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# Recent Trends in Microextraction Techniques Employed in Analytical and Bioanalytical Sample Preparation

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Received: 16 October 2017; Accepted: 27 November 2017; Published: 1 December 2017

**Abstract:** Sample preparation has been recognized as a major step in the chemical analysis workflow. As such, substantial efforts have been made in recent years to simplify the overall sample preparation process. Major focusses of these efforts have included miniaturization of the extraction device; minimizing/eliminating toxic and hazardous organic solvent consumption; eliminating sample pre-treatment and post-treatment steps; reducing the sample volume requirement; reducing extraction equilibrium time, maximizing extraction efficiency etc. All these improved attributes are congruent with the Green Analytical Chemistry (GAC) principles. Classical sample preparation techniques such as solid phase extraction (SPE) and liquid-liquid extraction (LLE) are being rapidly replaced with emerging miniaturized and environmentally friendly techniques such as Solid Phase Micro Extraction (SPME), Stir bar Sorptive Extraction (SBSE), Micro Extraction by Packed Sorbent (MEPS), Fabric Phase Sorptive Extraction (FPSE), and Dispersive Liquid-Liquid Micro Extraction (DLLME). In addition to the development of many new generic extraction sorbents in recent years, a large number of molecularly imprinted polymers (MIPs) created using different template molecules have also enriched the large cache of microextraction sorbents. Application of nanoparticles as high-performance extraction sorbents has undoubtedly elevated the extraction efficiency and method sensitivity of modern chromatographic analyses to a new level. Combining magnetic nanoparticles with many microextraction sorbents has opened up new possibilities to extract target analytes from sample matrices containing high volumes of matrix interferents. The aim of the current review is to critically audit the progress of microextraction techniques in recent years, which has indisputably transformed the analytical chemistry practices, from biological and therapeutic drug monitoring to the environmental field; from foods to phyto-pharmaceutical applications.

**Keywords:** MEPS; FPSE; DLLME; magnetic nanoparticles; MIP; extraction procedures; green analytical chemistry; quantitative analyses

## 1. Introduction

The development of analytical methods for quantitative analyses in environmental water, biological sample matrices, and in food or food supplements with a reduced amount of toxic solvents, and the replacing with non-toxic ones, without loss of efficacy in the extraction procedure, are important aims for contemporary researchers [1,2]. These aspects are deeply valued during method development and validation in all fields [3].

Often, these aspects lead to the development of new approaches for analyte extraction and clean-up involved in the development of better sorbent coating technology for solid phase microextraction and stir bar sorptive extraction. The use of novel devices, like packed sorbent (in microextraction by packed sorbent, MEPS), fabric phase sorptive extraction media (in fabric phase sorbent extraction, FPSE), and imprinted polymer (in molecularly imprinted polymer extraction), as well as the use of combined strategies with magnetic elements, can enhance the efficiency and the recovery of the target analyte.

Liquid phase microextraction methods have demonstrated important innovations for the extraction and pre-concentration of analytes from different matrices. Dispersive liquid-liquid microextraction (DLLME) and its modifications, such as ultrasound-assisted DLLME (UA-DLLME), ionic liquid-based dispersive liquid–liquid microextraction (IL-DLLME), deep eutectic solvent-based dispersive liquid-liquid microextraction (DES-DLLME), and sugaring-out assisted liquid-liquid extraction (SULLE), can offer unique benefits, such as a high pre-concentration factor for the target analytes, low cost, simplicity and combined use with almost every analytical measurement technique [4].

A large number of solvent microextraction techniques, including single-drop microextraction, DLLME, and liquid-phase microextraction (LPME), have been reported. Implementation of these techniques can vary widely, but common features remain the same, including the use of only a small amount of organic solvents and a high sample-to-acceptor volume ratio. The organic phase, which extracts and pre-concentrates the target analyte(s), can be used for quantification by means of different types of instrument configurations [5]. LPME is usually performed to analyze water samples or aqueous solutions. Analysis of solid samples is commonly done in two steps: the solid sample is converted to aqueous solution using a suitable pretreatment procedure, and then the LPME is applied. Direct analysis of solid samples is somewhat exceptional, rather than common. Several works have been reported for the determination of different analytes in complex matrices, such as phenolic compounds in plant materials [6] and food samples [7,8] by using DLLME in combination with High Performance Liquid Chromatography-UltraViolet/Visible detector (HPLC-UV/Vis) [6] and Gas Chromatography-Mass Spectrometry detector (GC-MS) [7] instrument configurations.

Replacing hazardous solvents with ionic liquids (IL) or natural deep eutectic solvents (NADES) is another important task available in DLLME, and was recently reviewed by Shishov and co-workers [9]. It is possible to modify the IL's properties depending on the analytical purpose, due to the cation's fine structure and the anion's identity [10], but high cost and toxicity remain as the main disadvantages [11]. Recently, NADESs have been rapidly developed as a new type of green solvents, as an alternative to ILs. NADESs are based on primary metabolites, such as organic acids, amino acids and sugars, but limited data are available for these solvents' properties.

The aim of this review is to report the recently applied protocols and devices used in the extraction (and clean-up) procedures for quantitative analyses in complex matrices, with the main goal being the reduction of time, sample manipulation, solvent consumption and use of non-toxic solvents, in accordance with Green Analytical Chemistry (GAC) concepts.

## 2. Sorbent-Based Sorptive Microextraction Techniques

Sorbent-based sorptive microextraction techniques utilize a solid/semi-solid organic polymer as the sorbent, immobilized on a substrate (such as fused silica fiber, silica particles, glass-coated bar magnet, cellulose/polyester/fiber glass fabric etc.), and include solid phase microextraction (SPME) and its different modifications and implementations, stir bar sorptive extraction (SBSE), microextraction by packed sorbent (MEPS), thin film microextraction (TFME), and fabric phase sorptive extraction (FPSE). Sampling and sample preparation using these techniques are often carried out either by (1) headspace extraction; or by (2) direct immersion extraction. Due to the glue-like, highly viscous polymeric sorbents are prone to irreversibly adsorb matrix interferents from the sample matrix, direct immersion extraction can only be done when the aqueous sample is free from particulates

or macromolecules. As such, biological, environmental and food samples require rigorous sample pretreatment prior to analyte extraction such as filtration, centrifugation, protein precipitation, etc. Once the analytes are extracted into these devices, desorption can be carried out by applying thermal shock or by exposing to an organic solvent. Due to the special geometrical advantage (fiber retractable inside a syringe needle), SPME fiber can be introduced directly into GC inlet or into the HPLC system via a special interface. For SBSE or FPSE, a thermal desorption unit can be used. Alternatively, solvent mediated desorption can be used followed by injecting an aliquot into GC or HPLC for chromatographic separation and analysis.

### *2.1. Fiber-Based Solid-Phase Microextraction, Capillary Solid-Phase Microextraction, and Related Techniques*

Solid-phase microextraction (SPME), invented by J. Pawliszyn in 1987, undoubtedly deserves the credit for beginning a new era in analytical sample preparation characterized by solvent-free extraction, miniaturization and automation. SPME integrates sampling, extraction and analyte preconcentration into a single step. Due to this ease of interfacing with other analytical systems, as well as many other advantages, SPME has been enjoying exponential growth in applications in many different areas since its inception.

The miniaturization of sample preparation techniques and the integration, particularly in *on-line* configuration, of chromatographic instruments that could allow a reduction in labor-intensive manual operation and help to enhance the overall analytical performance [12] still remain the major focus in academic and industrial research. In this scenario, even if MEPS is more easily automated than SPE, and more robust than solid-phase microextraction (SPME) [13], sorbent-based techniques and their different formats certainly represent a valid choice. These techniques provide simplicity in their operation, consume no solvent or minimize solvent usage, allow the separation and pre-concentration of the analytes using different commercial fibers, and the possibility of automating the entire process could be successfully applied in food, environmental, clinical, pharmaceutical and bioanalysis applications [14–16], as recently reviewed by Silva and co-workers [17].

The fibers, which are commercially available, may be different based on their type:

- non-bonded phases: stable with some water-miscible organic solvents, although some swelling may occur when used with non-polar solvents,
- bonded phases: stable with all organic solvents, except for some non-polar solvents,
- partially cross-linked phases: stable in most water-miscible organic solvents and some polar solvents,
- highly cross-linked phases: similar to the partially cross-linked phases, except that some bonding to the core may occur.

All of these phases have been strongly and deeply studied and implemented for analysis of volatile components and in different applications—e.g., food, food supplements, and bioanalysis—but all show the same limitation with regard to handling of large sample volumes as for the main SPE/SPME procedure. These procedures (also capillary-like) could easily be used in biological and food analyses due to the relatively low sample volume, but in environmental applications, where large sample volumes are required in order to obtain higher pre-concentration factors, their limitations are highlighted.

Even if these "limitations" are present, fiber-based solid-phase microextraction and capillary solid-phase microextraction represent valid alternatives to conventional approaches due to the wide range of phases commercially available, their better stability and reproducibility (both between lots and analyses), and their unique characteristic of being solvent-less.

The latter techniques, capillary solid-phase microextraction, consist of an inert liner with a packet of coated open capillary tubes inside. The main advantage in comparison to the other reported microextraction procedures is that the surface areas of the extraction phase are more than two orders and one order of magnitude higher, respectively, than that of fiber-SPME. Hence, an equal extraction quantity can be obtained in a lower time. Another advantage is represented by the large cross-section

area, resulting in a lower flow resistance; consequently, water samples are able to flow through the cartridge independently, without the need for an auxiliary apparatus. Using capillary solid-phase microextraction, the extraction phase is protected from damage in the liner, so no heightened precautions are needed during application. Furthermore, the cartridge shows a small-bore diameter, which ensures the retention of trace and ultra-trace compounds using limited sample amounts, allowing high absolute recovery. The advances in SPME in terms of new coatings, formants and applications have been reviewed in a large number of articles; only a few are referenced here [18–21].

Although SPME offers numerous advantages over conventional sample preparation techniques, it suffers from significant shortcomings, including (1) relatively low operating temperature; (2) instability and swelling of the coating if exposed to organic solvents; (3) low sorbent loading results and poor extraction sensitivity; (4) high run-to-run and batch-to-batch variability; (5) the fact that the slow diffusion of the analyte(s) into viscous sorbents often leads to a long extraction equilibrium time; and (6) the fact that physically holding sorbent to the inert support results in a short life time for the SPME fiber. The majority of the shortcomings stem from the sorbent coating technology used in manufacturing the SPME fibers. However, the coating-related deficiency has been duly addressed by the sol-gel-based coating technology developed by Malik and his research groups [22]. This technology subsequently aided in the development of hundreds of sorbents possessing unique selectivity, as well as unprecedented thermal, solvent and chemical stability. A large number of review articles have critically evaluated these SPME coatings [23–27].

### *2.2. Stir Bar Sorptive Extraction (SBSE)*

Stir bar sorptive extraction was developed by Pat Sandra and his research group [28] with the aim of increasing the extraction sensitivity of SPME by incorporating substantially higher sorbent loading compared to SPME. In the original invention, poly(dimethylsiloxane) (PDMS) was coated onto a glass-coated magnetic bar. The unique design of SBSE makes it an independent sample preparation device, capable of diffusing the sample matrix by itself on a magnetic stirrer without requiring any external magnet. Extraction and preconcentration of the analyte is carried out by introducing the SBSE device directly into the aqueous sample. The analytes are extracted and preconcentrated when the SBSE spins inside the solution. Following the analyte extraction (driven by equilibrium), the SBSE device is withdrawn from the sample, rinsed with deionized water to clean matrix interferents, and dried with a Kim wipe. Subsequently, the extracted analytes are desorbed using a thermal desorption unit coupled to gas chromatography, or can be subjected to solvent desorption by exposing it to a small volume of a suitable organic solvent. The eluent is typically dried under nitrogen, and the sample is reconstituted in smaller-volume solvent. The sample can be analyzed in a gas or liquid chromatographic system. SBSE devices are commercially available under the trade name Twister®. Among others, a major drawback of this technique is the availability of only two phases: PDMS and Poly(ethylene glycol) in PDMS [29]. The high viscosity of both of these phases slows down analyte diffusion during extraction, resulting in a long extraction equilibrium time. As such, the extraction sensitivity in SBSE has not been improved proportionately with the sorbent loading, compared to SPME. Several review articles have discussed recent developments in SBSE [29–33]. As in the case of SPME, the efficiency of SBSE has been substantially improved by adopting sol-gel coating technology [34–38].

### *2.3. Micro Extraction by Packed Sorbent Procedures (MEPS)*

Recently, Abdel-Rehim and coworkers [39] reviewed the literature published on Micro Extraction by Packed Sorbent (MEPS) methods. This extraction procedure shows some very interesting potential benefits, such as low solvent consumption, small sample volume (10–250 µL), and the ability to be directly injected into the HPLC system without further treatments, with solvent volumes being compatible with several instrumental configurations and analyses. Figure 1 shows the device and the general procedure applied in MEPS extraction.

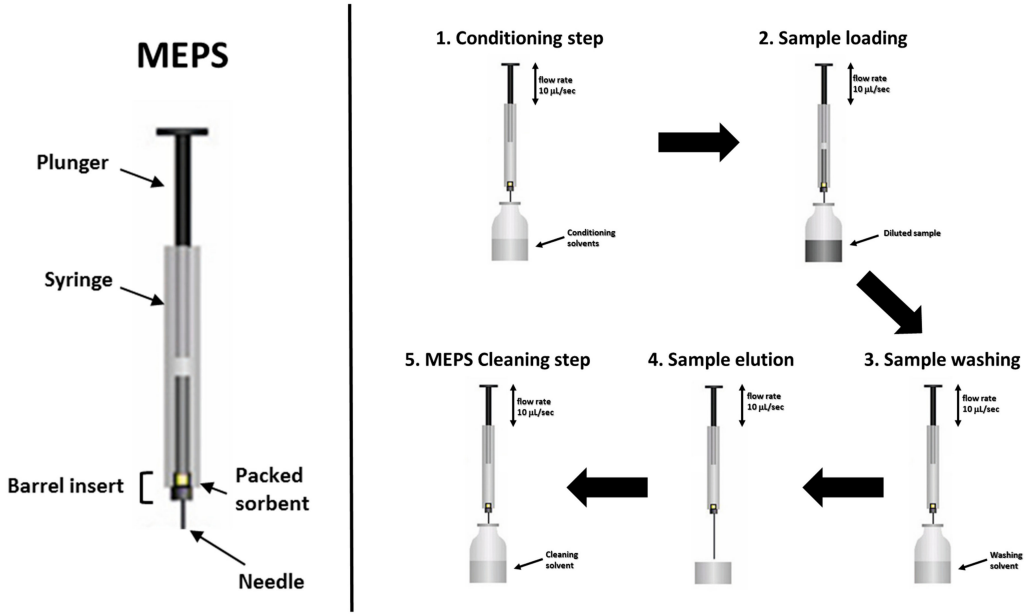


**Figure 1.** Device (**left**) and general procedure (**right**) applied in MEPS extraction.

This device is used in different fields, from biological applications to food and food supplement analyses. The main drawback is also related to its advantages. In fact, the possibility of using small sample volumes permits its application in analyses where only small volumes are available, for example plasma. In the case of higher volumes (such as in the environmental field), this device often shows its limitations.

Nowadays, several types of packing materials are available, including:

- Silica-based sorbents SIL (unmodified silica),
- C2(ethyl),
- C8 (octyl),
- C18 (octadecyl);
- Mixed-mode C8 and ion exchange (SCX),
- Mixed-mode M1 (80% C8 and 20% SCX with sulfonic acid bonded silica);
- Polystyrene-divinylbenzene (PS-DVB),
- Porous graphitic carbon,
- Molecular imprinted polymers (MIPs) based on different templates,
- Metal organic framework (MOF)-based MIPs [40,41],
- Monoclonal antibodies (mAbs) for immunoaffinity sorbents production.

Additionally, other commercial sorbents, such as new kinds of graphitic sorbent, polypyrrole/polyamide, polyaniline nanowires, CMK-3 nanoporous materials, functionalized silica monoliths, APS (amino-propyl silane), and cyanopropyl hybrid silica have been successfully applied in MEPS devices to extract different groups of analytes, as recently reviewed [39,42].

To aid and improve the reproducibility during the extraction process, MEPS devices are also coupled to syringes in semi-automated and/or fully automated configurations. In fact, the main critical point during extraction relates to the reproducibility of the flow rate (generally µL $s^{-1}$) used in the different steps (Figure 1). A MEPS syringe and a one-way check valve [43] was used for the realization of automated or semi-automated MEPS extraction, both for *on-line* and *off-line* instrument configurations.

Table 1 presents selected MEPS applications in different fields and the performances obtained when applying this device.

**Table 1.** Some recent MEPS applications (2012–2017, not previously reviewed) [39,43] in different fields, and the performances obtained when applying this device.

| Field | Analyte | MEPS | Matrix | Sample Volume | LOQ (LOD) | Reference |
|---|---|---|---|---|---|---|
| Biological | NSAIDs | C18 | Plasma Urine | 100 µL | 0.10 µg/mL (0.03 µg/mL) | [44] |
| | Fluoroquinolones | C18 | Sputum | 200 µL | 0.05 µg/mL (0.017 µg/mL) | [45] |
| | NSAIDs and Fluoroquinolones | C18 | Plasma Urine | 200 µL | 0.10 µg/mL (0.03 µg/mL) | [46] |
| | Imidazoles and Triazoles | C18 | Plasma Urine | 200 µL | 0.02 µg/mL (0.007 µg/mL) | [47] |
| | New psychoactive substances | mixed-mode C8/SCX | Oral fluid | 300 µL | 0.5 ng/mL (n.r.) | [48] |
| | Trans,trans-muconic acid | MIP-MEPS | Urine | 100 µL | 0.05 µg/mL (0.015 µg/mL) | [49] |
| | Statins | C18 | Plasma | 100 µL | 10–20 ng/mL (n.r.) | [50] |
| | Drugs of abuse | C8/SCX | Plasma | 300 µL | 0.01 µg/mL (0.005 µg/mL) | [51] |
| | Cocaine and metabolites | Mixed mode M1 | Urine | 200 µL | 25 ng/mL (n.r.) | [52] |
| Food and Food Supplements | Melatonin and other antioxidants | C8 | Foodstuffs | 100 µL | 0.05 ng/mL (0.02 ng/mL) | [53] |
| Environmental | Brominated diphenyl ethers | C18 | Sewage sludge | 15 mL reduced to 1 mL | n.r. (3 pg/mL) | [54] |
| | Chlorophenols | C18 | Soil samples | 1 mL | 0.353 µg/kg (0.118 µg/kg) | [55] |
| | Sulfonamides | C8 | Wastewater | n.r. | 5 ng/mL (n.r.) | [56] |
| | Phtalate esters | graphene and CNT/CNF–G nanostructures | Water | 10 mL reduced to dry | 0.02 ng/mL (0.004 ng/mL) | [57] |
| | Parabens | graphene supported on aminopropyl silica | Water | 1 mL | 0.2 µg/mL (n.r.) | [58] |

n.r. not reported.

As previously mentioned, applications in environmental fields are very limited due to the large volumes that are necessary for the trace analysis of pollutants, both organic and inorganic. Additionally, applications are relatively limited for foods and food supplements due to difficult application of MEPS, which requires a longer time in the pre-analytical steps.

### *2.4. Fabric Phase Sorptive Extraction Procedures (FPSE)*

Fabric Phase Sorptive Extraction (FPSE) is a novel sample preparation procedure that mitigates the drawbacks of MEPS. In fact, it allows small and large volumes to be treated, and could be usefully applied in all fields where a very high pre-concentration factor is required, from environmental to biological, from toxicological to food and food supplement quality control. The common drawbacks encountered in conventional sample preparation techniques can be conveniently overcome by using FPSE—developed by Kabir and Furton [59], and recently reviewed by the inventors [60]—which does not require any matrix modifications or clean-up. FPSE successfully integrates the advantages of equilibrium-based extraction (SPME/SBSE) and exhaustive extraction (SPE) without the necessity of time-consuming sample pretreatment procedures such as protein precipitation. The sorbent is covalently bonded to the substrate surface, and therefore offers high chemical, physical, and thermal stability. In addition, the open geometry of the media facilitates fast analyte sorption and desorption. The substrate used in FPSE is not inert, and contributes synergistically to the overall polarity of the FPSE media. Fabric phase sorptive extraction substantially simplifies the sample preparation workflow in comparison to other available and recent techniques, as demonstrated in Figure 2.

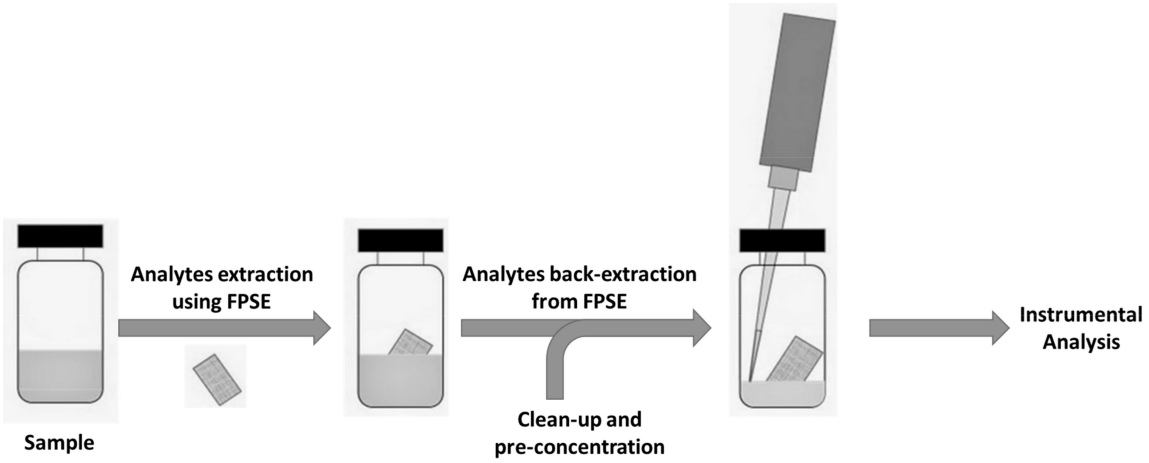


**Figure 2.** General procedure (**right**) applied in FPSE extraction.

Using FPSE devices, both large sample volumes (such as in the environmental field) and small sample volumes (generally applicable in the biological and pharmaceutical fields) can be easily handled, maintaining very good analytical performances in terms of LOQ, linearity and low pre-analytical steps, as reported in Table 2.

**Table 2.** Some recent FPSE applications in different fields, and the performances obtained when applying this device.

| Field | Analyte | FPSE | Matrix | Sample Volume | LOQ (LOD) | Reference |
|---|---|---|---|---|---|---|
| Biological | Imidazoles and Triazoles | sol-gel Carbowax® 20 M | Plasma Urine | 500 µL | 0.10 µg/mL (0.03 µg/mL)<br>0.05 µg/mL (0.015 µg/mL) | [61] |
| | Ciprofloxacin Sulfasalazine Cortisone | sol-gel Carbowax® 20 M | Whole blood Plasma Urine | 100 µL 500 µL 500 µL | 0.25 µg/mL (0.10 µg/mL)<br>0.10 µg/mL (0.03 µg/mL) | [62] |
| | Anastrozole Letrozole Exemestane | sol-gel PEG-PPG-PEG | Whole blood Plasma Urine | 200 µL 500 µL 1 mL | 0.1 µg/mL (0.03 µg/mL)<br>0.025 µg/mL (0.008 µg/mL)<br>0.025 µg/mL (0.008 µg/mL) | [63] |
| | Benzodiazepines | sol-gel PEG | Blood serum | 50 µL | 0.03 µg/mL (0.01 µg/mL) | [64] |
| | Selected estrogens | sol-gel PTHF | Urine | 10 mL | 0.066 ng/mL (0.020 ng/mL) | [65] |
| | Androgens and progestogens | sol-gel PTHF | Urine | 2 mL | 29.7 ng/L (8.9 ng/L) | [66] |
| Food and Food Supplements | Non-volatile plastic additives | sol-gel PDMS | Aqueous food simulants | 10 mL | 3 ng/g (1 ng/g) | [67] |
| | Amphenicols | sol-gel PEG | Milk | 0.5 g | 20 µg/kg | [68] |
| | Sulfonamides residues | sol–gel short-chain PEG | Milk | 1 g | 30 µg/kg (n.r.) | [69] |
| | Volatile compounds | sol-gel Carbowax® 20 M | Orange | 75 mL | n.r. | [70] |
| | Penicillin antibiotics | sol-gel PEG | Milk | 0.5 g | 10 µg/kg (3 µg/kg) | [71] |
| | Bisphenol A and residual dental restorative material | sol–gel graphene | Cow and human breast milk | 0.5 g | 50 µg/kg (16.7 µg/kg) | [72] |
| Environmental | Pharmaceuticals and personal care products | sol-gel Carbowax® 20 M | Water | 50 mL | 20 ng/mL (2 ng/mL) | [73] |
| | Selected estrogens | sol-gel PTHF | Water | n.r. | 0.066 ng/mL (0.020 ng/mL) | [65] |
| | Alkyl phenols | sol-gel PTHF | Water Soil | n.r. 1 g | n.r. (0.161 ng/mL) n.r. (1 ng/g) | [74] |
| | NSAIDs | sol-gel PTHF | Water | 30 mL | 3 ng/L (0.8 ng/L) | [75] |
| | Triazine herbicides | sol-gel PTHF | Water | 100 mL | 0.26 µg/L | [76] |
| | Benzotriazole UV stabilizers | sol–gel PDMDPS | Sewage | 10 mL | 24.5 ng/L (7.34 ng/L) | [77,78] |
| | Pharmaceuticals and personal care products | sol-gel Carbowax® 20 M | Water | 10 mL | 0.1 µg/L (0.01 µg/L) | [79] |
| | Cadmium | sol-gel PDMDPS | Water | 13.5 mL | 1.2 µg/L (0.4 µg/L) | [80] |
| | Androgens and progestogens | sol-gel PTHF | Waters | 2 L | 5.7 ng/L (1.7 ng/L) | [66] |
| | Co(II), Ni(II) and Pd(II) | sol-gel PTHF | Water | 10 mL | 1 ng/mL (n.r.) | [81] |
| | Pheromones | sol-gel PDMDPS | Air | - | 2.6 µg (0.8 µg) | [82] |

n.r. not reported; PEG polyethylenglycol; PDMS poly(dimethylsiloxane); PTHF polytetrahydrofuran; PDMDPS polydimethyldiphenylsiloxane.

### *2.5. Magnetic Nanoparticle Extraction*

Recently these applications were reviewed [9], and in particular, a review focused on using magnetic nanoparticles for the selective extraction of trace species from a complex matrix was reported [83].

The main advantage of this last configuration is the possibility of retaining the analytes adsorbed on magnetic stationary phase directly in the tube, cleaning the sample from the matrix and the interference compounds, and analyzing the extract directly for trace species.

To date, no other innovative applications—except for those reported in very recent review papers—have been reported in the literature for food analysis [84], for drugs in biological matrices [85], or in other research fields [86,87].

All of these papers clearly report the great advantages in using magnetic devices to allow the total recovery of the extracted analytes by using a strong magnet during the cleaning process. In this way, it could be possible to retain the analytes without any loss related to the wash step.

Additionally, it is also possible to dry the extracted samples and re-suspend them in a mobile phase more suitable for the instrumental analysis, thus also obtaining a great pre-concentration factor for trace analyses.

## 3. Solvent-Based Microextraction Techniques

Due to its high toxicity, expensive disposal requirements, and contribution to further environmental pollution, liquid-liquid extraction and its various modifications have undergone critical evaluation during the last decade, leading to the introduction of liquid phase microextraction (LPME). In a very short period, a number of techniques evolved, with the common goal of minimizing solvent consumption in the sample preparation process.

### *3.1. Liquid-Liquid Micro Extraction (LPME)*

Considering the principles of Green Analytical Chemistry [88], the development of analytical methods that reduce the amount of toxic solvents, or replace them with non-toxic alternatives without sacrificing the efficacy of the extraction procedure, is a major aim for researchers.

Liquid phase microextraction methods (LPME), in comparison to solid phase (micro) extraction, have shown important innovations for trace analytes in different matrices. LPME is utilized for organic compounds and inorganic trace elements in several application fields, such as the environmental, biological, and food fields. LPME can be divided into three different procedure modes: headspace LPME (HS-LPME), direct-immersed LPME (DI-LPME), and hollow fiber LPME (HF-LPME). In HS-LPME, a drop of extraction solvent—which can be either an organic solvent or a water solution—is suspended at the tip of a micro-syringe needle and exposed to the headspace of the sample; this is very suitable for analyses of volatile compounds. DI-LPME is very similar, except that the extraction solvent must be immiscible with aqueous solutions, and is directly immersed into a stirred sample solution. HF-LPME uses a hollow fiber in order to stabilize and protect the extraction solvent, while the small fiber pore size avoids the interference of large molecules and particles, which could result in a more extensive clean-up of the sample during the extraction process. Sharifi and co-workers [89] recently reviewed the principal applications in which these LPME techniques are applied.

### *3.2. Dispersive Liquid-Liquid Microextraction (DLLME)*

Dispersive liquid-liquid microextraction (DLLME) and its modifications—such as ultrasound-assisted DLLME (UA-DLLME), ionic liquid-based dispersive liquid-liquid microextraction (IL-DLLME), deep eutectic solvent-based dispersive liquid-liquid microextraction (DES-DLLME), and sugaring-out assisted liquid-liquid extraction (SULLE)—offer unique benefits, such as a high pre-concentration factor for the target analytes, low cost, simplicity, and the possibility of combined use with almost every analytical measurement technique [4,90,91]. A large number of solvent microextraction techniques,

including single drop microextraction, DLLME, liquid phase microextraction (LPME), have been reported. This extraction procedure allows a better analytical performance in comparison to HF-LPME, as reported by Xiong and Hu [92]. The organic phase, which contains the target analyte(s), can be used for quantification by means of different types of instrument configurations [5]. LPME is usually performed to analyze water samples or aqueous solutions. Analysis of solid samples is commonly done in two steps; the solid sample is converted to aqueous solution using a suitable pretreatment procedure, and then LPME is applied.

## 4. Conclusions

As is clearly highlighted in this review paper, the extraction (and clean-up) procedures applied to complex matrices are the real rate-limiting step in sample preparation, particularly related to the overall analytical performance of the developed (and validated) method. Several procedures that have recently been applied, their main aim being the reduction of time, sample manipulation, solvent consumption, and use of toxic solvents, in accordance with the Green Analytical Chemistry (GAC) concepts. A good idea of the advantages/disadvantages of the different procedures treated herein is reported in Table 3.

**Table 3.** A comparison of some characteristics of sample preparation techniques [17,93,94].

| Feature | MEPS | FPSE | DLLME | SPE | SPME |
|---|---|---|---|---|---|
| Phase amount | 0.5–4 mg | n.a. | n.a. | 50–10,000 mg | 150 mm thickness |
| Principle-separation | no emulsion | no emulsion | emulsion | no emulsion | no emulsion |
| Procedure time | 1–2 min | 5–30 min | 5–15 min | 10–15 min | 10–40 min |
| Re-use | 40–100 times | 30–50 times | Single use | Single use | 50–100 times |
| Recovery | + | + | + | + | − |
| Carryover | − | − | n.a. | + | + |
| Solvent consumption | − | +/− | + | + | solventless |
| Sensitivity | − | + | + | + | − |
| Easy-to-use | − | + | − | + | − |
| Sample quantity | − | +/− | +/− | + | + |
| Easily adaptable to | GC or HPLC | GC or HPLC | GC or HPLC | GC or HPLC | GC |
| Automatable | + | − | − | + | + |
| Target analytes | polar and charged analytes may be extracted | polar and charged analytes may be extracted | polar analytes difficult to extract | polar and charged analytes may be extracted | polar and charged analytes may be extracted |
| Cost | − | n.a. | + | + | + |
| Commercially available | + | − | + | + | + |

n.a. not applicable; + high; − low; +/− high or low depend to the application field.

These innovative procedures also allow analytical performance to be improved by using well-known instrument configurations—such as HPLC-UV/Vis—while avoiding the use of more complex and expensive ones (HPLC-MS, UPLC-MS, etc.). Additionally, these instrumentations can also be used by non-expert operators in routine analyses, both in clinical and in quality-control procedures.

**Acknowledgments:** This work was supported by University "G. d'Annunzio" of Chieti-Pescara, Chieti, Italy.

**Author Contributions:** All Authors contributed equally to the present work.

**Conflicts of Interest:** The authors declare no conflict of interest.

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