to facilitate the transfer of analytes into the gas phase. GC has been the sole separation technique reported, primarily coupled with MS detectors, though flame ionization detectors (FID) [45] have also been used. Recoveries are generally between 87 % and 117 %. However, Yin et al. [18] reported recoveries ranging from 16 % to 89 %, likely due to the high number of analytes studied [40].

### 3.1.1. *Hollow-fiber solid-phase microextraction (HF-SPME)*

Polypropylene hollow fibers (PP-HFs) have become a popular choice in hollow-fiber liquid-phase microextraction (HF-LPME) due to their cost-effectiveness, low carry-over, reduced organic solvent use, and enhanced sample enrichment and clean-up properties [52,53]. Initially, fused-silica or steel fibers were either expensive or had fragile polymer coatings, making PP-HF an attractive alternative because of its affordability, durability, and reusability. However, PP-HF suffers from low selectivity and limited surface area for absorption, which reduces its extraction efficiency. To enhance its performance, it can be modified by bonding or immobilizing it with other absorbent materials. Using this as a template, zirconia hollow fibers in the macro range were successfully synthesized for the first time through a sol–gel process, resulting in fibers with a similar morphology and a hollow lumen structure [53]. Consequently, HF-SPME was developed, and it currently represents a novel configuration that simplifies the extraction process by eliminating centrifugation or filtration steps, as well as initiating the creation of a variety of inorganic hollow fiber structures with controlled walls and porous substructures.

Although it has not been widely applied in food analysis, it has been employed to analyse pesticides [44,54] and polycyclic aromatic hydrocarbons (PAHs) [52] in different food matrices, achieving recovery rates ranging from 79 % to 107 %. In all cases, the separation technique utilized was HPLC coupled with DAD [54] and UV [44,52] detectors.

### 3.1.2. *Solid-phase microextraction Arrow (SPME-Arrow)*

The SPME-Arrow method is a recent innovation from conventional fiber-based SPME, designed to enhance extraction capacity and sensitivity through a larger volume of sorbent phase immobilized on a stainless-steel rod [32]. The term “Arrow” reflects the visual and structural similarity of the device’s lower end to an arrowhead. The enhanced sorbent capacity of the SPME-Arrow is evident when comparing its phase volume (3.8 mL) for a 1.1 mm version with that of a traditional 1 cm long SPME fiber (0.6 mL), both of which are coated with a 100 μm layer of PDMS [55]. Moreover, the arrow-like tip facilitates gentle penetration of silicon septa in both vials and injectors, while also reducing the fragility commonly associated with SPME fibers. Because of the coating and enclosing the stainless-steel rod with a protective

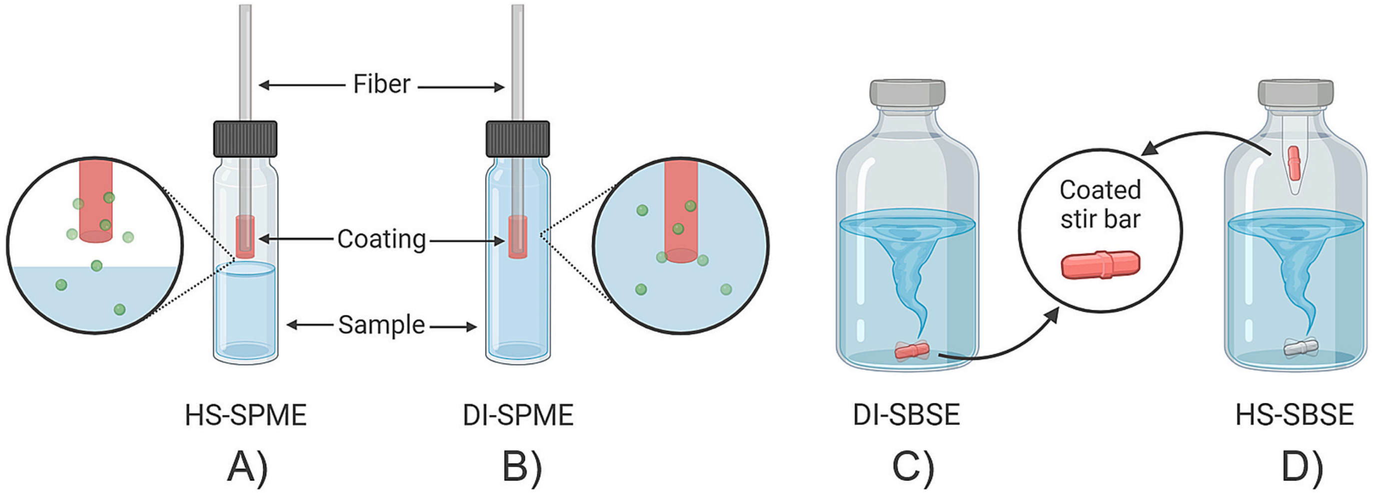

**Fig. 2.** A) Headspace SPME configuration. B) Direct immersion SPME configuration. C) Direct immersion SBSE configuration. D) Headspace SBSE configuration.

sheath, it is better protected from contamination and mechanical damage. Additionally, the SPME-Arrow shows extraction efficiencies similar to SBSE, but it is easier to implement and fully automatable with autosamplers [56]. However, a key disadvantage is the need to widen the injection port before use due to the larger dimensions of the fiber, though this can be addressed by using modified injectors provided by GC manufacturers, a trend that is becoming more common with newer instruments [57].

SPME-Arrow has been applied to analyse volatile and aroma compounds in beverages [32,58] and fish [56], utilizing GC as the separation technique without the use of organic solvents during sample preparation in accordance with GAC principles. Castro et al. [56] applied this extraction technique in a HS configuration to quantify synthetic musk fragrances (cashmeran, celestolide, phantolide, tonalide, musk ketone, and musk xylene) in various fish samples (cod, sole, and hake), using gas chromatography-tandem mass spectrometry (GC–MS/MS) achieving limit of detection (LOD) values between 0.5 and 2.5 ng g$^{-1}$. The sample preparation involved 250 mg of lyophilized fish, magnetically stirred for 45 min.

### 3.1.3. *Pipette tip solid-phase extraction (PT-SPE)*

Pipette tip or in-syringe SPE is a miniaturized adaptation of the conventional cartridge-based SPE technique, where the sorbent is placed within plastic micropipette tips or syringe needles. By using either single-channel or multichannel pipettes and syringes, the sample solution is repeatedly aspirated and desorbed, allowing for analyte extraction (see Fig. 3) [1].

This approach offers several advantages, including [11]:

1. Simplicity of the method.
2. Reduced use of sorbent material, which is especially favourable for handling small sample volumes and minimizing the use of an elution solvent.
3. Lower operational costs.
4. The ability to process multiple samples simultaneously with a multichannel pipette.
5. Faster extraction times.
6. High recovery efficiency.
7. The possibility of directly injecting the eluates into GC or LC systems.
8. Ease of automation.

There are some limitations to this sample preparation method, including high fragility, the risk of clogging, significant plastic waste, and a limited number of commercially available tips. Nevertheless, numerous options are nowadays available from various manufacturers, offering a wide range of volumes (from 1 to 200 mL) and varying amounts of sorbent material inside the tips [11].

In food matrices, this technique has been applied to seafood [59], vegetables [34], and animal products such as meat and eggs [60]. As shown in Table 3, the sample and solvent amounts vary depending on the specific work, as does the analytical technique used, with HPLC being the most commonly employed for separation. Notably, LODs can be as low as 5 pg mL$^{-1}$ [59], and recoveries consistently range between 76 % and 114 %. Li et al. [60] determined fipronil residues in chicken eggs by combining this technique with dispersive solid-phase extraction (D-SPE), achieving rapid analyte extraction with only 3 mg of adsorbent. In this study, the sample amount was 5 g, which is relatively high, and 30 mL of acetonitrile was required for extraction prior to PT-SPE. Nevertheless, the results were satisfactory, with LODs of 4.76 μg kg$^{-1}$ and recoveries between 84 % and 98 %. It must be mentioned that such quantities are not needed for every matrix, considering that Sun et al. [34] used only 5 mg of sample and a total of 1600 μL of solvents, achieving results comparable to those previously discussed.

### 3.1.4. *In-tube solid-phase microextraction (IT-SPME)*

In-tube (IT) techniques use an alternative to coated fibers, which are internally coated capillaries or needles. IT-SPME employs open-tubular capillary columns to retain analytes and was originally designed to facilitate automation for fiber-based SPME-HPLC systems [61]. For this reason, as shown in Table S2, all methods use LC-based instrumentation for the analysis. This approach addresses several limitations of traditional SPME fiber, including its fragility, limited sorption capacity, and issues with thick-film coating stability. IT techniques can be categorized into two types: a) extraction coatings, which utilize an internal layer as the sorption phase immobilized on the needle or capillary walls. b) extraction fillings, which rely on packed sorbent materials as the sorption phase [62]. Furthermore, these systems can operate in two modes, static or dynamic. In the static mode, analytes are transferred via diffusion, while in the dynamic mode, they are actively transported by pumping or using gravitational flow of the sample through the needle or tube [63]. Additionally, IT-SPME offers the potential for improved sensitivity by employing longer tubes and larger quantities of sorbent material. However, it requires the removal of particulates from the sample through filtration or centrifugation to avoid clogging the extraction capillary. SPME fibers do not require these preparatory steps and can simply be rinsed with water before entering the desorption chamber which leads to a need for less sophisticated instrumentation [12].

As shown in Table S2, IT-SPME has been frequently applied to liquid matrices such as milk [64,65], wine [66], coffee [29,67], and juices [65,68], as well as solid matrices like meat [36], rice [69], and corn [70] to determine a broad variety of analytes. Sample amounts rarely exceed 2 g, and organic solvents are typically used in small volumes, often measured in microliters. However, some authors like Wang et al. [64] used large organic volumes (75 mL of acetonitrile) in the sample preparation step. Moreover, diethyl ether was employed in two studies for extraction [29,30], despite being classified as highly hazardous by the CHEM21 solvent guide (see Table 2) [21]. Recovery values were generally high (73–119 %), and LODs were as low as 0.32 pg mL$^{-1}$ [71].

### 3.1.5. *Solid-phase dynamic extraction (SPDE)*

SPDE is an alternative mode of HS-SPME. It uses a sorbent to coat the

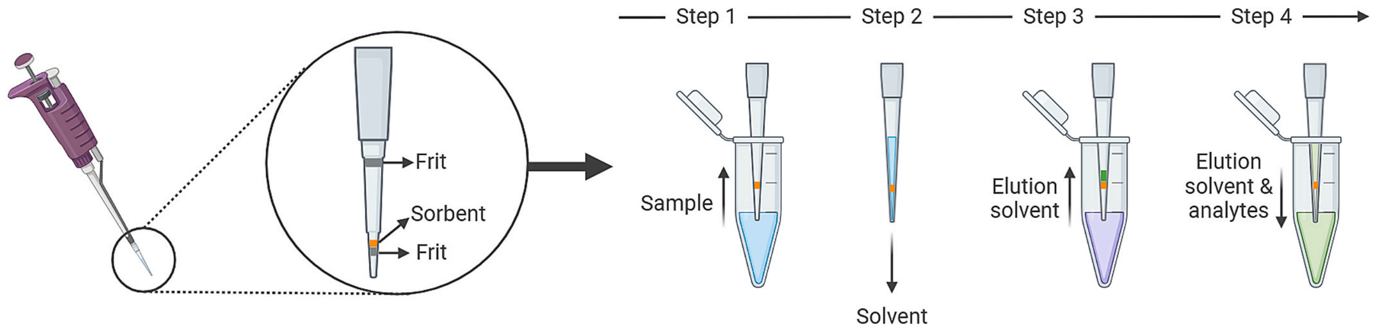

**Fig. 3.** Steps in PT-SPE procedures.

**Table 3**
Representative works using PT-SPE and μSPE for the analysis of food matrices.

| | Compound Group | Food Matrix | Sample amount | Organic Solvent (volume) | Instrumentation | LOD | Recovery (%) | Ref. |
|---|---|---|---|---|---|---|---|---|
| PT-SPE | B | Vegetable oils | 100 mg | 150 μL of BSTFA (1 % TMCS), 150 μL of pyridine, 5 mL HX, 4.5 mL HX: $Et_2O$ (99:1, v:v) | GC × GC–MS/FID | NS | 97–100 | [183] |
| | M | Seafood | 5 g | 20 mL MeOH:$H_2O$ (1:1, v/v) | HPLC-MS/MS | 5 pg $mL^{-1}$ | 86–107 | [59] |
| | P | Tomato, apple, cucumber and pear | 5 mg | 1 mL MeOH, 600 μL ACN | GC-FID | 0.08–0.32 mg $kg^{-1}$ | 81–119 | [34] |
| | PH | Meat, egg and milk | 5 g (chicken and beef), 10 mL (milk), 7 g (egg) | 30 mL ACN:5%HAcO (19:1, v/v) (chicken and beef), 25 mL ACN (milk), 30 mL ACN (egg) | HPLC-DAD | 0.1–0.28 μg $L^{-1}$ | 76–114 | [184] |
| | P | Chicken eggs | 5 g | 30 mL ACN, 300 μL MeOH:$H_2O$ (3:7, v/v), 5.3 mL MeOH | HPLC-UV–Vis | 4.76 μg $kg^{-1}$ | 84–98 | [60] |
| | M | Peanut kernel | 1 peanut kernel | NS | HPLC-MS/MS | 0.04 ng $mL^{-1}$ | NS | [185] |
| | PH | Pork meat | 300 μL | 300 μL ACN:$H_2O$ (50:50, v/v), 2.3 mL MeOH:HCl (90:10, v/v) | LC-UV | 0.009 μg $kg^{-1}$ | 87–91 | [186] |
| μSPE | PH | Milk | 0.06–0.18 mL | ACN | CE-UV | 0.03 μg $L^{-1}$ | 92–119 | [79] |
| | M | Maize | 5 g | 20 mL ACN:$H_2O$ (80:20, v/v), 100 μL MeOH | HPLC-FLD | 0.0075–0.03 μg $kg^{-1}$ | 91–105 | [76] |
| | E | Milk | 5 mL | 100 μL ACN | GC–MS | 0.01–1.2 μg $L^{-1}$ | 77–103 | [25] |
| | P | Milk | 10 mL | 300 μL TOL | GC–MS | 0.19–1.64 ng $mL^{-1}$ | 85–102 | [187] |
| | PH | Meat | 1 g | >2.6 mL MeOH | HPLC-UV | 7.4–16.3 ng $g^{-1}$ | 92–105 | [78] |
| | M | Coffee and malt beverage | 10 mL | 350 μL ACN | LC-MS/MS | 0.12–0.76 ng $g^{-1}$ | 86–109 | [77] |
| | PH | Cow milk | 5 g | 100 μL MeOH | HPLC-UV–Vis | 0.8–1.5 μg $kg^{-1}$ | 88–102 | [80] |
| | M | Coffee and grape juice | 10 g (coffee), 10 mL (juice) | – | HPLC-FLD | 0.02–0.06 ng $g^{-1}$ | 91–102 | [81] |

*The empty cells in the Organic Solvent column indicate that the method is solvent-free. **ACN** – acetonitrile; **B** – biological & functional compounds; **BSTFA** – N,O-Bis(trimethylsilyl)trifluoroacetamide; **CE-UV** – capillary electrophoresis with ultraviolet detector; **E** – endocrine disruptors & plasticizers; **$Et_2O$** – diethyl ether; **GC-FID** – gas chromatography with flame ionization detector; **GC–MS** – gas chromatography-mass spectrometry; **GC × GC–MS/FID** – comprehensive two-dimensional gas chromatography-mass spectrometry/flame ionization detector; **$H_2O$** – water; **HAcO** – acetic acid; **HCl** – hydrochloric acid; **HPLC-DAD** – high-performance liquid chromatography with diode array detector; **HPLC-FLD** – high-performance liquid chromatography with fluorescence detector; **HPLC-MS/MS** – high-performance liquid chromatography-tandem mass spectrometry; **HPLC-UV** – high-performance liquid chromatography with ultraviolet detector; **HPLC-UV–Vis** – high-performance liquid chromatography with ultraviolet–visible detector; **HX** – hexane; **LC-MS/MS** – liquid chromatography-tandem mass spectrometry; **LC-UV** – liquid chromatography with ultraviolet detector; **M** – mycotoxins & biotoxins; **MeOH** – methanol; **NS** – not specified; **P** – pesticides & related substances; **PH** – pharmaceuticals & antibiotics; **PT-SPE** – pipette tip solid-phase extraction; **TMCS** – trimethylchlorosilane; **TOL** – toluene; **μSPE** – micro solid-phase extraction.

internal surface of the needle, enhancing interphase contact [4]. Compared to classical SPME, it offers shorter analysis times and significantly lower sample capacity. Additionally, SPDE fibers exhibit superior mechanical resistance in the sorption element compared to traditional extraction fibers. However, the primary drawback of this extraction method lies in the complex retention and elution process associated with these fibers and the potential for carry-over issues because analytes tend to adhere to the inner walls of the needle after thermal desorption [12]. Due to its similarity to HS-SPME, it has primarily been used to analyse volatile compounds in beverages such as beer, barley, malt, and red wine [72–74], utilizing significant sample volumes, between 5 and 10 mL but no organic solvents, thanks to the HS configuration of the technique. GC–MS [73,74] and GC-FID [72,75] have been the main analytical methods employed for the analysis. Additionally, it has been applied for the determination of pesticides (atrazine, simazine, cyanazine, ametryn, prometryn, and terbutryn) in grape juice and tap water by Djozan et al. [73].

### 3.1.6. *Micro-solid-phase extraction (μSPE)*

In this extraction method, a small quantity of sorbent is enclosed within sorbent bags (1–4 cm$^2$), which are made of porous membranes such as polypropylene or composite materials combining polyamide and nylon fibers, as shown in Fig. 4A. This design offers several important advantages [12]:

1. It can be applied to semisolid, solid, or suspension matrices, as the porous membrane prevents sorbent contamination, which helps eliminate matrix effects and reduce blockages commonly observed in other SPE techniques.
2. High preconcentration factors can be achieved.
3. The method is cost-effective.
4. It requires minimal amounts of organic solvent.
5. Each device can be reused up to 20 times.
6. The procedure is less time-consuming than conventional SPME.
7. It addresses analyte carryover and the fragility of fibers, drawbacks associated with conventional SPME.

Despite its merits, the implementation of μSPE also has notable drawbacks, such as carry-over, and a limited range of the stationary phases [10].

In food matrices (see Table 3), this technique has been primarily applied to milk, but maize [76], coffee [77], and meat [78] have also

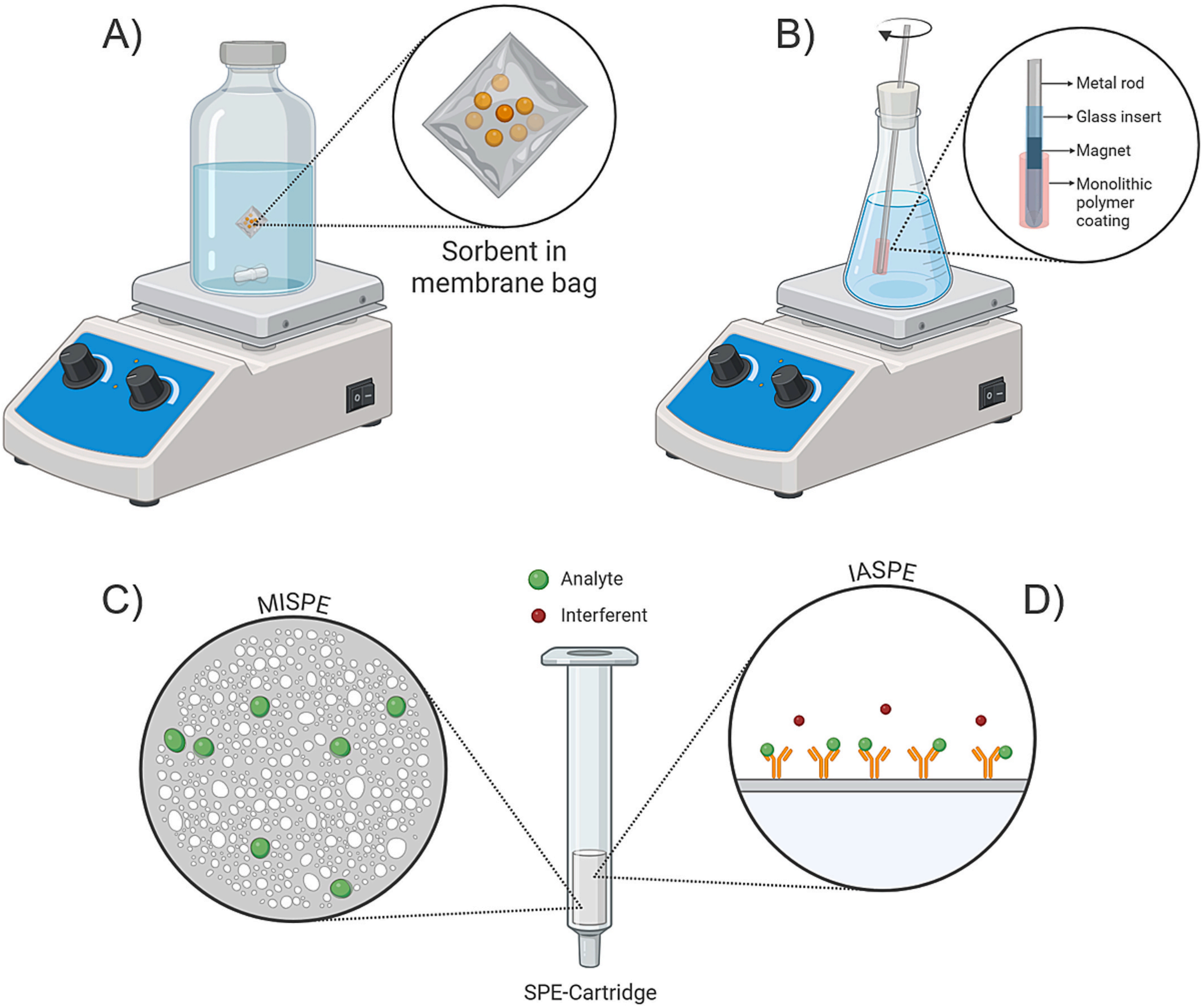

**Fig. 4.** A) Experimental setup for μSPE. B) Experimental setup for SRSE. C) Molecularly imprinted polymers in SPE-derived methods. D) Immunosorbents in SPE-derived methods.

been reported. The analytes studied encompass antibiotics and pharmaceuticals, including fluoroquinolones [79] and compounds from the penicillin family [80], as well as mycotoxins and biotoxins, such as ochratoxin A [81] and aflatoxins [76,77]. The most commonly used analytical techniques are GC and LC coupled with MS, FLD or UV detectors [77]. Solvent volumes are notably low, typically in the microliter range, aligning GAC principles. However, some commonly used solvents, such as acetonitrile and toluene, are considered problematic according to the CHEM21 solvent guide [21] (see Table 2). In contrast, sample amounts generally range from 5–10 g or 5–10 mL, except for the work of Martínez-Pérez-Cejuela et al. [79], who used 0.06–0.18 mL. Some variations of this technique include the incorporation of MIPs [81], or the combination with PT-SPE [80].

### *3.1.7. Adsorptive microextraction (AμE)*

AμE is an alternative to SBSE, which faces significant limitations in the sampling, concentration, and determination of analytes with high octanol–water partition coefficients [12]. This extraction method can be coupled with different analytical devices with appropriate geometries, where specific sorbents are held in place using sticking-based technologies. In most cases, the sorbent is physically attached to the substrate and immersed in the aqueous solution, which is then stirred with a stir bar or vortexed. Since many polar analytes are non-volatile and some are sensitive to heat, liquid desorption followed by HPLC is often the preferred analytical approach [3]. In practice, AμE can be performed using two geometrical variants: bar AμE (BAμE) and multi-sphere AμE (MSAμE). The latter provides multiple benefits, such as excellent recovery rates for polar analytes, ease of preparation, cost-effectiveness, and selectivity, as the sorbent can be chosen based on the target analyte. However, the primary limitation is the device's stability, which should be assessed individually for each application. In terms of stability, MSAμE devices also provide with better results than BAμE when thermal support is applied, because it enhances the device's robustness related to fixation. This is especially noticeable for challenging matrices such as foods [1].

AμE has been applied to determine an extensive variety of analytes in matrices such as wines [82], corn [83], baby food [23], condiments [84], and honey [85]. Chromatography has been the most commonly used separation technique, including GC–MS [82,84] and HPLC coupled with DAD [83] and FLD [23]. Sample amounts as low as 10 μL have been used [84] with methanol being the main organic solvent. Timofeeva et al. [23] determined volatile phenols (phenol, guaiacol, *o*-cresol, and *p*-cresol) in baby food using $Fe_3O_4@Cr(OH)_3$ nanoparticles for magnetic HS-AμE. The authors used 500 mg of meat sausages and 10 mg of nanoparticles were evenly distributed across the entire cap surface of the system, forming a thin layer that was held in place by an external magnetic tape outside of the cap. The particles were used only once, as their efficiency dropped to nearly 50 % of the initial when reused this issue is not consistent with GAC nor the practicality principles [86].

### *3.1.8. Stir-cake sorptive extraction (SCSE)*

SCSE was developed as a refinement of the SBSE technique, addressing some of its limitations. This method relies on a specially crafted holder for the stationary phase, which incorporates an iron core coated with a protective glass layer positioned at the base of the cake holder. Unlike SBSE, the extraction process in SCSE takes longer due to the deliberate prevention of contact between the sorptive element and the vessel bottom [3]. However, due to the protection provided, the sorptive phase can be reused up to 300 times, which is five times the usual lifespan of a stir bar [87]. SCSE uses of monoliths as the extractive

**Table 4**
Representative works using SCSE and MEPS for the analysis of food matrices.

| | Compound Group | Food Matrix | Sample amount | Organic Solvent (volume) | Instrumentation | LOD | Recovery (%) | Ref. |
|---|---|---|---|---|---|---|---|---|
| SCSE | H, D | Tap water, juices and soybean sauce | NS | MeOH:$H_2O$ (95:5) | HPLC-DAD | 0.0893–0.334 μg L$^{-1}$ | 69–120 | [188] |
| | D | Juices and soft drinks | 10 mL | NS | HPLC-DAD | 0.16–1.08 μg L$^{-1}$ | 63–107 | [92] |
| | PH | Water, honey and milk | 100 mL solution | 3 mL ACN:0.1 %FA (85:15, v/v) | HPLC-DAD | 0.020–0.10 μg L$^{-1}$ | 70–118 | [88] |
| | D | Orange juices and tea | 10 mL | 3 mL MeOH:HAcO (99:1, v/v), 3 mL MeOH | HPLC-DAD | 0.012–0.23 μg L-1 | 72–116 | [93] |
| | PH | Milk, chicken egg, chicken muscle and chicken kidney | 10 mL solution | 2 mL MeOH:FA (80:20, v/v), 0.2 mL MeOH | HPLC-FID | 1.9–4.6 ng mL$^{-1}$ (milk, egg), 1.8–3.7 ng g$^{-1}$ (chicken muscle and kidney) | 87–111 | [90] |
| | PH | Water and milk | 20 mL | 3 mL MeOH, 0.5 mL MeOH:0.5 %FA (8:2, v/v) | HPLC-DAD | 0.1–0.26 μg L$^{-1}$ | 69–120 | [89] |
| | B | Milk | 5 mL | 6 mL MeOH, 1 mL MeOH:$H_2O$ (80:20, v/v) | HPLC-MS/MS | 0.007–0.030 μg L$^{-1}$ | 50–113 | [91] |
| MEPS | B | Soy Juices | 2 mL | 2.8 mL MeOH | HPLC-MS/MS | 0.5–1.5 μg L$^{-1}$ | 93–123 | [144] |
| | P | Coffee | 2 g | 16 mL DCM, 4 mL ACN, 2 mL MeOH | GC–MS/MS | NS | 35–97 | [138] |
| | M | Wine | 600 μL | 200 μL MeOH:$H_2O$ (95:5, v/v) | UHPLC-DAD | 4.5–285.2 ng L$^{-1}$ | 84–99 | [140] |
| | B | Wine | 250 μL | 350 μL MeOH, 50 μL MeOH:$H_2O$ (95:5, v/v) | UHPLC-DAD | 0.01–0.2 μg mL$^{-1}$ | 77–100 | [141] |
| | B | Beer | 500 μL | 2.5 mL ACN | UHPLC-DAD | 0.4–0.9 ng mL$^{-1}$ | 67–100 | [142] |
| | B | Wine | 250 μL | 250 μL MeOH:$H_2O$ (95:5, v/v) | UHPLC-DAD | 0.21 μg mL$^{-1}$ | 95 | [139] |
| | P | Apple juice | 100 μL | 150 μL ACN | HPLC-UV | 0.005 μg mL$^{-1}$ | 76–96 | [145] |
| | P | Corn | 1 g | 5.5 mL ACN, 2.4 mL ACN:$H_2O$ (40:60, v/v) | LC-MS | 2.5 μg kg$^{-1}$ | 90–114 | [143] |

**ACN** – acetonitrile; **B** – biological & functional compounds; **D** – dyes, additives, & synthetic compounds; **FA** – formic acid; **GC–MS/MS** – gas chromatography-tandem mass spectrometry; **H** – heavy metals & inorganic substances; **$H_2O$** – water; **HAcO** – acetic acid; **HPLC-DAD** – high-performance liquid chromatography with diode array detector; **HPLC-FID** – high-performance liquid chromatography with flame ionization detector; **HPLC-MS/MS** – high-performance liquid chromatography-tandem mass spectrometry; **HPLC-UV** – high-performance liquid chromatography with ultraviolet detector; **LC-MS** – liquid chromatography-mass spectrometry; **M** – mycotoxins & biotoxins; **MeOH** – methanol; **MEPS** – microextraction by packed sorbent; **NS** – not specified; **P** – pesticides & related substances; **PH** – pharmaceuticals & antibiotics; **SCSE** – stir-cake sorptive extraction; **TFA** – trifluoroacetic acid; **UHPLC-DAD** – ultra-high-performance liquid chromatography with diode array detector.

medium that can be customized according to the properties of the target analytes, enabling a more tailored extraction. Among the commonly used extraction materials are poly(4-vinylbenzoic acid-DVB) sorbents derived from PILs, as well as monolithic discs fabricated from MIPs [12].

As shown in Table 4 the majority of food matrices analysed using this extraction technique are liquids, such as water [88,89], milk [88–91], and juices [92], which is reasonable given that the solid phase is embedded on a stirrer. Some studies have also focused on meats and eggs [90], but non-soluble matrices are less commonly analysed using this approach. Sample amounts typically range from 5 to 20 mL, with some involving solutions of non-liquid matrices where the weight was not specified [88,90]. The analytes primarily investigated include preservatives [92,93] and antibiotics, such as fluoroquinolones [89] and tetracyclines [90]. Organic solvent volumes reached up to 7 mL per sample preparation procedure, with methanol being the commonly preferred solvent [21]. Finally, HPLC was the predominant analytical technique, primarily coupled with DAD but also with FID [90] and MS/MS [91].

### 3.1.9. Rotating-disc sorbent extraction (RDSE)

RDSE is a highly effective extraction method for concentrating and isolating analytes with low polarity. This technique utilizes a rotating Teflon disk that has been modified with a stationary phase, which is where the extraction process takes place. After that, the disk is dried, and a small amount of solvent is applied to release the analytes from the sorbent material [87]. One of the key advantages of RDSE is the ability to reuse the disks, which enhances the method's practicality and cost-efficiency [86]. Furthermore, the disk design can be produced in a laboratory setting and provides a significantly larger active surface area for extraction than the stir-bar configuration used in SBSE [12]. Because of the previously mentioned aspects, and like SCSE, this method improves mass transfer during extraction, leading to higher analyte recovery, greater reproducibility, and a longer lifespan for the extraction material compared to conventional SBSE. Despite its significant merits, RDSE has been rarely used, particularly for food matrices. However, Fashi et al. [37] developed a rotating disk made of agarose gel to determine malondialdehyde in corn oil, olive oil, infant powdered milk, and some biological samples. The extraction process involved a derivatization step with 2-thiobarbituric acid, and it was carried out by attaching the gel disk to an electric stirrer using a rotating rod. Recoveries ranged from 88.3 % to 103.3 %, with LOD values between 12.5 and 17.5 ng $g^{-1}$. Analysis was performed using a single-beam UV–Vis spectrometer and a smartphone with an RGB-based program, both avoiding desorption steps as recommended by GAC principles. The high sorption performance observed was attributed to the gel's strongly hydrophilic nature and its high surface area-to-volume ratio.

### 3.1.10. Stir-rod sorptive extraction (SRSE)

SRSE was first proposed by Luo et al. to analyse fluoroquinolones in honey samples [94]. In this technique, the lower end of a metallic stir rod is coated with the extraction phase, a monolithic polymer-based adsorbent, which is rotated by a magnetic stirrer [3] (see Fig. 4B). The rod remains suspended without touching the extraction vessel, preventing any loss of the coating due to friction. The extraction process is carried out on this rod, which can be reused more than 60 times [94]. Five grams of samples were used with low volumes of organic solvents. LODs were low (0.06–0.14 ng $g^{-1}$), and recoveries were satisfactory (70.3–122.6 %) with HPLC-MS employed for separation and detection. Apart from this single study, the technique has not been widely applied to food matrices to date.

## 3.2. Stir-bar sorptive extraction (SBSE)

SBSE operates on principles similar to SPME, but instead of using a fiber coated with polymer, it employs stir bars (typically 1.5 cm long) covered with a thin layer of PDMS (0.5–1 mm), an apolar polymeric phase that facilitates hydrophobic interactions with the target analytes [9,11]. During the extraction process, the stir bar is usually immersed in the sample while it is stirred (DI, see Fig. 2C). Although less common, the stir bar can also be exposed to the HS of a vial containing a gaseous, liquid, or solid sample (see Fig. 2D) [95–97]. Once the adsorption step is completed, the stir bar is removed, rinsed with ultrapure water, and dried. For analytes that are stable at high temperatures, thermal desorption is used to transfer them from the sorbent phase to the injection port for GC or LC analysis [12]. The primary interactions between the sorbent and the analytes involve hydrogen bonding and Van der Waals forces [3]. SBSE offers some benefits, including its versatility for a comprehensive scope of analytes across gaseous, liquid and solid matrices, its potential for automation, and its ability to achieve high preconcentration factors. Additionally, the method is considered environmentally friendly due to the elimination of solvents [10]. However, this method also presents several drawbacks, such as a narrow range of analyte polarities that can be effectively extracted with the available stationary phases, significant matrix effects, and the need for strict control over extraction conditions. Highly complex matrices also limit the effectiveness in eliminating interferences due to its relatively low selectivity and specificity. Furthermore, there are other constraints to consider, such as the use of a single nonpolar polymer coating the stir bar, which restricts its application to semi-volatile, thermally stable compounds when thermal desorption is used. Nevertheless, integrating SBSE with derivatization procedures, such as on-stir, *in-situ* or post-extraction, can mitigate these challenges and broaden its applicability to polar and thermally labile compounds [12]. Recent advances in coating materials for magnetic stirrers have introduced a variety of innovative options, such as polyvinyl alcohol, poly(ethylene glycol)-modified silicone, polyacrylate, polyurethane foams, MIPs, and silicone-based materials.

In food matrices (see Table S3), liquids are the most studied, such as milk [98–100], juices [19,101–103], beer [96,104], or coffee [97]. This preference can be attributed to the technique's requirement for the solid phase to be placed on a magnetic stirrer, which facilitates pre-treatment when the matrix is already in solution and eliminates the need for additional preparation. Nevertheless, solid matrices like pork [31,105,106], fish [107,108], and apples [109,110] have also been reported. Volatile and aromatic compounds are the analytes most often analysed, as well as pesticides such as paraquat [111], thiabendazole, and carbendazim [112]. However, a great variety of other analytes have also been considered, as shown in Table S3. Sample amounts and solvent volumes vary considerably between studies but are not usually very high, with the exception of the work of. Ma et al. [98] who used 300 mL of acetonitrile. Recoveries are generally high and LODs can reach as low as pg $mL^{-1}$ [98]. Chromatographic techniques are the most commonly applied, with GC–MS being frequently used, especially for volatile compounds, followed by HPLC-UV. Notably, stir bars have been reused in some studies, with up to 50 [102], or even 150 uses [103] reported without compromising extraction efficiency, although the latter showed recoveries between 0.18 % and 49.5 %. MIPs have been widely used as a sorbent in food matrices as well [31,99,106,108,111,112]. It is worth mentioning that some authors have combined this technique with D-SPE to develop stir-bar sorptive dispersive microextraction (SBSDME) [113,114]. Abujaber et al. [114] analysed pineapple and orange juices using magnetic cellulose nanoparticles (MCNPs) to coat a stir bar, which dispersed into the solution during stirring. Once this process was completed, the MCNPs returned to the stir bar via magnetic attraction, allowing it to be removed from the solution as in standard SBSE procedures.

## 3.3. Magnetic solid-phase extraction (MSPE)

MSPE is a commonly used technique for separating and concentrating organic, inorganic, and bioactive compounds. The method relies on the adsorption and desorption of analytes onto magnetic adsorbents, which are introduced into the sample solution containing the target analytes. These magnetic particles (MPs) have a core coated with silica or alumina oxides, typically applied using the sol–gel process over which silanization can be utilized to immobilize specific functional groups [12]. In this approach, as shown in Fig. 5, the magnetic sorbent is introduced into the sample solution that contains the analytes of interest to then interact with the solution for a specific time, facilitating the adsorption of the compounds of interest. To improve the efficiency, speed, and ease of this interaction, the mixture is stirred using devices like a vortex, magnetic stirrer, or shaker. Once the adsorption phase is complete, the sorbent is separated from the sample solution using an external magnetic field. Then, an eluent is applied to the sorbent to separate the target analytes, and the sorbent is subsequently isolated from the previous using the same external magnetic field [115]. The separation process of the MPs relies on the nature of the sorbent and involves the interaction between analyte molecules and the functional groups fixed on the magnetic core. Various types of interactions have been identified, including ionic interactions, hydrogen bonding, dipole–dipole forces, dipole-induced dipole interactions, and dispersion forces [12]. In several applications, various polymers, nanomaterials, metals, and metal oxides that typically do not possess magnetic properties are enhanced with magnetic particles, enabling them to exhibit these. Different advanced sorbents are employed in these methods, including graphene-like materials. Additionally, mesoporous and nanoporous silicates, metal–organic frameworks, and MIPs are frequently used as well [3,116–118]. MSPE offers several advantages, providing a more efficient alternative to traditional SPE techniques by removing the need for sorbent-packed columns during batch processing, given that the phase separation process is both quick and efficient, as it is facilitated by an external magnetic field. By utilizing magnetic nanoparticles, the analysis time is reduced by minimizing the steps required for extraction and allowing simultaneous isolation and concentration of analytes. Furthermore, MSPE helps lower the consumption of organic solvents, thereby reducing hazardous waste production, in line with GAC principles [12].

As shown in Table S4, the food matrices most analysed are milk [119–125], meat [126], and fruits and vegetables such as apple [127], tomato [128], or carrots [129]. Biological and functional analytes, such as plant growth regulators [26,27,130] or pharmaceuticals like tetracyclines [119,121,123,131] or sulfonamides [126], have received the greatest attention, although pesticides have also been studied. Generally, good recoveries (69–122 %) and low LODs—as low as 0.89 pg mL$^{-1}$ [20]—have been reported. HPLC is the leading technique used, coupled with DAD and UV detectors. MIPs were included in this extraction technique by some authors [124,125,131,132].

### 3.4. Immunoaffinity solid-phase extraction (IASPE)

Antibodies are frequently employed as the active components in biosensors, playing a key role in affinity chromatography and immunoanalytical techniques such as the enzyme-linked immunosorbent assay (ELISA). Their exceptional specificity and selectivity make them ideal for use as sorbents in the extraction and concentration of trace-level antigen-target analytes from highly complex sample matrices. This has led to the development of IASPE, which can be conducted either on-line or off-line during the sample preparation process. The steps followed in this technique are equivalent to those in conventional SPE, and the determination of the analytes is often performed using HPLC, GC or CE [3]. Immunosorbents (ISs) are created by attaching antibodies, either monoclonal or polyclonal, to a solid support surface (see Fig. 4D). In order to choose the antibodies, it should be considered the physicochemical properties of both these and the support material, with careful control needed to prevent the deactivation of the formers. Common materials used for preparing supports include agarose gel and silica beads. While other solid supports, such as glass, alumina, and polystyrene (PV) DVB polymers, have been proposed in the literature, they have not demonstrated significant advantages over the previous [12]. Due to their nature, ISs have been primarily applied to biological compounds [133–136] and pharmaceuticals [137] in a wide range of matrices, including flours [134,135], meats [137], oranges [136], and milk [133]. The separation methods employed have included CE [134,135], LC [136,137], and matrix-assisted laser desorption/ionization (MALDI) [133] coupled with MS detectors, often achieving recoveries between 77 % and 115 %, and LOD values as low as 0.02 μg mL$^{-1}$ [133,137]. Although low sample amounts should be used in miniaturized techniques, Wang et al. [137] employed 10 g, which were subjected to different pre-treatments prior to extraction due to the complexity of meat matrices and the potential loss of analytes during pre-treatment processes, such as enzymatic or acid hydrolysis.

### 3.5. Microextraction by packed sorbent (MEPS)

MEPS is a scaled-down version of SPE that is more efficient, faster, environmentally friendly, and easy to use. In this method, a small amount of solid sorbent (approximately 1–4 mg) is placed inside a gastight syringe barrel or between the needle and barrel as a cartridge [6].

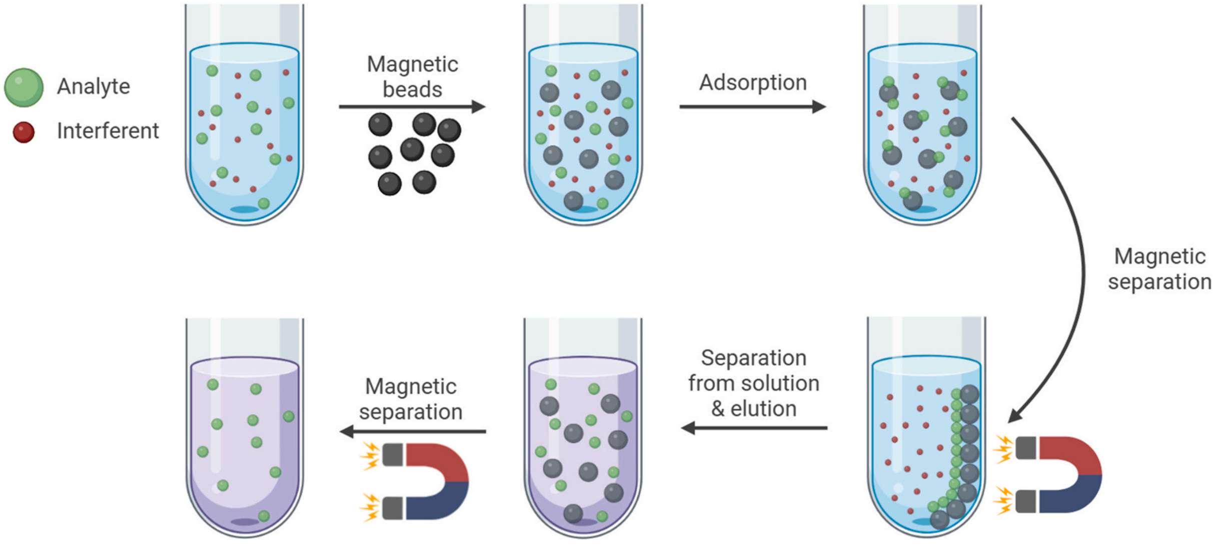

**Fig. 5.** Steps in MSPE procedures.

When the sorbent is spent or needs to be replaced, it can be quickly swapped out by unscrewing the locking nut and inserting a new barrel insert and needle. The MEPS protocol typically involves four main steps: conditioning the sorbent, loading the sample, washing, and elution. These steps are carried out by moving solutions up and down through the sorbent, in a similar way as in PT-SPE, optimizing the extraction for maximum efficiency and recovery. Additional parameters, such as sorbent, solvent, pH or ionic strength, must also be considered in order to reduce matrix effects, contaminants, and carry-over [1]. In MEPS, a variety of sorbents are employed, each with distinct particle sizes and adsorption properties. Commonly used sorbents comprise traditional silica matrices (unmodified silica, $C_{18}$, $C_8$, $C_2$), carbon, PV-DVB copolymers, strong and weak cation/anion exchange materials, restricted access materials, MIPs, and organic monolithic sorbents and mixed sorbents ($C_8$/SCX) are also utilized based on specific extraction needs [9,10]. MEPS offers several benefits when compared to other extraction techniques. These include [10]:

1. It is a versatile and simple technique that works with an extensive range of analytes and matrices.
2. The miniaturization of sorbent and solvent volumes.
3. The use of small sample volumes (20–50 μL of solvent in elution and washing steps, and 1–4 mg of sorbent), especially beneficial for limited or hard-to-collect samples.
4. MEPS sorbents can be reused up to 100 times or more, reducing the cost per analysis compared to techniques like SPE.
5. The two-directional flow in MEPS facilitates better sample loading, sorbent conditioning, and analyte elution.

However, despite these advantages, MEPS also has some drawbacks [10]:

1. Sorbent clogging, particularly with highly viscous or concentrated samples. Once clogged, the sorbent cannot be reused.
2. Not suitable for sample volumes above 500 μL, which can make the procedure time-consuming and labour-intensive in some cases.
3. Carry-over can occur, but it can be mitigated through carry-over studies and modifications to the washing steps before reusing the sorbent.

Regarding foodstuffs (see Table 4), MEPS has been primarily applied to liquids due to the requirement of suctioning the matrix into a syringe in each step. These matrices include coffee [138], wine [139–141], and beer [142], but also solid matrices like corn [143] were analysed. The most commonly determined analytes are biological and functional compounds, such as isoflavones [144], polyphenols [141], and prenylflavonoids [142], along with pesticides [138,145]. Sample amounts are lower than 2 g or 2 mL in all cases, and organic solvents are mostly used in very low quantities as well, although it must be mentioned that 16 mL of dichloromethane were used in one of the studies [138]. Gonçalves et al. [141] employed a $C_8$ sorbent and 50 μL of wine to determine hydroxybenzoic and hydroxycinnamic acids in wines, achieving recoveries between 77 % and 100 % and LODs ranging from 0.01 to 0.2 μg $mL^{-1}$ in 10 extraction cycles (5 min total). This procedure used a total of 350 μL of methanol (100 μL for conditioning and 250 μL for elution) and 50 μL of a methanol:water mixture, low volumes of solvents recommended by the CHEM21 solvent guide [21]. Moreover, the same packing bed was reused for approximately 100 extractions before replacement was required due to reduced analyte recovery and clogging. Dinali et al. [145] utilized MIPs on the surface of silica nanoparticles, requiring even less sample (100 μL) and 150 μL of acetonitrile, a lower volume but of a more problematic solvent. In this case, their recoveries ranged from 76.18 % to 96.12 %, with LODs as low as 0.005 μg $mL^{-1}$ in 5 extraction cycles.

### 3.6. Molecularly imprinted solid-phase extraction (MISPE)

MIPs are a type of polymer intentionally engineered to recognize a specific target molecule or group of compounds with high selectivity. These polymers are designed to be complementary in size, shape, and functional groups to the target molecule. The unique cavities created during the polymerization process allow the polymer to selectively bind with the target analyte(s) when introduced to the sample matrix [9] (see Fig. 4C). Due to the mentioned selectivity for a particular analyte or a group thereof, they have been applied to SPE methods, being effective for isolating trace-level compounds of interest. In practice, MISPE operates similarly to traditional SPE techniques. The process typically involves an extraction cartridge containing a small quantity of MIP (around 15–500 mg). Initially, the solid phase is conditioned to prepare it for extraction. Then, the sample solution is passed through the cartridge, where the target analytes bind to the polymer. After this, the analytes are eluted using an appropriate solvent and subsequently analysed with a compatible detection method [3]. MIPs offer several advantages, such as their ability to target a wide range of analytes, exceptional chemical and mechanical stability, low-cost and straightforward preparation processes, and their predetermined recognition capabilities for specific molecules. These features make them highly versatile and effective in various analytical applications. However, despite these benefits, a notable limitation of MIPs is the time-consuming nature of their preparation and use, which can reduce their practicality for applications requiring rapid analysis [12].

MISPE can be performed in two formats: off-line and on-line. The most used, off-line MISPE, is simple to operate, allows for the use of various solvents and additives without impacting subsequent chromatographic analysis, and provides high enrichment factors and selectivity. However, this method can be time-consuming, which may increase analytical errors. To address these limitations, on-line MISPE integrates the extraction process directly with the analytical system, reducing sample handling, minimizing compound loss and contamination risks, and improving accuracy and reproducibility. Additionally, on-line MISPE reduces preparation time, reagent consumption, and waste, while requiring only a small sample volume, as the entire extract is introduced into the analytical column [146]. There are two types of on-line MISPE procedures. The first uses a pre-column packed with MIP particles in the injection valve loop and is mostly used for multi-analyte determinations. The second does not use a pre-column, allowing preconcentration and separation on a single MIP column, and is typically used for extracting and determining a single analyte [12].

MISPE has been primarily applied to determine antibiotics and pharmaceuticals including ampicillin [147,148], chloromycetin [149], and oxacillin [147,150], as well as biological compounds like flavonoids [151]. In all cases, LC methods were employed, using MS [147,149] or spectroscopic detectors (UV, DAD) [148,150,151]. While milk has been the most studied matrix, Li et al. [151] applied the technique to *Ginkgo biloba* leaves. In this study, MIPs were synthesized using deep eutectic solvents, a novel class of biodegradable and low-toxicity solvents, to extract quercetin, isorhamnetin, and kaempferol. The procedure used 50 mg of sample and 1 mL of ethanol as the eluent, achieving recoveries between 99 % and 100 %. This demonstrates that miniaturized techniques using minimal sample and solvent amounts, even alongside innovative solvents, can yield excellent results. Conversely, Soledad-Rodríguez et al. [148] used 20 g of milk as sample, which is a significantly large amount to still be considered as miniaturized. However, they employed 350 mg of dry MIP for the extraction, that could be regenerated by passing 5 x 2 mL of acetonitrile, finally achieving recoveries above 95 %.

### 3.7. Dispersive micro-solid-phase extraction (D-μSPE)

D-SPE is already considered a miniaturized technique [62] and has been applied to various food matrices, including vegetables and fruits

[152–155], honey [156], beverages [28,33,157], and meat [158], to determine analytes such as pesticides [153–155,157,159] and endocrine disruptors [158,160]. D-SPE used sample amounts as low as 500 mg [156] and total organic solvent volumes of 220 μL [157]. Additionally, MIPs have been incorporated in several studies [28,155]. However, as analytical chemistry continues to advance toward more environmentally friendly approaches, D-μSPE has been more recently developed [161]. This technique relies on dispersing a microgram-level amount of sorbent into the solution containing the analyte. This approach generates a significantly larger surface area compared to conventional SPE methods, enabling quicker equilibration and enhancing the equilibrium ratio. As a result, it delivers improved extraction efficiency and reduces the overall sample preparation time. To achieve this, the sorbent is introduced into the sample solution using a dispersing liquid phase [2]. Enhanced distribution of the sorbent within the solution is achieved through methods such as ultrasonic vibration (ultrasound-assisted dispersive micro-solid-phase extraction, UA-D-μSPE) or vortex mixing (vortex-assisted dispersive micro-solid-phase extraction, VA-D-μSPE). However, these techniques can take time and risk degrading thermally sensitive analytes due to heat generation. Alternatively, air-assisted dispersive micro-solid-phase extraction (AA-D-μSPE) employs rapid cycles of aspiration and ejection using a syringe (30 cycles) for efficient dispersion. Once the sorbent has trapped the analytes, separation from the sample matrix is typically achieved through centrifugation, filtration (e.g., with a syringe filter) or an external magnetic field when magnetic sorbents are involved (magnetic micro solid-phase extraction, M-m-dSPE). Finally, the analytes are eluted from the sorbent using a suitable organic solvent, allowing the organic extract to be analysed further [11]. As mentioned before, the solid sorbents employed in D-μSPE must possess a high capacity and extensive surface area to ensure rapid and complete sorption and elution, along with excellent dispersibility in liquid samples. Given these factors, nanoparticles, such as carbon-based materials—e.g., carbon nanotubes, graphene, or fullerenes—and inorganic nanoparticles, are ideal candidates for these applications [12].

Regarding food analysis (see Table S5), milk [162–166], along with other liquid matrices such as juices [167–169] and tea [167,169–171] are frequently studied. Solid matrices, including rice [172], tomato [172,173], and cucumber [172], have also been examined. The biological and functional compounds most commonly determined include flavonoids [167,169], followed by pesticides such as fipronil [166] and chlorpyrifos [174]. Sample sizes ranged from as low as 30 mg [175] to as high as 10 g [176], with methanol being the most broadly used solvent in these analyses. HPLC and UHPLC are the predominant techniques employed, often coupled with spectroscopic detectors like UV, DAD, or FLD. Additionally, less frequently used methods, such as inductively coupled plasma optical emission spectroscopy (ICP-OES) [177] and circular dichroism coupled with ion mobility spectrometry (CD-IMS) [174] have been documented. Pezhhanfar et al. [178] combined D-μSPE with dispersive liquid–liquid microextraction (DLLME), achieving LODs between 0.88 and 1.04 μg $L^{-1}$, and recovery rates ranging from 40 % to 68 %. This technique has been modified with magnetic materials [169,174,176], and MIPs [166,171].

## 4. Future trends

Despite the advances made until now, challenges remain, particularly in the synthesis and characterization of pure, high-performing materials, and so, the future of miniaturized SPE-based extraction methods lies in the development of innovative sorbents designed to enhance retention efficiency, loading capacity, and selectivity. The application of nanomaterials and their derivatives, thanks to their exceptional surface area and unique physicochemical properties, has shown significant promise for improving selectivity and sensitivity in the extraction of analytes across diverse matrices. Additionally, combining different materials with complementary properties offers the potential to analyse diverse compounds using a single device. Among the most promising innovations, the use of 3D-printed sorbents is gaining attention, enabling the creation of customized geometries and controlled porosity to fine-tune extraction performance. These materials can be tailored to specific analytical needs and may support the design of more compact and integrated extraction platforms.

However, there are two main issues in terms of the application of these new materials. Firstly, the synthesis, purification, and even activation of the sorbents is not always carried out using green methodologies. Secondly, there is a lack of commercial availability for many advanced sorbents, and this restricts accessibility for both laboratories and industries. Moreover, the scalability of these materials and miniaturized systems remains a key challenge. While many developments show outstanding performance at the lab scale, transferring them into industrial workflows often requires addressing robustness, reproducibility, cost-effectiveness, and compliance with strict quality standards. To address this, future research should emphasize the development of greener and more sustainable sample preparation methods that can be applied to larger developments and further use by the scientific community.

Direct sampling techniques, such as in vivo SPME, are also gaining traction as transformative tools in analytical chemistry [179–182]. These methods allow for the extraction of analytes directly from various surfaces and textures without requiring precise sample positioning or extensive sample preparation. In vivo SPME, for instance, facilitates the direct sampling of biological fluids or tissues, offering rapid and minimally invasive analysis, and it is currently being studied in order to work with more complex matrices. Furthermore, as the demand for automation and high-throughput analytical systems grows, the integration of these advanced materials—and the entire sample preparation step—into automated workflows and analytical instruments is likely to shape the next generation of extraction techniques. Aside from reducing the consumption of solvents and minimizing waste generation, this also protects operators from exposure to harmful reagents as it reduces sample manipulation. In this regard, AI-driven automation may enhance decision-making and optimization throughout the sample preparation process, especially when integrated with technologies such as microfluidics and smartphone-based detectors. These developments could lead to more user-friendly, decentralized analytical tools. Nevertheless, the regulatory framework for novel sorbents and extraction platforms is still under development. Challenges related to validation protocols, safety assessments, and international standardization must be addressed to ensure their successful translation into routine analytical and industrial environments.

## 5. Conclusions

The development and application of miniaturized sample preparation techniques in analytical chemistry, such as SPME and related methods, has revolutionized the analysis of complex matrices, particularly in food science. These techniques offer significant advantages, including simplicity, high sensitivity, and efficiency in extracting analytes across a wide range of polarities and structures. Their ability to eliminate labour-intensive steps like centrifugation and filtration, coupled with reduced organic solvent consumption, makes them faster, more cost-effective, and more environmentally friendly. Furthermore, the adaptability of these techniques—as they can be seamlessly coupled with advanced analytical instruments such as GC, HPLC or UHPLC—has broadened their applicability in detecting both organic and inorganic compounds in diverse food matrices. These attributes have established miniaturized sample preparation techniques as indispensable tools in modern analytical workflows, combining efficiency, sustainability, and adaptability to address the challenges posed by complex sample matrices.

## CRediT authorship contribution statement

**Ana Jano:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Adrián Fuente-Ballesteros:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Methodology, Investigation, Formal analysis, Conceptualization. **Ana M. Ares:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Conceptualization. **José Bernal:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Project administration, Funding acquisition, Conceptualization.

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## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

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## Data availability

Data will be made available on request.

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