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Review

Alternative Green Extraction Phases Applied to Microextraction Techniques for Organic Compound Determination

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Abstract: The use of green extraction phases has gained much attention in different fields of study, including in sample preparation for the determination of organic compounds by chromatography techniques. Green extraction phases are considered as an alternative to conventional phases due to several advantages such as non-toxicity, biodegradability, low cost and ease of preparation. In addition, the use of greener extraction phases reinforces the environmentally-friendly features of microextraction techniques. Thus, this work presents a review about new materials that have been used in extraction phases applied to liquid and sorbent-based microextractions of organic compounds in different matrices.

Keywords: biosorbents; microextraction; organic compounds; green extraction phases

1. Introduction

Sample preparation is a crucial step in analytical methods for determining organic compounds. The isolation of the analytes from the matrix is a major task to ensure the quantification and unambiguous identification of such compounds [1]. Classical sample preparation techniques, such as liquid–liquid extraction (LLE) and solid-phase extraction (SPE), are usually time-consuming and labor-intensive. These techniques usually use large volumes of organic solvents, which are expensive and generate a considerable amount of waste that is harmful for human health and the environment [2].

Microextraction techniques such as those based on sorbent microextraction and liquid-phase microextraction are considered of great importance, since they represent an environmentally friendly alternative to classical extraction methods [3]. There are different microextraction configurations and modes of use. Sorbent microextraction may be considered as an advanced and miniaturized solid phase extraction (SPE) technique. Solid phase microextraction (SPME) [4] and thin film microextraction (TFME) [5] belong to this category. Similarly, liquid phase microextraction (LPME) can be considered as miniaturized liquid–liquid extraction procedures [6]. Most LPME techniques used include dispersive liquid–liquid microextraction (DLLME) [7] and single drop microextraction (SDME) [8,9].

In general, microextractions are carried out using an appropriate extraction phase, which can be a liquid [6] or a solid material [10], depending on the technique chosen. There is a large variety of extraction phases commercially available. However, in the last decade, efforts have been devoted to the development of new materials to be used as "greener" extraction phases. The green aspects of these alternative materials contribute to a less harmful and lower-cost analysis [3]. Furthermore, their usage reinforces the environmentally friendly character of microextraction techniques. In some specific cases, it increases selectivity and hence applicability for treating complex samples. For example, ionic liquids (ILs) and their tunable properties meet the criteria for extracting some compounds.

Based on that, the aim of this work is to review the new materials used as green extraction phases for the determination of organic compounds by microextraction and chromatographic techniques. Furthermore, some recent applications of these materials in various matrices are presented.

2. Biosorbent-Based Extraction Phases

Natural, renewable and biodegradable sorbents are denominated biosorbents and have attracted a great deal of attention in the sample preparation area, due to their low cost, non-toxicity and high availability [11]. There are several materials from different sources that can be used as biosorbents, such as agricultural waste products, industrial by-products and biomass derived from usually discarded materials [12]. Some materials such as cork, bamboo charcoal, bract, and recycled diatomaceous earth have already been applied in extraction phases to a large number of microextraction techniques based on solid phase extraction. Thus, in the following topics, the characteristics and some relevant recent applications of these materials in the biosorbent-based extraction phase will be discussed. More information about the applications and validation parameters of the reported methods are summarized in Table 1.

2.1. Cork as a Biosorbent

Cork is the bark of the cork oak tree (*Quercus suber* L.) and as a lignocellulosic material, it is composed of 40% suberin, 24% lignin, 20% cellulose and hemicellulose and 15% of other extractives [13]. In 2013, Dias et al. [14] proposed, for the first time, the use of a cork-based biosorbent as a coating for the solid phase microextraction technique (SPME) introduced by Pawliszyn et al. in 1990 as a miniaturized technique [4]. The procedure to obtain SPME cork fiber involves immobilization of the cork powder (approx 200 mech) on a nitinol wire of 0.2 mm thickness and approximately 2 cm length. After this, the wires with biosorbent are heated at a temperature of 180 °C for 90 min. Before use, the cork fibers produced are conditioned at 260 °C for 60 min in a gas chromatograph (GC) injection port [14].

The fiber characterization conducted using Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) showed a heterogeneous chemical composition. Lignin presents several aromatic rings that may allow π-π interactions between sorbent phase and analytes, mainly the non-polar compounds. On the other hand, cellulose and hemicellulose exhibit a number of O–H groups in their structure, allowing for hydrogen-bonding and dipole–dipole interactions with the compounds presenting intermediate polarity. Furthermore, a homogeneously distributed coating and a porous structure are reported for the surface of the fiber. The coating thickness obtained for the proposed fiber was about 55 µm [14].

The SPME biosorbent-based fiber has already been successfully applied for the determination of polycyclic aromatic hydrocarbons (PAH) [14], organochloride pesticides (OCPs) [15] and UV filters such as 3-(4-methylbenzylidene) camphor (4-MBC) and 2-ethylhexyl 4-(dimethylamino) benzoate (OD-PABA) [16] (Table 1). In the work proposed by Dias et al. [14], the cork fiber extracted the PAHs by adsorption through π-π interactions and suberin was reported to play a more important role than lignin, in this case. The cork fiber was compared to commercially available fibers such as polydimethrylsiloxane/divinylbenzene (PMDS/DVB), divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) and polydimethylsiloxane (PDMS), presenting similar or better extraction efficiency for most compounds. An advantage reported by the authors was the lifetime of the coating layer, which was higher than the commercial ones, 50–100 times against 40 times, respectively.

Table 1. Applications and validation parameters of different microextraction techniques using biosorbents as the extraction phase for organic compound determination. SPME—solid phase microextraction; TFME—thin film microextraction; BAμE—bar-adsorptive microextraction; SPE—solid-phase extraction.

Biosorbent	Technique	Analyte	Matrix	LOQ	LOD	Linear Range	Recovery (%)	Precision (RSD%)	Method	Ref.
Cork	SPME	polycyclic aromatic hydrocarbons (PAHs)	River water	0.1 μg L^{-1}	0.03 μg L^{-1}	0.1–10 μg L^{-1}	70–103	1.9–15.7	GC-MS	[14]
		Organochlorine pesticides	River water	1–10 ng L^{-1}	0.3–3 ng L^{-1}	1–50 ng L^{-1}	60–112	0.5–25.5	GC-ECD	[15]
		UV filters	River water	0.01–0.1 μg L^{-1}	0.004–0.03 μg L^{-1}	0.01–0.5 μg L^{-1}	67–107	3–18	GC-MS	[16]
	TFME	Emerging contaminants	River water	0.8–15 μg L^{-1}	0.3–5.5 μg L^{-1}	5–400 μg L^{-1}	72–125	4–18	HPLC-DAD	[17]
	BAμE	Parabens, benzophenone and triclocarban	Lake water, effluent, wastewater	1.6–20 μg L^{-1} (15 mm)	0.5–6.5 μg L^{-1} (15 mm)	1.6–500 μg L^{-1} (15 mm)	65–123 (7.5 mm)	3–22 (7.5 mm)	HPLC-DAD	[18]
				0.64–8 μg L^{-1} (7.5 mm)	0.2–2.5 μg L^{-1} (7.5 mm)	0.64–400 μg L^{-1} (7.5 mm)				
		Hexanal and heptanal	Human urine	2.19–3 μmol L^{-1}	0.73–1 μmol L^{-1}	2.19–8 μmol L^{-1}	88–111	3–7	HPLC-DAD	[19]
Bract	SPME	Organochlorine pesticides	River and lake water	0.65–2.38 ng L^{-1}	0.19–0.71 ng L^{-1}	5–100 ng L^{-}	60–110	5–19	GC-ECD	[20]
		PAHs	Lake water	0.01–0.1 μg L^{-1}	0.003–0.03 μg L^{-1}	0.01–4 μg L^{-1}	68–117	0.6–17	GC-MS	[21]
	TFME	Steroid estrogens	Human urine	0.1–10 μg L^{-1}	0.3–3 μg L^{-1}	0.1–400 μg L^{-1}	71–105	1–17	HPLC-FLD	[22]
Diatomaceous earth	SPME	PAHs	River water	0.1–0.5 μg L^{-1}	0.03–0.16 μg L^{-1}	0.1–25 μg L^{-1}	83–100	2–15	GC-MS	[23]
	TFME	Endocrine disruptors	River water	3–23 μg L^{-1}	1–8 μg L^{-1}	5–285 μg L^{-1}	70–117	1–21	HPLC-DAD	[24]
	BAμE	Methyl and ethyl paraben, benzophenone, triclocarban	Lake water	0.63–6.9 μg L^{-1}	0.19–2 μg L^{-1}	0.63–100 μg L^{-1}	63–124	1–20	HPLC-DAD	[25]
Bamboo charcoal	SPME	Phthalate esters	Tap and river water		0.004–0.023 μg L^{-1}	0.1–100 μg L^{-1}	61–87	1.89–9.85	GC-MS	[26]
Moringa oleifera seeds	μ-SPE	Phthalate esters	Milk	0.1–3.7 μg L^{-1}	0.01–1.2 μg L^{-1}	1–100 μg L^{-1}	77–103	3.6–9.4	GC-MS	[27]
MMT clay	RDSE	polychlorinated biphenyl (PCB)	Wastewater	6.5–103.8 ng L^{-1}	3 ng L^{-1} to 43 ng L^{-1}		80–86	2–24	GC-ECD	[28]
Cork and MMT clay	RDSE	Parabens	River and tap water	0.8 μg L^{-1} (cork)	0.24 μg L^{-1} (cork)	0.8–75 μg L^{-1} (cork)	80–118 (cork)	1.15–14.29 (cork)	LC-MS/MS	[29]
				3 μg L^{-1} (MMT clay)	0.90 μg L^{-1} (MMT clay)	3–100 μg L^{-1} (MMT clay)	80–119 (MMT clay)	3.24–18.14 (MMT clay)		

When used for OCP determination [15] the extraction efficiency of the cork fiber was attributed mostly to dipole–dipole interactions with the analytes. The authors also reported the occurrence of hydrogen bonds with the compounds containing oxygen atoms. In the work of Silva et al. [16], the cork fiber extraction efficiency for 4-MCB and OD-PABA was compared with PDMS/DVB and PDMS fibers, and the results showed a better extraction efficiency when the cork fiber was used, for both analytes.

Cork has also been used with thin film microextraction (TFME) [17]. TFME comprises a new geometry for SPME, aiming to provide more sensitivity for this technique. The device used in TFME consists of a support coated with a thin layer of a sorbent phase that can be used in headspace or immersion mode. Moreover, this technique has been designed to fit a commercially available 96-well plate system providing high-throughput analyses. To date, there has been only one study published using cork with TFME, by Morés et al. in 2017 [17]. The TFME cork coating coupled with 96-well plate system was used as a high-throughput method for the extraction of emerging contaminants in a water sample by high-performance liquid chromatography-diode-array detector HPLC-DAD (Table 1). In this work, analytes with the log K_{ow} ranging from 2.49 to 5.92 were successfully extracted by the cork sorbent phase.

Another microextraction technique that used cork as the sorbent phase is called bar-adsorptive microextraction (BAμE) [18]. The BAμE device consists of a finely divided powder (up to 5 mg) fixed with suitable adhesives in polypropylene supports with cylindrical bar format. In the experimental procedure, the adsorbing bars are placed in direct contact with the sample, under constant stirring. Due to the low density of the polypropylene support, this floats just below the vortex formed by agitation, preventing direct contact of the bar with the flask's walls containing the sample, thus increasing the useful life of the device. After extraction, the desorption step consists of completely inserting the bar into vials containing a few microliters of a suitable extraction solvent.

Cork biosorbent has been used twice with BAμE. It was first used in 2015 for determination of polar and intermediate polarity compounds (parabens, benzophenone and triclocarban) in water samples by HPLC-DAD [18]. In this study, bars of 7.5 and 15 mm in length were used. Hollow cylindrical polypropylene tubes (15 mm length and 3 mm diameter) were coated with adhesive films followed by a layer of the cork powder (200 mesh). Before use, the bars were conditioned under ultrasound agitation with 250 μL of acetonitrile (ACN) for 15 min. The half bars (length of 7.5 mm) were obtained by cutting the 15 mm length bar in half. As shown in Table 1, the quantification limits ranged from 1.6 to 20 μg L^{-1} using a bar of 15 mm and 0.64 to 8 μg L^{-1} using a bar of 7.5 mm.

The second study was published in 2017. At this time, the use of cork BAμE bars was extended to biological samples for determination of two potential lung cancer biomarkers (hexanal and heptanal) in human urine by HPLC-DAD [19]. In this study, the adsorptive bar surface was impregnated with 2,4-dinitrophenylhydrazine (DNPH) so that derivatization and extraction were accomplished simultaneously on the surface of the bar under acidic conditions. Relative recoveries in urine samples varied from 88 to 111% (Table 1). Figure 1 illustrates a scheme of the biobased BAμE procedure used. According to the authors, one of the main advantages was the low cost of the method, since polypropylene tubes, adhesive and cork obtained from cork stoppers were used to produce the devices.

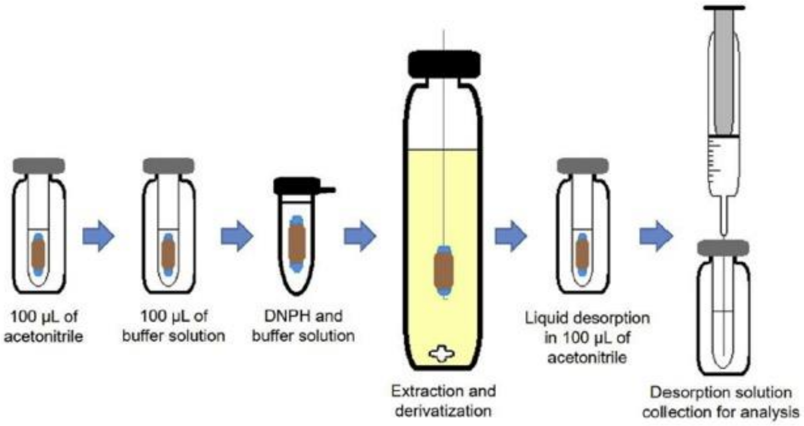

Figure 1. Scheme of the biobased bar-adsorptive microextraction (BAµE) procedure to determine hexanal and heptanal in human urine by HPLC-DAD. Reproduced with permission from [19], Copyright Elsevier, 2017.

2.2. Bract as a Biosorbent

Another lignocellulosic material was reported in 2017 as a green extraction phase for SPME [20]. The material, called bract, is the non-developed seeds obtained from the tree *Araucaria angustifolia* (Bert) O. Kuntze, a conifer found in the south and southeast of Brazil and in eastern Argentina. This material is composed of 45% lignin, 46% holocellulose (cellulose and hemicellulose) and 15% total extractives. The process for obtaining bract-based fibers is similar to those already described for cork fibers. Both materials are similar; however, the cork powder presents a better attachment to the nitinol wire, so it is easier to handle. Bract has been used as an environmentally friendly and low-cost biosorbent coating for SPME for the determination of OCPs in river and lake water [20] and PAH's in river water [21] (Table 1). The characterization of bract fiber carried out by thermogravimetric analysis (TGA), SEM and FTIR showed that the fiber offers satisfactory thermal stability with no decomposition observed up to 260 °C. SEM micrographs presented a highly porous and rough morphology and a film thickness of approximately 60 µm [20]. Like cork, bract is also a lignocellulosic material. The FTIR spectrum revealed peaks related to O–H bond and C–H stretching assigned to polysaccharides and lignin. C=C stretching from the aromatic rings and a peak related to C–O–C bond were also identified. Figure 2 shows a scheme of the preparation (2A) and SEM micrographs obtained for bract SPME fiber (2B).

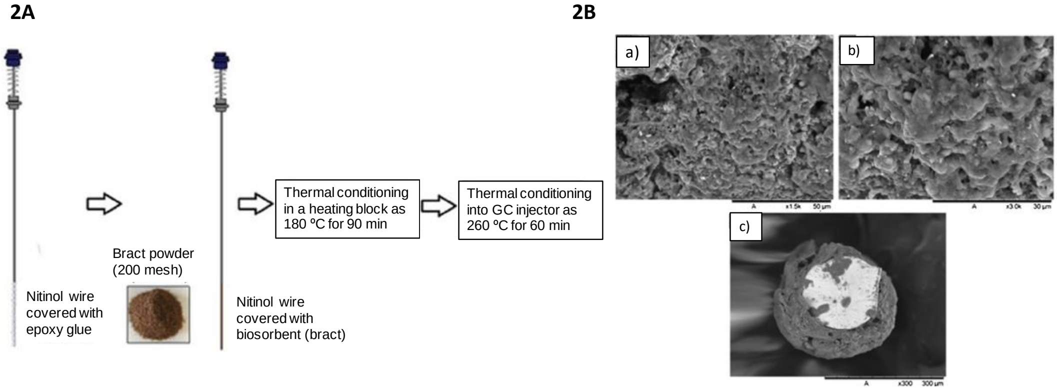

Figure 2. (**2A**) Scheme of the preparation of SPME fibers and (**2B**) SEM micrographs obtained for bract fiber (**a**) magnification of 1500× (**b**) magnification of 3000× and (**c**) a cross-section of the proposed fiber at magnification of 300×. Reproduced with permission from [20], Copyright Elsevier, 2017.

When applied to the determination of OCPs in water samples by gas chromatography–electron capture detection (GC-ECD), a satisfactory analytical performance was reported with limits of detection

(LODs) ranging from 0.19 to 0.71 ng L^{-1}. In addition, the biosorbent-based fiber provided efficient extractions when compared with the commercial mixed coating fiber DVB/Car/PDMS. In 2018, bract fiber was used for the determination of PAH's in water samples by gas chromatography–mass spectrometry (GC-MS) [21]. In this study, the LODs varied from 0.003 to 0.03 μg L^{-1} (Table 1).

Bract has also been used with TFME combined with a 96-well plate for the determination of steroid estrogens in human urine by liquid chromatography fluorescence detector (HPLC-FLD) [22]. At this time, the target compounds presented intermediate polarity with log $P \leq 4.12$. The extraction efficiency of the bract layer was explained by the π-π interactions between lignin and the analytes. The LODs of the method varied between 0.3 μg L^{-1} for 17-β-estradiol and 3 μg L^{-1} for estrone (Table 1). As an advantage, in this study, the authors reported the use of the 96-well plate system, allowing for 1.7 min/sample turnaround times for the proposed method.

2.3. Recycled Diatomaceous Earth as a Biosorbent Material

Diatomaceous earth is an amorphous silicate sediment originating from fossilized unicellular microorganisms on algae of the class Bacillariophyceae centricae. This material is composed mainly of silica dioxide and small amounts of aluminum, iron, calcium, magnesium, sodium and potassium. After being used for the filtration and clarification of beer in a brewery, the diatomaceous earth was subject to thermal treatment and then used as the extraction phase for SPME [23]. The FTIR characterization of the material revealed O–H bonds from silanol groups. Moreover, asymmetric stretching was reported assigned to Si–O–Si bonds, frequently found in silicate materials. This biosorbent has been used along with SPME for the determination of PAH's in river water samples by GC–MS [23]. In the comparison with the commercial fibers PDMS/DVB and PDMS, the biosorbent showed better extraction efficiency for most compounds, except for acenaphthylene ($C_{12}H_8$), fluorene ($C_{13}H_{10}$) phenanthrene ($C_{14}H_{10}$) and pyrene ($C_{16}H_{10}$), for which PDMS/DVB was better. In this work, the authors did not provide a possible explanation for the interactions between analytes and the biosorbent. However, a fiber limitation was reported regarding the use of salt in the optimization step. According to the authors, salt particles added to the samples can remain adsorbed in the surface of the extraction phase, causing fiber damage. In this case, if the salt addition is necessary to improve extraction efficiency, a cleaning step with water may be done before the fiber insertion into the GC injection port.

Other applications of this sorbent include TFME with 96-well plate system for the determination of endocrine disruptors in water samples by HPLC-DAD [24] and with BAμE in the determination of methyl and ethyl paraben, benzophenone and triclocarban in water by HPLC-DAD [25] (Table 1). In the work of Kirschner et al. [24], bisphenol A (BPA), benzophenone (BzP), triclocarban (TCC), 4-methylbenzylidene camphor (4-MBC) and 2-ethylhexyl-p-methoxycinnamate (EHMC) were successfully determined from environmental water samples. Considering the analyte structure, the authors attribute the extraction efficiency of diatomaceous earth to the O–H moieties presented in the sorbent and the O–H and N–H groups in the target compounds. In this work, information about the extraction phase stability in the presence of organic solvents was provided. After successive extractions, the biosorbent blades were able to be used without expressive loss in the extraction efficiency for at least 20 extraction/desorption cycles. The proposed method exhibited satisfactory analytical performance, with LODs varying between 1 and 8 μg L^{-1} and determination coefficient ranging from 0.9926 to 0.9988.

2.4. Other Materials Used as Biosorbents

A range of other materials characterized as biosorbents have also been used in combination with microextraction techniques for organic compound determination. Although there are still few applications involving these materials, a brief description is provided, along with the existent applications.

Bamboo plants are characterized by rapid growth and are widely distributed in China. Bamboo charcoal is obtained by submitting the bamboo to high temperatures (over 800 °C), producing a material with high density, porous structure and a large surface area. Bamboo charcoal was proposed as a novel and inexpensive SPME coating material for determination of 11 phthalate esters (PAE) in water samples by GC-MS [26].

Another material used as a biosorbent was obtained from powdered seeds of the *Moringa oleifera* tree. This material is considered to possess a highly fibrous and naturally functionalized surface. The characterization of the moringa-based biosorbent using SEM and FITR showed a porous framework of interconnected fibers, and various functional moieties were identified such as O–H, N–H and C–H and CH_2 groups. The first application for organic compound determination was in 2016, as a sorbent for the determination of 13 phthalate esters (PE) in a milk sample by micro-solid phase extraction (μ-SPE) and GC-MS [27]. The relative polar PEs interacted with the sorbent through the functional moieties identified. The more the alkyl chain of PEs increased, the lower the extraction efficiency became.

An eco-material denominated montmorillonite (MMT) clay, modified through the intercalation of ionic liquids (IL), has also been applied in the extraction phase [28,29]. MMT is a clay mineral composed of structural layers consisting of an octahedral alumina sheet sandwiched between two tetrahedral silica sheets. MMT is found in sediments, soils or rock and has been modified to adsorb organic compounds of low polarity from aqueous solutions. In 2016, Fiscal-Ladino et al. [28] used rotating-disk sorptive extraction (RDSE) and MMT in the extraction phase for the determination of polychlorinated biphenyl (PCB) compounds in water samples with GC-ECD (Table 1). The RDSE device consists of a rotating Teflon disk containing an embedded miniature magnetic stirring bar. In this study, SEM was employed to characterize the novel sorbent, and the results showed clusters of particles with a narrow size distribution of approximately 25 mm. The extraction efficiency achieved for the MMT modified with 1-hexadecyl-3-methylimidazolium bromide (HDMIM-Br) phase was compared with commercial phases and showed the highest response for all the studied analytes.

Very recently, the viability of MMT-HDMIM-Br as a green sorbent for RDSE was again investigated [29]. In this study, cork and montmorillonite clay modified with ionic liquid were explored for the determination of parabens in water samples by high-performance liquid chromatography—tandem mass spectrometry (LC-MS/MS). The proposed method presented limits of detection of 0.24 $\mu g\ L^{-1}$ for the cork and 0.90 $\mu g\ L^{-1}$ for the MMT-HDMIM-Br with correlation coefficients higher than 0.9939 for both biosorbents.

2.5. Concluding Remarks about Biosorbents

In general, biosorbents demonstrated great versatility for the extraction of the different classes of compounds. Lignocellulosic biosorbents, such as cork, bract and *Moringa oleifera* seeds, are mainly composed of lignin, cellulose and hemicellulose. These macromolecules have a number of chemical groups that are capable of interacting with a wide range of analytes with different polarities. The works reported in this review showed studies in which cork was able to satisfactorily extract non-polar compounds, such as PAH's, and compounds with intermediate polarity, such as parabens, benzophenone and triclocarban. Bract biosorbent demonstrated similar behavior, presenting satisfactory extraction for compounds with low polarity, such as OCPs, and for those with intermediate polarity, such as steroid estrogens.

The extraction efficiency of these lignocellulosic materials is mostly explained by the π-π interactions between lignin and the analytes, or through hydrogen-bonding and dipole-dipole interactions between O–H groups presented in the cellulose and hemicellulose with the O–H, N–H bonds and Cl present in the analytes. When biosorbents were used with SPME for PAH extraction in water samples, bract fiber showed lower LODs than cork and diatomaceous earth fiber. The same was observed for OCP determination in water samples. Bract has a higher percentage of lignin in its structure than cork, which could explain the higher extraction efficiency for the non-polar compounds.

By using BAμE as the microextraction technique, the diatomaceous earth bar provided lower LODs than the cork bar for the extraction of parabens, benzophenone and triclocarban in water samples. Although diatomaceous earth has been used for PAHs determination, it has shown good extraction efficiency for compounds with intermediate polarity, which was mainly due to interactions through O–H groups. It is also worth mentioning that the porous structure of these biosorbents plays an important role in the extraction through physical interaction with the analytes.

As a final remark, cork has been the material most used with different microextraction techniques and for a large variety of compounds. This fact can be related to the ease with which it is obtained through the reuse of wine bottle corks. The other biosorbents are more limited, such as bract, which is obtained from trees in southern Brazil and in eastern Argentina. Similarly, diatomaceous earth is a sub-product from the beer filtration and clarification process. Most of the works report the comparison with commercial extraction phases. In general, the results are similar or even better, in some cases. However, the procedures employed in the preparation of the devices, in particular for SPME, may be a limitation for the widespread use of these bio-based extraction phases.

3. Ionic Liquids (ILs) as Green Extraction Phase

Ionic liquids (ILs) are non-molecular solvents with melting points below 100 °C, negligible vapor pressure at room temperature, high thermal stability and variable viscosity. The ILs' miscibility in water and organic solvents can be controlled by selecting the cation or anion combination or by the addition of certain functional groups in the IL molecule. Most often, ILs are composed of large asymmetric organic cations and inorganic or organic anions. The most usually employed IL anions are polyatomic inorganic species, such as $PF6^-$ and $BF4^-$, and the most relevant cations are a pyridinium and imidazolium ring with one or more alkyl groups attached to the nitrogen or carbon atoms [30]. ILs have been successfully applied to the liquid phase microextraction technique (LPME) as a less toxic alternative to conventional organic solvents. Considering these most notable properties, the potential usage of ILs as the extraction phase for LPME and applications has already been extensively reviewed by different authors [31–35]. The successful use of ILs in extraction phases is related to their structure. In addition to the common interactions existing in conventional solvents, ILs also have ionic interactions which confer miscibility when dissolved in polar substances. At the same time, the presence of alkyl chains in the cation determines the solubility in less polar substances. A review by Han and coworkers in 2012 presents the physical properties of some of the most commonly used ILs [32].

In 2003, Liu et al. [36] reported the first application of ILs in the extraction phase in single drop microextraction (SDME). SDME is a simple, easy-to-operate and reliable LPME-based method developed in the 1990s [8]. In this report, IL-based SDME coupled with HPLC was applied for the preconcentration and analysis of polycyclic aromatic hydrocarbons (PAHs) using the IL 1-octyl-3-methylimidazolium PF_6 [C_8C_1IM-PF_6] as the extraction solvent. Compared with 1-octanol, ILs provided higher enrichment factors (EFs), enabling the use of extended extraction times and larger drop volumes. In 2015, Marcinkowski et al. reviewed the analytical potential of ILs in SDME [37].

One of the most relevant applications of ionic liquids concerns their use as the extraction phase in dispersive liquid-liquid microextraction (DLLME). DLLME is a powerful extraction technique in which microliter volumes of an extraction solvent are dispersed in the sample to extract and preconcentrate the analytes [7]. The tunable properties of ILs have made these solvents particularly attractive for DLLME applications. Trujillo-Rodríguez et al. [38] reviewed in 2013 the use of ILs in the different types of DLLME and Rykowska et al. [39] recently reviewed modern approaches for IL-DLLME. In a recent application, IL-DLLME was used for the first time in the extraction phase for cortisone and cortisol determination from human saliva samples by HPLC-UV. The method provided high selectivity and EFs to achieve biological levels [40].

3.1. Magnetic Ionic Liquids (MILs) as Green Extraction Phase

A subclass of the ILs, denominated magnetic ionic liquids (MILs), has also been used as a green alternative to conventional organic solvents in LPME applications. Their physicochemical properties are similar to conventional ILs; nonetheless, MILs exhibit a strong response to external magnetic fields. MILs are obtained by the introduction of a paramagnetic component into the cation or anion of the IL structure. Often the paramagnetic component is comprised of a transition or lanthanide metal ions [41]. Synthesis, properties and analytical applications of MILs, including micro extractions, have been already reviewed [42].

MILs have been applied to many LPME techniques. Table 2 shows the most recent applications (since 2017). However, most of the MIL-based extraction approaches are performed using DLLME. In this case, a mixture containing the MIL, dissolved in a small amount of an organic solvent, is dispersed in the sample and then recovered with a magnetic rod. The first application of MIL-DLLME was described in 2014 for the extraction of triazine herbicides in vegetable oils using 1-hexyl-3-methylimidazolium tetrachloroferrate ([C6mim] [FeCl$_4$]) as the extraction phase [43]. Very recently, Sajid et al. [44] reviewed significant milestones of employing MILs for analytical extraction application and the main drawbacks of using MILs with DLLME.

Among the most recent applications, one in particular has attracted significant attention, since a new generation of MILs suitable for in situ DLLME were presented. MILs comprising paramagnetic cations containing Ni(II) metal centers coordinated with four N-alkylimidazole ligands and chloride anions were used for in situ DLLME and extraction of both polar and non-polar pollutants in aqueous samples. In this work, a metathesis reaction was originated by mixing a water-soluble MIL into the aqueous sample followed by the addition of bis [(trifluoromethyl) sulfonyl] imide ([NTf2-]) anion. This reaction produced a water-immiscible extraction solvent containing the preconcentrated analytes. The MIL was then isolated by magnetic separation and subjected to analysis using reversed-phase HPLC-DAD. The proposed methodology achieved higher extraction efficiency when compared to the conventional MIL-dispersive liquid-liquid microextraction. Extraction efficiencies ranging from 46.8 to 88.6% and 65.4 to 97.0% for the $[\mathrm{Ni(C_4IM)_4}^{2+}]2[\mathrm{Cl}^-]$ and the $[\mathrm{Ni(BeIM)_4}^{2+}]2[\mathrm{Cl}^-]$ MILs were obtained [45].

MILs have also been successfully applied to the SDME technique. In a recent study, a high-throughput parallel-single-drop microextraction (Pa-SDME) was developed [46]. According to the authors, Pa-SDME combines some advantageous features of trihexyl (tetradecyl) phosphonium tetrachloro manganite (II) ($[\mathrm{P6,\ 6,\ 6,\ 14}^+]_2[\mathrm{MnCl_4}^{2-}]$) MIL such as drop stability and extraction capacity with the 96-well plate advantages for obtaining high-throughput analysis. In this study, the determination of parabens, bisphenol A, benzophenone and triclocarban was conducted from environmental aqueous samples by HPLC-DAD. The method validation was carried out after the optimization step, and LODs ranging from 1.5 to 3 μg L^{-1} were achieved. Coefficients of determination were higher than 0.994, and intraday and interday precision ranged from 0.6 to 21.3% (n = 3) and 10.4–20.2% (n = 9), respectively. Relative recovery ranged between 63% and 126%. Figure 3 shows the Pa-SDME lab-made extraction apparatus used for the extractions.

Table 2. Recent applications of magnetic ionic liquids (MILs) for extraction of different analytes from various matrices. DLLME—liquid–liquid dispersive microextraction.

Method	MIL	Analyte	Matrix	LOD	Instrumentation	Ref.
In situ DLLME	$[\mathrm{P_{6,6,6,14}}^+]_2[\mathrm{CoCl_4}^{2-}]$	Biogenic amines	Wine fish	1.3–3.9 μg L^{-1} 1.2–3.8 μg kg^{-1}	HPLC-UV	[47]
DLLME	$[\mathrm{P_{6,6,6,14}}^+]$ $[\mathrm{Cl}^-]$	Estriol Estrone Parabens Carbamazepine Diazepam Ketoprofen Ibuprofen 17α-Ethynylestradiol Triclocarban Aldicarb Methyl parathion Metolachlor Diuron Bisphenol A	River water	1.5–15 μg L^{-1}	HPLC-DAD	[48]

Table 2. *Cont.*

Method	MIL	Analyte	Matrix	LOD	Instrumentation	Ref.
In situ SB-DLLME	$[Ni(C_4IM)_4{}^{2+}]2[Cl^-]$ $[Ni(C_8IM)_4{}^{2+}]2[Cl^-]$ $[Co(C8IM)_4{}^{2+}]2[Cl^-]$	Naphthalene Acenaphthene Fluorene 1-chloro-4-nitrobenzene Biphenyl 5-Bromoacenaphthene 3-Tert-butylphenol	Tap and mineral water	4.8–15 μg L^{-1} 1–10 μg L^{-1} 5.9–30 μg L^{-1}	HS-GC-MS	[49]
DLLME	$P_{66614}{}^+]$ $[Dy(III)(hfacac)_4{}^-]$	Triazines and sulfonamides	Lake water, effluent wastewater	0.011–0.03 μg L^{-1}	HPLC-DAD	[50]
DLLME	$[P_{6,6,6,14}{}^+]_2[MnCl_4{}^{2-}]$	Estrogens	Human urine	2 ng mL^{-1}	HPLC-DAD	[51]
SB-DLME	$[P6,6,6,14^+]$ $[Ni(II)(hfaca)_3{}^-]$	PAHs	River water and rain water	1.7–28.7 ng L^{-1}	GC-MS	[52]
HS-SDME and DLLME	$[P_{6,6,6,14}{}^+]_2[MnCl_4{}^{2-}]$	Aromatic compounds	Lake water	0.005–1 μg L^{-1} and 0.04–1 μg L^{-1}	HPLC-DAD	[53]
SB-DLME	$[P_{6,6,6,14}{}^+]$ $[Ni(hfacac)_3{}^-]$	UV filters	River and sea water	9.9–26.7 ng L^{-1}	GC-MS	[54]
Vacum-HS-SDME	$[P_{6,6,6,14}{}^+]$ $[Mn(hfacac)_3{}^-]$	Free fatty acids	Milk	14.5–216 μg L^{-1}	GC-MS	[55]

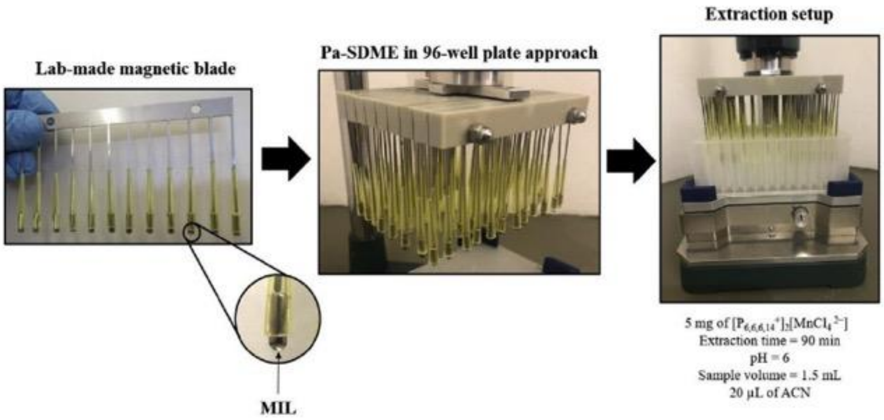

Figure 3. An overview of the extraction procedure using the novel parallel-single-drop microextraction (Pa-SDME)/MIL-based approach. Reproduced with permission from [46], Copyright Elsevier, 2017.

3.2. *Deep Eutectic Solvent (DES) and Natural Deep Eutectic Solvents (NADES) as a Green Extraction Solvent*

The concept of deep eutectic solvents (DESs) was first introduced by Abbot et al. in 2003 [56]. DESs consist of two solid compounds interacting via hydrogen bonds to form a liquid phase with a lower melting point compared to each individual component [57]. The most popular DES involves the combination of choline chloride (ChCl) with urea, carboxylic acids (e.g., citric, succinic, and oxalic acids) and glycerol acting as hydrogen bond donors (HBDs). The use of ChCl has been related to some advantages for DES production, including ease of preparation, biocompatibility, non-toxicity and biodegradability. Although DESs are considered a subclass of IL, they are cheaper and easier to prepare due to the lower cost of the raw materials. Also, they present less toxicity and are often biodegradable, which makes them valuable alternative solvents. One of the most attractive features of these solvents is that, like ILs, their chemical properties can be tuned through the manipulation of their chemical structures (HBA and HBD) to interact more effectively with the target analytes. Florindo et al. (2018) [58] provide a closer look into DES intermolecular interactions; however, there is still a lack of knowledge regarding this topic.

In 2017, Shishov et al. published a review of the applications of DES in analytical chemistry, including their use in the extraction phase in microextraction techniques [59]. Nowadays, these solvents represent a very promising alternative in the sample preparation area, mainly due to their easy acquisition and versatility for extract different classes of compounds. In the work of Farajzadeh et al., a gas-assisted DLLME method using a mixture of ChCl and 4-chlorophenol (1:2 molar ratio) as the extraction solvent was developed for pesticide residue determination in vegetable and fruit by GC-FID [60]. The proposed method was optimized, and enrichment factors and extraction recoveries were achieved in the range of 247–355 and 49–71%, respectively.

Two hydrophobic deep eutectic solvents were synthetized and used as the extraction solvent with air-assisted DLLME (AA-DLLME) for pre-concentration and extraction of benzophenone-type UV filters from aqueous samples and determination by HPLC-DAD [61]. DESs were obtained by mixing DL-menthol and quaternary ammonium salts with a straight-chain monobasic acid. After optimization, a DES consisting of DL-menthol and decanoic acid mixture (1:1) was chosen for UV-filter extraction. Analytical parameters of merit were evaluated, and the developed method exhibited low limits of detection (0.5 to 0.02 ng mL^{-1}) and repeatability in the range of 1.5–4.9 and 0.6–5.6% for intraday ($n = 6$) and interday ($n = 6$) determinations, respectively. The method was applied to determine the benzophenone-type filters in environmental water samples, and relative recoveries ranged from 88.8 to 105.9%.

Recently, a novel approach for effective liquid-liquid microextraction based on DES decomposition was reported [62]. In this work, DESs were synthesized from tetrabutylammonium bromide and long-chain alcohols. Afterwards, they were decomposed in the aqueous phase, resulting in an in-situ dispersion of organic phase and extraction of hydrophobic analytes. The method was applied to 17b-estradiol microextraction from transdermal gel samples. Efficient extraction of 95 ± 5% and reproducibility of 6% were obtained. Figure 4 shows a scheme of liquid-liquid microextraction based on in-situ decomposition of deep eutectic solvent.

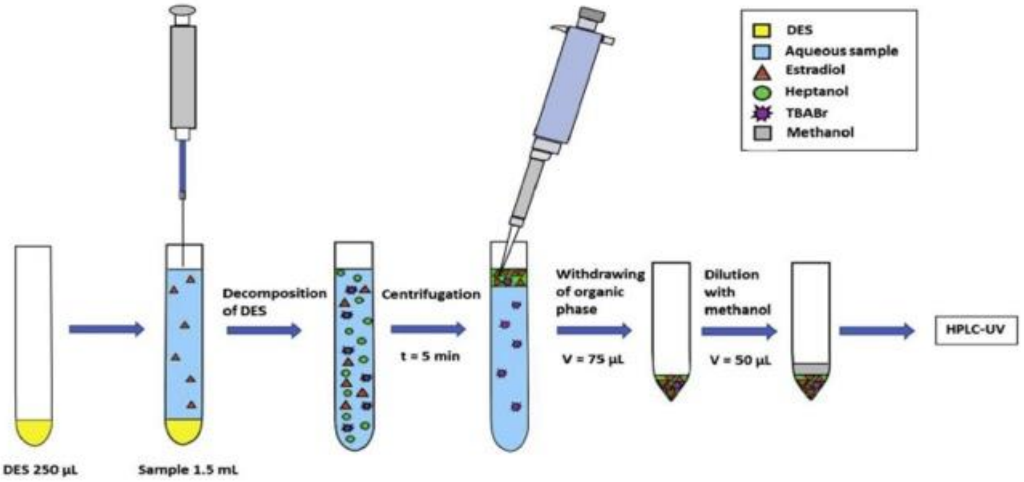

Figure 4. Schema of liquid-liquid microextraction based on in situ decomposition of deep eutectic solvent. Reproduced with permission from [62], Copyright Elsevier, 2019.

Natural deep eutectic solvents (NADESs) are considered a sub-class of DESs, and they consist of a mixture of cheap and natural compounds such as sugars, alcohols, organic acids, and amino acids [63]. The most significant features of NADESs include adjustable viscosity, since they are liquid at temperature below 0 °C, sustainability, and the capability of dissolving a diverse range of analytes with different polarities. In a review by Hashemi et al., (2018) [63] the authors show the most common compounds for preparation of DES and the chemical structure of the most used NADES components. Cunha et al., 2018 [64] presented the main LPME techniques using DES or NADES as extraction solvents to determine several polar volatile and non-volatile compounds from food and water matrices. Table 3 shows some recent applications of DES/NADES (since 2017) with microextraction techniques for the determination of organic compounds in various matrices by chromatographic methods.

Table 3. Recent applications of deep eutectic solvents (DES)/natural deep eutectic solvents (NADES) for extraction of different analytes from various matrices.

Technique	DES/NADES Composition	Analytes	Matrix	LOD	Instrumentation	Ref.
DES-ALLME	Ch-Cl: TNO [1]	Methadone	Water and biologic	0.7 μg L^{-1}	GC-FID	[65]
UA-DLLME	trioctylmethylammonium chloride: decanoic acid	UV filters	Water	0.15–0.30 ng mL^{-1}	HPLC-UV	[66]
VA-LLME	Decanoic acid: Methyltrioctylammonium bromide	Malondialdehyde (MDA) and Formaldehyde (FA)	Human urine, apple juice and rain water	2.0 and 10.0 ng mL^{-1}	HPLC-UV	[67]
AA-EME	ChCl: Ph-EtOH	Amphetamine-type stimulants (Ats)	Human plasma and pharmaceutical wastewater	2.0–5.0 ng mL^{-1}	HPLC-UV	[68]
SFO–AALLME	Ch-Cl: n-butyric acid	Aromatic amines	Aqueous samples	1.8–6.0 ng L^{-1}	GC-MS	[69]
UA-DLLME	thymol, ±camphor, decanoic: 10-undecylenic acids	PAHs	Industrial effluents	0.0039–0.0098 μg L^{-1}	GC-MS	[70]
DSPE-DES-AALLME	ChCl: 4-chlorophenol	Tricyclic antidepressant drugs	Human urine and plasma	8–15 and 32–60 ng L^{-1}	GC-MS	[71]
DES-GALLME	Mixture of two or three different carboxylic acids (C8, C9, C10, C11 and C12)	Phenolic compounds	Water	0.22–0.53 μg L^{-1}	HPLC-UV	[72]
VA-RP-LLME	[N4444]Cl, TBA [2]: ethylene glycol (EG)	Triazine herbicides	Vegetable oil samples	0.60–1.50 μg L^{-1}	HPLC-UV	[73]
MA-in syringe DLLME	ChCl: phenol and ChCl: butyric acid	Herbicides	Wheat	1.6–12 ng kg^{-1}	GC-MS	[74]
DLLME	Hexafluoro isopropanol: l-carnitine/betaine	Pyrethroids	Tea beverages and fruit juices	0.06–0.17 ng mL^{-1}	HPLC	[75]
UA-DLLME-DES	Quaternary phosphonium salts: straight-chain monobasic acids	Pyrethroids	Water	0.30–0.60 μg/L	HPLC-UV	[76]

1—5, 6, 7, 8-Tetrahydro-5, 5, 8, 8-tetramethylnaphthalen-2-ol; 2—tetrabutylammonium chloride ([N4444] Cl, TBA).

4. Supramolecular Solvent (SUPRAS) as Extraction Phase

Supramolecular solvents (SUPRASs) are nano-structured liquids in which the spontaneous association of different molecules self-organizes in a biphasic system formed by a continuous and a dispersed phase. SUPRASs' amphiphilic nature highlights one of their main advantages, providing excellent solvation for a wide range of organic and inorganic compounds. This characteristic is due to the presence of supramolecular aggregates, promoting a solvent with different degrees of polarity [77–79]. Supramolecular solvents have already been used in the determination of several classes of compounds such as parabens, pesticides, polycyclic aromatic hydrocarbons and bisphenols [80–83].

A very recent SUPRAS paper showed SUPRAS applicability with LPME as the extraction solvent. In this work, cationic surfactants didodecyldimethylammonium bromide (DDAB) and dodecyltrimethylammonium bromide (DTAB) were used in the extraction solvent mixture. SUPRAS-based liquid phase microextraction (SUPRAS-LPME) was also used in the preconcentration of five TCs (tetracycline, oxytetracycline, chlortetracycline, methacycline and doxycycline) in milk, egg and honey samples. An alkaline solution of the analytes was preconcentrated via electrostatic and hydrophobic interactions in the presence of the SUPRAS extraction solvent. The extraction mechanism was confirmed by the exploration of SUPRAS' Zeta potential and particle size. According to the authors, the results showed an excellent quantification method using SUPRAS and LPME for the determination of TCs in various matrices [84].

Recently, an innovative study proposed the application of a novel hexafluoroisopropanol (HFIP)/Brij-35 based SUPRAS in the determination of some organic compounds in water samples also using LPME. Brij-35 is a budget-friendly and non-toxic anionic surfactant that has a high cloud point (>100 °C). Presenting characteristics of a strong hydrogen-bond donor, elevated density and high hydrophobicity, HFIP was used in Brij-35's density regulation and cloud-point reduction to below room temperature. The HFIP/Brij-35 SUPRAS-based LPME procedure allowed its preparation at room temperature with centrifugation only, making it very simple. Quantification of parabens with HFIP/Brij-35 showed good linearity and correlation coefficients higher than 0.9990. Spiked samples provided recoveries from 90.2% to 112.4% and relative standard deviation of lower than 9% [85].

5. Bio-Based Solvents

Bio-based solvents are a group of green solvents that have several advantageous characteristics such as low toxicity and non-flammability, besides being biodegradable and renewable, as they are produced from biomass and agricultural materials [86]. One example is ethanol, which has been used for decades in classical liquid-liquid extraction. Among others, glycerol, 2-methyl tetrahydrofuran (meTHF), ethyl lactate, p-cymene, and terpenes are part of the bio-based solvent groups that have attracted interest for applications in separation methodologies due to their characteristics [87]. A very interesting bio-based solvent is D-Limonene. It is derived from citrus peel and, like other bio-solvents, is low-cost and biodegradable and exhibits low toxicity. Its main attraction has been in the substitution of traditional solvents such as acetone, toluene, and chlorinated and fluorinated solvents in several applications. Due to its characteristics as a degreaser, this solvent has been applied to the removal of oils and fats [88]. In addition, D-Limonene may be a substitute for toxic organic solvents in Soxhlet extraction procedures [89].

Recently, a liquid–liquid dispersive microextraction (DLLME) method applying D-Limonene and B-carotene for the determination of b-cyclodextrin (b-CD) was developed [90]. These two mixed bio-solvents show a strong adsorption characteristic. When placed in the presence of b-CD, B-carotene forms a complex that increases the absorbance of the extracted phase, generating an excellent analytical signal for the determination of the target compound. The validation of the method presented an excellent limit of detection (0.00004 mol L^{-1}) with a linear range from 0.0004 to 0.006 mol L^{-1}. The method was applied for the determination of b-CD in water and pharmaceutical samples, obtaining recovery values between 94.2 and 108.0%, confirming the efficiency of the method.

Despite the advantages, these solvents are still poorly explored as the extraction phase for microextraction techniques, mainly with chromatography techniques. Some drawbacks may have to be overcome, such as the high viscosity that causes poor analyte mass transfer and also the incompatibility with analytical instrumentation [91]. Nevertheless, an alternative would be their combination with other green solvents or their use as modifiers of solid sorbents, as already proposed by Hashemi et al. (2018) [63].

6. Conclusions

The development of alternative green extraction phases represents an important research field in chemical analysis for the determination of different analytes from various matrices. This approach has been exploited in several recent publications and highlighted in this article. The use of biosorbents in analytical chemistry, mainly applied to microextraction techniques, is a very promising eco-friendly and cheap alternative. Cork, bract and diatomaceous earth have shown tremendous potential as alternative sorbents to commercial phases (PDMS/DVB, DVB/Car/PDMS and PDMS). However, preparation of the fibers may limit their use. Additional efforts need to be made in order to expand the applicability of the existing biosorbents to different groups of analytes. The use of green extraction phases as an alternative to conventional organic solvents has led to remarkable improvements with regard to environmentally friendly aspects. DES/NADES and SUPRAS are a very promising alternative in sample preparation. Additional research is needed to exploit their interactions with the analytes and also to expand their applicability. The application of bio-based solvents in the extraction phase should be further investigated, since there are only a few reports regarding these subjects.

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