Deep eutectic solvents in analytical sample preconcentration

Part B: Solid-phase (micro)extraction

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Abstract

One of the key challenges of modern analytical chemistry is the monitoring of trace amounts of contaminants using sensitive and selective instrumental techniques. Due to the variety and complexity of some samples, it is often necessary to properly prepare a sample and to perform a preconcentration of trace amounts of analytes. In line with the principles of Green Analytical Chemistry (GAC), it is important for an analytical procedure to reduce labor and time consumption and to decrease the use of volatile and hazardous solvents. Therefore, solvent-free extraction techniques, such as SPE, μSPE, SPME and their various modifications, which are mainly aimed at increasing their "greenness", have been very popular for many years. Deep eutectic solvents fit perfectly into GAC principles, which is why they have been used as extractants in liquid-phase microextraction techniques for a long time.

This review is a follow-up to our recently published article on the use of deep eutectic solvents (DESs) in liquid-phase microextraction techniques and summarizes the most important applications of DES in solid-phase (micro)extraction techniques.

Keywords: solid-phase extraction; micro solid-phase extraction; solid-phase microextraction; deep eutectic solvents; sorbents; dispersing agents; eluting solvents

1. Introduction

Sample preparation is a key part in any analytical procedure, because it can improve both their selectivity and sensitivity by eliminating interferences and the preconcentration of analytes [1]. Sample preparation is often time-consuming and requires the use of large amounts of hazardous and volatile organic solvents [2]. Therefore, in order to reduce the negative impact of solvents and chemical reagents on the environment and human health, the principles of Green Analytical Chemistry (GAC) were introduced in 2013 to analytical practice based on the known principles of Green Chemistry [3,4]. In line with these principles, it would be ideal to avoid the sample preparation step, including the use of extraction techniques. However, if this is not possible, solvent-free extraction techniques are recommended. In addition, according to GAC, the use of volatile and often hazardous organic solvents should be limited by using more “environmentally friendly” substitutes [5,6]. An ideal “green” solvent intended for analytical tasks should be cheap, low-toxic, biodegradable, reusable, easy to obtain from renewable sources and characterized by high extraction capacity and selectivity towards a selected groups of analytes [3,4,7]. Deep eutectic solvents (DESs) are one of the groups of compounds that have gained a lot of interest in recent years due to their designability, ease of preparation (with no need for purification) and their variety of physicochemical properties. DESs are synthesized by mixing a hydrogen bond acceptor (HBA) with a hydrogen bond donor (HBD), such that the melting point of the DES is much lower than the melting points of HBD and HBA, which is called reaching the eutectic point [8]. This relatively new class of solvents is currently a very popular group of extractants in liquid-phase microextraction techniques (which we discussed in detail in a previous review [9]). However, even though the use of DESs in solid-phase extraction and solid-phase microextraction techniques is not so common at present, everything points to their great potential for use in solvent-free techniques in the future.

This review paper summarizes the latest (i.e. from 2017 to April 2023) possibilities of using DESs, both as a key ingredient for the preparation or modification of solid sorbents, as well as a dispersing agent or solvent for elution of analytes from sorbents (Fig. 1). Both the advantages and disadvantages of these green solvents in different variations of solid-phase extraction and microextraction techniques have been discussed.

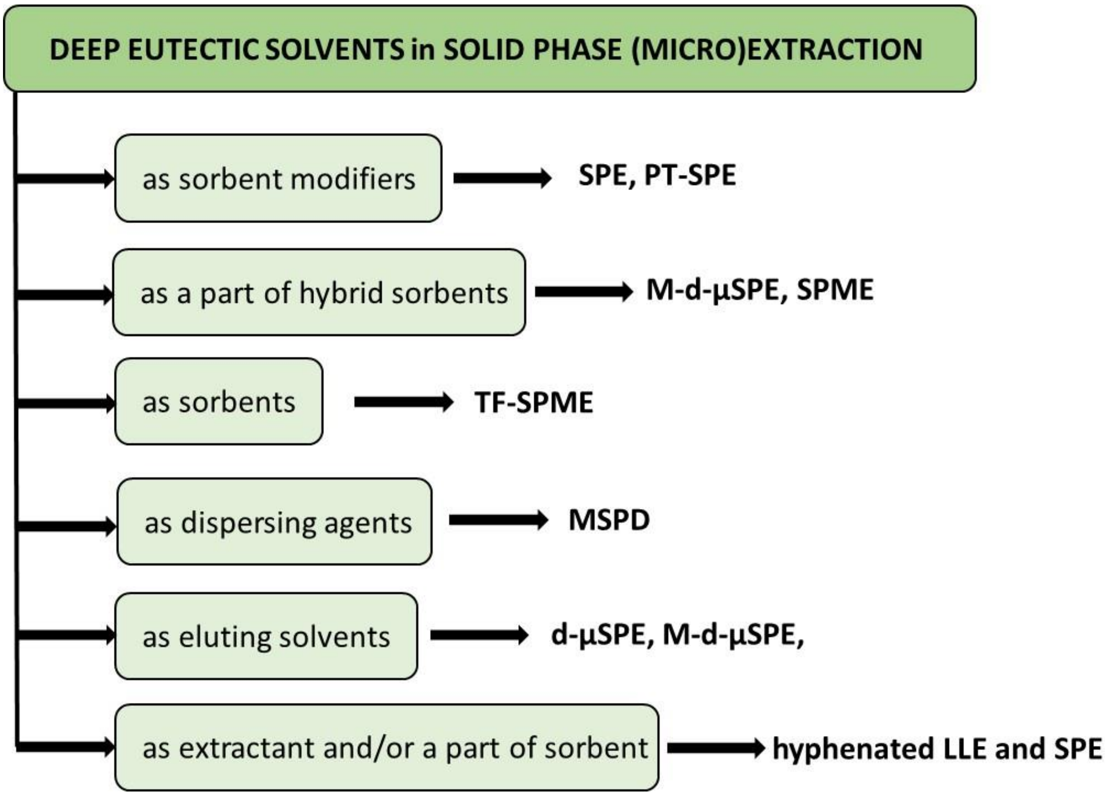

Figure 1. Role of deep eutectic solvents in different variants of solid-phase (micro)extraction techniques.

2. Use of deep eutectic solvents as sorbent modifiers

In this section several examples of DES application as sorbent modifiers in SPE and PT-SPE techniques are described.

2.1. Solid-phase extraction

Currently, one of the most frequently used sample pretreatment techniques is solid-phase extraction (SPE) due to its major advantages, such as high recoveries, ease of use, environmental friendliness, as well as cost and time efficiency [10]. Nevertheless, the performance of SPE depends primarily on the selection of a suitable sorbent to control the selectivity and capacity in order to achieve high extraction efficiency [11]. Many new sorbents have been developed for this purpose, including those containing DESs, as shown in Table 1.

The simplest usage of DESs in SPE involves the modification of existing commercial sorbents. The most frequently studied DESs are those based on choline chloride (ChCl). Fu et al. prepared DESs based on ChCl and various HBDs, such as glycerol, ethylene glycol or phenol, and subsequently used them to modify the octyl- and octadecyl-functionalized silica SPE sorbents. The resulting product was used to perform the pretreatment of palm samples for determination of polyphenols. The highest amount of extracted analytes was obtained by using a sorbent modified with ChCl:phenol (1:1) due to a more porous surface than the original sorbent (41 m^2g^{-1} compared to 10 m^2g^{-1}) and the presence of the benzene ring, which promotes the interaction with polyphenols [12]. The combinations of ChCl with glycerol, ethylene glycol as well as 1,4-butanediol were prepared by Wang et al. and used in DES-modified monolithic sorbents. The sorbents were synthesized by adding DESs to the methacrylic acid and glycidyl methacrylate monomers with an ethylene glycol dimethacrylate (EGDMA) cross-linker. The resulting monolithic SPE sorbent was applied to the determination of quercetin from *Ginkgo biloba* [13].

Deep eutectic solvents are also used to modify natural, renewable materials, such as cotton, which is considered one of the biopolymers occurring in the greatest amounts worldwide and has various applications, including being used as a sorbent in SPE. The disadvantage of cotton, however, is its low selectivity and capacity. Therefore, Karimi et al. modified cotton fibers with a DES composed of ChCl and urea (1:2). The DES was deposited on the cotton by evaporating its methanolic solution. This simple method of immobilizing the DES on the cotton fibers resulted in obtaining a very rough structure and thus increased the surface area from 4 to 45 m^2g^{-1}. The modified cotton sorbent was packed into microcolumns and used for SPE of copper and nickel from real water samples, serum and urine. The significantly higher extraction recoveries for modified cotton compared to bare material resulted from the creation of a complex between the determined ions and nitrogen donor moieties in a ChCl:urea DES [14].

Several studies have discussed the use of DESs in the synthesis of molecularly imprinted polymers (MIPs), which are described as stable polymers characterized by their high ability to recognize specific, targeted molecules. The main principles of molecular imprinting are based on the reaction of a functional monomer and a cross-linking agent in the presence of a template molecule (analyte). The monomer molecules assemble around the template and are then polymerized and cross-linked to form a mechanically stable structure. The entrapped template molecule is subsequently removed from the polymer network, leaving recognition regions which exhibit high complementarity in terms of size, shape and spatial distribution [15,16]. As a result, a highly selective sorbent in comparison with other materials of similar structure is obtained. MIPs are gaining increasing attention due to their benefits, such as chemical and mechanical durability, thermal stability, high loading capacity and low cost of preparation [16]. Recently, DESs have been introduced into the synthesis of MIPs to enhance the selectivity and affinity of sorbents [17].

Liang et al. used a DES based on ChCl and ethylene glycol in the synthesis of molecularly imprinted polymers applied for the SPE isolation of clorprenaline and bambuterol from urine. The material synthesized in the DES exhibits increased adsorptive capacity and higher sorption compared with materials prepared in alcoholic solvent systems [15]. The application of DESs in the synthesis of a MIP sorbent was also tested by Li et al., who prepared a set of DESs based on ChCl and formic, acetic and propionic acids or urea. The ChCl:urea (1:2) DES was used in the synthesis of a MIP sorbent. The study confirmed that the modification by DESs significantly improved the affinity and selectivity of the MIPs used for the SPE of fucoidan and laminarin from marine kelp [11]. Sanjari et al. prepared ternary DESs, i.e. ChCl:ethylene glycol:methacrylic acid, ChCl:ethylene glycol:caffeic acid, ChCl:formic acid:methacrylic acid and ChCl:formic acid:caffeic acid (all in a 6:6:2 molar ratio). Taking advantage of the ability of these DESs to both interact with imprinted molecules and form polymeric structures due to their double bonds, they were used as a base to synthesize MIPs. Thus, the ternary DESs were mixed with metronidazole (as the imprinting molecule) and EGDMA as the cross-linker. The authors not only demonstrated experimentally the prevalence of ChCl:ethylene glycol:methacrylic acid over the other DESs but also explained the interactions based on computational methods. The developed method was used for the determination of metronidazole in plasma samples [16].

The DES-based modification of a hybrid organo-silica MIP and mesoporous siliceous material (MSM) was performed by Li and Row in order to create novel sorbents for the extraction of levofloxacin and tetracycline using the SPE technique. Both MIP and MSM demonstrated the potential to be efficient sorbents due to their uniform ordered structure, high surface area and high pore volume. A betaine:ethylene glycol:water (1:2:1) DES was introduced in the preparation, resulting in remarkable selectivity and binding capability in comparison with non-modified materials [17,18].

2.2. Pipette-tip solid-phase extraction

Pipette-tip solid-phase extraction (PT-SPE) is a miniaturized version of SPE in which the sorbent is packed into the pipette tip. As a result, the sorbent mass may be very low, even below 1 mg, resulting in low solvent usage and time consumption. DESs have also found their place in this miniaturized version of SPE (Table 1). Liu et al. synthesized a graphene@DES sorbent containing ChCl:ethylene glycol (1:2). The sorbent mass in the tip was 2 mg, and the river water sample volume for the determination of sulfamerazine was only 0.5 mL [19]. Yuan et al. used a DES on graphene oxide. The allyltriethylammonium bromide:ethylene glycol (1:2) DES was polymerized on the surface of graphene oxide using a reversible-addition fragmentation chain-transfer polymerization that improves grafting. The resulting sorbent, because of the presence of different surface groups, provides different intermolecular interactions, thus supporting better sorption of analytes due to the possible synergistic extraction mechanisms. The pipette tip was loaded with 2 mg of the sorbent and used to process a 0.5 mL urine sample for the determination of hippuric acid and methylhippuric acid as biomarkers of toluene and xylene exposure [20].

Apart from the carbon-based sorbents, molecularly imprinted sorbents were also proposed for use in PT-SPE. Tang et al. prepared three DESs based on ChCl with ethylene glycol, glycerol or propylene glycol (all in a 1:1 molar ratio). The polymerization process involved the use of a DES, an acrylamide monomer, a template molecule and a divinylbenzene cross-linker. The resulting polymer was ground and washed to remove the template. Of the three DESs tested, the one composed of ChCl with ethylene glycol was found to be suitable for the extraction of chloramphenicol from milk samples. The sorbent mass was 3 mg, which allowed the successful processing of a 1 mL milk sample [21].

Table 1. Summary of studies using deep eutectic solvents as sorbent modifiers in SPE and PT-SPE techniques.

Analytes	Samples	Extraction method	Sorbent	DES (molar ratio)	Detection	LOD [ng mL^{-1}]	Extraction recovery [%]	RSD [%]	Ref.
Clorprenaline, bambuterol	Urine	SPE	MIP	ChCl:EG (1:2)	HPLC-UV	3.9	91.7–100.1	≤7.6	[15]
Fucoidan, laminarin	Marine kelp	SPE	MIP	ChCl:Urea (1:2)	HPLC	-*	33.1–95.5	≤4.23	[11]
Levofloxacin	Green bean	SPE	MIP, MSM	Betaine:EG:water (1:2:1)	HPLC-UV	10	97.2–100.2	0.7–1.8	[18]
Levofloxacin, tetracycline	Millet	SPE	MIP	Betaine:EG:water (1:2:1)	HPLC-UV	10	95.7–100.2	0.3–1.8	[17]
Polyphenols	Palm	SPE	P123:1,3,5-TMB:ES	ChCl:Ph (1:1)	HPLC-MS	-*	60–117	-*	[12]
Quercetin	*Ginkgo biloba*	SPE	DES-M	ChCl:Gly (1:3)	HPLC	-*	-*	-*	[13]
Copper, nickel	Water and biological samples	Online SPE	Cotton fibers	ChCl:Urea (1:2)	FAAS	0.05–0.6	95–105	1.5–6.8	[14]
Polycyclic aromatic hydrocarbons	Lake water	SPE	pAS-COOH-GO	ChCl:EG (1:3)	HPLC	0.01–0.2	90.3–102.8	2.1–4.9	[22]
Proteins	Biological samples	SPE	poly(APTES-MAA-co-DES-co-EDMA)	ChCl:MAA	UV-VIS	-*	95.5	2.2–7.2	[23]
Aflatoxins	Cereals	SPE	MoF-DES-MIPs	ChCl:Gly (1:2)	HPLC-FLD	0.023-0.033**	95.3–98.5	4.3–6.7	[24]
Imidacloprid	Tea infusions, tap and well water	SPE	MoF-DES	ChCl:Urea (1:2)	HPLC-DAD	0.144	90–98	-*	[25]

Sulfamerazine	River water	PT-SPE	DES-Graphene	ChCl:EG (1:2)	HPLC-UV	10	91–97	≤3.8	[19]
Chloramphenicol	Milk	PT-SPE	DES-MIP	ChCl:EG (1:1)	HPLC-UV	10	96.5	<3.5	[21]
Toluene and xylene	Urine	PT-SPE	DES-GO	ATEAB:EG (1:2)	HPLC-UV	1.66–2.89	90.9–99.1	≤5.2%	[20]

* – not given; ** ng g^{-1}; 1,3,5-TMB – 1,3,5-trimethylbenzene; ATEAB – allyl triethylammonium bromide; Chal – chalcone; ChCl – choline chloride; GO – graphene oxide; DES-M – DES modified monolithic polymer; EG – ethylene glycol; ES – ethyl silicate; FA – formic acid; FAAS – flame atomic absorption spectrometry; Gly – glycerol; MAA – methacrylic acid; MSM – mesoporous siliceous material; P123 – polyethylene-polypropylene-polyglycol triblock copolymer; pAS-COOH-GO – carboxylated graphene oxide modified with p-aminostyrene; Ph – phenol; poly(APTES-MAA-co-DES-co-EDMA) – 3-aminopropyl triethoxysilane-methacrylic acid with DES and ethylene glycol dimethacrylate; PT-SPE – pipette-tip solid-phase extraction.

3. Use of deep eutectic solvents as a part of sorbents or eluting agents

This section focuses on the application of deep eutectic solvents as a part of sorbents or eluting agents.

3.1. Dispersive micro solid-phase extraction and magnetic dispersive micro solid-phase extraction

Dispersive micro solid-phase extraction (d-μSPE) has emerged as an alternative to conventional SPE. While the latter is one of the most widely used sample preparation techniques, it requires disposable cartridges and relatively large volumes of eluting solvents and is often time-consuming. Therefore, the low cost and short sample preparation time characteristic of d-μSPE has led to its growing use. In d-μSPE, the solid sorbent is dispersed directly into the sample. After the adsorption of analytes, it is collected and the compounds being determined are eluted. Three main types of sorbent separation techniques are used in d-μSPE: it may be filtered, centrifuged or collected taking advantage of its magnetic properties. Deep eutectic solvents can be applied to solid sorbents and used as dispersing agents or as eluting solvents (Table 2).

Currently, magnetic dispersive micro solid-phase extraction (M-d-μSPE) is the most widely used version of d-μSPE, with DESs applied on the surface of solid sorbents or used to form a magnetic fluid. The magnetic core of sorbents is almost always composed of Fe_3O_4 as an inexpensive and easy-to-synthesize material. In the simplest version, Fe_3O_4 is directly covered by a DES [26], suspended in a DES [27] or synthesized in a one-pot process by mixing a DES with substrates for Fe_3O_4 formation [28]. However, most often Fe_3O_4 is modified before a DES is applied to its surface. This Fe_3O_4 modification may be done during its preparation, for example, as co-precipitation with multi-walled carbon nanotubes [29,30], activated charcoal [31] or chitosan [32,33]. Such modifications are often only the first step in obtaining more complex sorbents. For example, Ma et al. synthesized a chitosan/Fe_3O_4 composite and then used a DES (ChCl:methacrylic acid, 1:1) with an EGDMA cross-linker to form a surface layer of the molecularly imprinted polymer used for the extraction of catechins [32], while Zhang et al. covered chitosan/Fe_3O_4 particles with a DES (L-proline:methacrylic acid, 3:1) cross-linked with EGDMA for the determination of the pharmacologically active ingredients of *Epimedium folium* [33].

Alternatively, Fe_3O_4 can be synthesized separately and only then modified. It may be functionalized with silanes, including 3-aminopropyl triethoxysilane [34] and vinyl triethoxysilane [35], or its surface may be covered by silica synthesized from tetraethoxysilane [36–39] or by polydopamine [40–42]. These modifications are often followed by other steps, e.g., Li et al. extracted tanshinones from plants using silica-modified Fe_3O_4, covered with a layer of a molecularly imprinted polymer formed from a DES (ChCl:glycerol, 1:2), methacrylic acid and EGDMA [36], and Wei et al. determined cationic dyes using 3-aminopropyl-modified Fe_3O_4 covered with a metal-organic framework and a surface layer of a polymerized DES (3-acrylamidopropyl trimethylammonium chloride:D-sorbitol, 2:1) [34].

Apart from applying the DES on the sorbent, it can also be used for the elution of analytes from sorbents. In this case, sorbents are also based on the Fe_3O_4 core with specific modifications [43,44]. For instance, Fe_3O_4 nanoparticles modified in a one-pot preparation with agarose were used for the extraction of phenolic compounds, which were then eluted with a DES (tetramethylammonium chloride:ethylene glycol 1:3) [44]. More complex sorbents used with a DES elution of analytes may also be encountered. Ge et al. synthesized a sorbent core from milled *Pericarpium granati* soaked with a ferric oxalate solution [45]. This advanced sorption material was then used for the extraction of aristolochic acids from rat urine, and the analytes were desorbed using a DES (ChCl:ethylene glycol, 1:2) before chromatographic determination [45]. On the other hand, less complicated and “greener” materials have also been used. Rao Pasupuleti et al. used dried coffee waste with ferric chloride to produce a magnetic sorbent subsequently used for the extraction of parabens. The extracted analytes were then eluted from the sorbent using a natural DES composed of DL-menthol and acetic acid (1:1) before chromatographic determination [46].

Non-magnetic sorbents have also been used in d-µSPE methods. Nemati et al. proposed using activated carbon for the extraction of tetracycline antibiotics from milk. Trichloroacetic acid was added to milk samples to precipitate proteins, and the supernatant was shaken mechanically in a homemade device in the presence of activated carbon dispersed using lauryl betaine surfactant. After extraction, the sample was purged with air to form a surface layer of activated carbon, which was collected with a spatula and extracted with a DES (tetrabutylammonium chloride:propionic acid, 1:2) [47].

Among sorbents formed *in situ,* two polymers were used. The polystyrene polymeric sorbents were centrifuged, and after discarding the supernatant, the analytes were desorbed using appropriate DESs [48,49]. Alternatively, polyvinylpyrrolidone was dissolved directly in a water sample and formed finely dispersed particles after the addition of NaCl. The extracted compounds of interest were desorbed from the surface of polyvinylpyrrolidone using selected DESs [50,51]. Apart from polymers, curcumin was also used in d-µSPE methods, and the analytes adsorbed on the fine curcumin particles were desorbed using DESs [52,53].

4. Use of deep eutectic solvents as dispersing agents in matrix solid-phase dispersion

Matrix solid-phase dispersion (MSPD) is a technique based on the extraction of analytes to a solid sorbent (dispersant). The sample with a solid sorbent is placed in a mortar, where it is mixed and crushed with a pestle. The sorbent facilitates the breaking up of the sample material, and any material that may be lost is immediately adsorbed on the sorbent. The resulting mixture is then subjected to extraction (Table 2). In the basic version of the method, it is packed into an empty SPE column and eluted with a solvent. Wu et al. used this methodology to determine aflatoxins in crops. They added 200 µL of a DES (tetrabutylammonium chloride:hexyl alcohol) to 1.0 g of sample and 0.5 g of diatomite. The mixture was blended and placed in an empty SPE column. It was then eluted with acetonitrile, evaporated, reconstituted and subjected to analysis. This method resulted in twice the amount of recovery than when a DES was not used for the extraction [54]. Li et al. used a similar methodology in the determination of triazine herbicides in brown sugar. The authors mixed 1.0 g of sugar with 3.6 g of a DES-impregnated silica gel in a mortar. Out of four different DESs tested the one formed from tetraethylammonium chloride:ethylene glycol (1:2) was used. The mixture obtained in the mortar was loaded into an SPE column, washed with hexane, eluted with acetonitrile, evaporated, reconstituted and subjected to analysis [55].

Alternatively, the mixture of the sample with the sorbent, instead of being packed in a column, may be subjected to the d-µSPE process. Yang et al. used MSPD to determine flavonoids in *Scutellariae* Radix. The authors mixed 20 mg of a powdered sample with 40 mg of silica gel-based mesoporous molecular sieve and 10 µL of a DES (menthol:acetic acid). The resulting mixture was transferred to a centrifuge tube and sonicated with 1 mL of ethanol. The centrifuged and filtrated sample was analyzed. Interestingly, each of the four DESs tested by the authors (ChCl:formic acid, ChCl:urea, menthol:acetic acid and ChCl:propanetriol) resulted in a similar analytical signal [56]. Likewise, Nedaei et al. determined nitrotoluene in soil samples by mixing 20 mg of soil with 60 mg of graphitic carbon nitride and 30 µL of a DES (borneol:menthol, 1:1) in a mortar and homogenizing it with a pestle. The resulting mixture was transferred to a 1.5 mL centrifuge tube and sonicated with 150 µL of acetonitrile. The centrifuged and filtered sample was then analyzed. The authors also pointed out that an inappropriate DES may overlap with the signal of the analytes being determined [57].

Table 2. Summary of studies using of deep eutectic solvents as part of sorbents, as dispersing agents or as eluting solvents in d-µSPE, M-d-µSPE and MSPD techniques

Analytes	Samples	Extraction method	Sorbent	DES (molar ratio)	Detection	LOD [ng mL^{-1}]	Extraction recovery [%]	RSD [%]	Ref.
DESs as a part of sorbents									
Copper and lead	Water (lake, tap), soil	M-d-µSPE	Fe_3O_4@DES	ChCl:Urea (1:2)	ICP-OES	0.29−0.51	94−102	≤3.55	[26]
Cobalt	Urine	Mgel-d-µSPE	Fe_3O_4@DES	ChCl:Ph (1:3)	SQT-FAAS	4.6	97−105	≤3.3	[27]
Organophosphorus pesticides	Vegetables	M-d-µSPE	Fe_3O_4@DES	SS:DDA (1:5)	GC-MS	0.03−0.1 µg kg^{-1}	80−119	≤14.4	[28]
Organochlorine pesticides	Water (lake, river, rural, farm)	Mgel-d-µSPE	MWCNT/ Fe_3O_4@DES	ChCl:Urea (1:2)	GC-µECD	0.03−0.27 ng L^{-1}	83−119	≤6.8	[29]
Nitroaromatic compounds	Industrial water	Mgel-d-µSPE	MWCNT/ Fe_3O_4@DES	ChCl:Urea (1:2)	GC-µECD	0.8−12.4 ng L^{-1}	90−110	≤8.5	[30]
Warfarin	Water, plasma, urine	M-d-µSPE	DES@AC/ Fe_3O_4	TMAC:thymol (1:4)	HPLC-UV	0.3−1.6	94.3−98.4	≤4.5	[31]
Catechins	Black tea	M-d-µSPE	chitosan/ Fe_3O_4@DES/ EDMA	ChCl:MAA (1:1)	HPLC-UV	150−500	88.3−98.1	≤6.84	[32]
Pharmaceutically active ingredients	*Epimedium* folium	M-d-µSPE	chitosan/ Fe_3O_4@DES/ EDMA	L-proline:MAA (3:1)	HPLC-UV	0.5−2.1	80−108	≤7.52	[33]
Cationic dyes	Fish	M-d-µSPE	Fe_3O_4-NH_2@MOF@PDES	APTMACl:D-sorbitol (2:1)	UV-VIS	24.0−98.2	89.4−100.7	≤0.7	[34]

Organophosphorus pesticides	Fruits and vegetables	M-d-µSPE	Fe_3O_4-vinyl@MIP/PDES	ChCl:caffeic acid:formic acid (3:1:1.5)	HPLC-UV	0.015−0.030	80−117	≤9.8	[35]
Diterpenoids, isoflavones, flavan-3-ols	Plants	M-d-µSPE	Fe_3O_4@SiO_2@MIP DES	ChCl:glycerol (1:2)	HPLC-UV	5	81−93	≤4.62	[36]
Theophylline, theobromine, (+)-catechin hydrate, and caffeic acid	Green tea	M-d-µSPE	Fe_3O_4@SiO_2@MIP/TDES	ChCl:OA:PG (1:1:1)	HPLC-UV	0.05−0.49	90−92	≤4.76	[37]
Morin	Plants	M-d-µSPE	SiO_2@ Fe_3O_4 DES	TMAC:EG (1:3)	HPLC-UV	0.91	97.7	3.8	[38]
Meloxicam	Biological samples	M-d-µSPE	SiO_2@ Fe_3O_4 DES	ChCl:EG (1:2)	HPLC-UV	1.5−3.0	89.2	≤6.2	[39]
Sulfonylurea herbicides	Water (lake, rice field)	M-d-µSPE	Fe_3O_4@ PDA-DES	DDAC:4ClPh (1:5)	UPLC-UV	0.0098−0.0110	61.3−108.6	≤3.6	[40]
Sulfonylurea herbicides	Water (lake, rice field)	M-d-µSPE	Fe_3O_4@ PDA-DES	ChCl:EG (1:2)	UPLC-UV	0.0092−0.0113	61.9−101.9	≤3.6	[41]
Sulfonylurea herbicides	Water (lake, rice field, drinking)	M-d-µSPE	Fe_3O_4@ PDA-DES	ChCl:Urea (1:2)	UPLC-UV	0.0074−0.0100	70.6−109.4	1.1–3.6	[42]
Non-steroidal anti-inflammatory drugs	Lake and river water	M-SPE	Fe_3O_4@ MIL-101(Cr)/DES	menthol:LA (1:2)	HPLC-UV	0.2−1.1	3.2−8.2	83.6–110.4	[58]
Organochlorine pesticides	Honey and tea samples	M-SPE	Fe_3O_4@ MIL-101(Cr)-NH_2/TDES	menthol:thymol:DDA (3:5:5)	GC-MS	0.07–0.80**	81.7−107.3	≤10	[59]
DESs as eluting solvents									

Flavonoids	Edible natural samples	M-d-μSPE	Fe_3O_4@ agarose	*TMAC:LA (1:3)	HPLC-UV	0.2–1.1	>91	2.6–5.7	[43]
Phenolic compounds	Fruit juice	M-d-μSPE	AD@Fe_3O_4	*TMAC-EG (1:3)	HPLC-UV	0.3–2.0	>91	≤4.8	[44]
Aristolochic acid I and II	Rat urine	M-d-μSPE	MMC@MIP	*ChCl:EG (1:2)	HPLC-UV	30 170	86.7–94.3	≤4.85	[45]
Parabens	Water (river, swimming pool), urine	M-d-μSPE	MAC	*DL-menthol:AcA (1:1)	HPLC-UV	0.1–0.3	82.6–114.4	3.49–9.15	[46]
Phenolic compounds	Food sample	M-d-μSPE	CS@Fe_3O_4	*β-CD:LA (DESP)	HPLC-UV	0.02–0.16	>94.8	≤2.9	[60]
Tetracycline antibiotics	Milk	F-d-μSPE	AC	*TBAC:PA (1:2)	HPLC-UV	0.1–0.3 μg kg^{-1}	80–91	≤9.8	[47]
Pesticides	Honey	d-μSPE	PS	*lysine: AcA (1:1)	LC-MS/MS	0.06–0.20 μg kg^{-1}	70–99	≤7.1	[48]
Pesticides	Milk	d-μSPE	PS	*TBAC:DCA (1:1)	LC-MS/MS	0.09–0.27	81–94	≤9	[49]
Phenolic compounds	Wastewater	d-μSPE	PVP	*ChCl:α-terpineol (1:2)	GC–MS	0.13–0.36	60–92	≤6	[50]
Metabolites of PAHs	Urine	d-μSPE	PVP	*ChCl:BA (1:2)	HPLC-FLD	0.014-0.028	74–96	≤6.2	[51]
Pesticides	Honey	d-μSPE	Curcumin	*TBAC:DCA (1:2)	GC–MS	0.22–0.81 μg kg^{-1}	70–83	≤10.2	[53]
PAHs	Honey	d-μSPE	Curcumin	*TBAC:EG (1:2)	GC–MS	0.14–0.37 μg kg^{-1}	72–81	≤7.5	[52]
Heavy metals	Juices, wastewaters, tap waters	d-μSPE	$CoFe_2O_4$	*ChCl:p-AP (1:2)	ICP-OES	0.54–1.33	72–90	1.1–2.1	[61]
DESs as dispersing agents									

Aflatoxins	Crops	MSPD	Diatomite	TBAC:HA	HPLC-FLD	0.03–0.10 μg kg^{-1}	93.7−98.1	≤7.5	[54]
Triazine herbicides	Brown sugar	MSPD	SG@DES	TEAC:EG (1:2)	HPLC-UV	1.59–3.77 μg kg^{-1}	95.0–101.7	≤9.1	[55]
Flavonoids	*Scutellariae* Radix	MSPD	Molecular sieve ZSM-5	Menthol:AcA	HPLC-UV	40−1030	95.9−102.31	<2.24	[56]
Nitrotoluenes	Soil samples	MSPD	Graphitic-carbon nitride	Borneol:DL-menthol (1:1)	HPLC-UV	120−330 μg kg^{-1}	78−96	<9.3	[57]

* – DES used as an eluent; **ng g^{-1}; 4ClPh – 4-chlorophenol; AC – activated carbon; AcA – acetic acid; AD – adipic acid; APTMACl – 3-acrylamidopropyl trimethylammonium chloride; β-CD – β-cyclodextrin; BA – butyric acid; ChCl – choline chloride; CS – chitosan; DCA – dichloroacetic acid; DDAC – dimethyldioctadecylammonium chloride; DDA – dodecanoic acid; DESP – deep eutectic supramolecular solvent; EDMA – ethylene glycol dimethacrylate; EG – ethylene glycol; F-d-μSPE – floating dispersive solid-phase extraction; HA – hexanoic acid; ICP-OES – Inductively Coupled Plasma Optical Emission Spectrometry; LA – lactic acid; MAA – methacrylic acid; MAC – magnetic-activated carbon; Mgel-d-μSPE – magnetic gel dispersive solid-phase extraction; MIP – molecularly imprinted polymer; MMC – magnetic mesoporous carbon; MOF – metal-organic framework; MSPD – matrix solid-phase dispersion; MWCNT – multi-walled carbon nanotubes; OA – oxalic acid; PA – propionic acid; PAHs – polycyclic aromatic hydrocarbons; p-AP – p-aminophenol; PDA – polydopamine; PDES – polymerized DES; PG – propylene glycol; Ph – phenol; PS – polystyrene; PVP – polyvinylpyrrolidone; SG – silica gel; SQT-FAAS – slotted quartz tube-flame atomic absorption spectrophotometry; SS – silicone surfactant; TBAC – tetrabutyl ammonium chloride; TDES – ternary deep eutectic solvent; TEAC – tetraethylammonium chloride; TMAC – tetramethylammonium chloride;

5. Use of deep eutectic solvents as a part of hybrid sorbents or as sorbents in SPME techniques

One of the most popular techniques of solvent-free sample preparation is solid-phase microextraction (SPME), which in its first form was developed over 30 years ago by Arthur and Pawliszyn [62]. At that time, the SPME device was made of a quartz fiber coated with a thin layer of sorbent and fixed in a needle. The essence of the SPME technique is the extraction of analytes from a sorbent-coated support immersed in the sample solution or inserted in the headspace of the sample solution. In the next step, the analytes are desorbed from the sorbent directly in the gas chromatograph (thermal desorption) or into a solvent for determination by HPLC. The SPME technique fits with the trends of GAC, mainly due to the solvent-free adsorption, the use of a small volume of solvent or a solventless desorption, as well as the limited amount of waste and the possibility of repeated use of the fiber after cleaning and conditioning [63–65]. Since the introduction of the first device to SPME, many solutions have been proposed to increase the efficiency of this process, such as changing the geometry and materials of supports, automation or introducing selective sorbents (e.g. carbon nanotubes, graphene, molecularly imprinted polymers, polymeric ionic liquids) [65–67].

It may seem that DESs can be dedicated only to solvent microextraction techniques [9], but in recent years their use in solvent-free techniques has been increasing. DESs have been used as a component of polymer monolith columns [68–70], hybrid aerogel with calcium alginate [71], as a monomer for the preparation of hybrid materials with graphene oxide [72–74] and with molecular imprinted polymers [75–77]. DESs can also be used directly as sorbents [78–80] and as hybrid materials with commercial polymers [81,82]. Even though the use of DESs in the SPME technique is a relatively new solution, it has a great potential in the search for task-specific sorbents selective towards chosen groups of analytes.

One of the first reports on the use of a DES in SPME was the study presented by Zhou et al. [68]. The authors prepared an inorganic-organic hybrid monolith with stellate mesoporous silica nanoparticles (SMSN), which they used as a sorbent in the SPME technique for the extraction of alkylbenzenes, anilines, naphthalenes and phenols from complex matrices. The monolith with SMSN was prepared by dispersing the modified SMSN in a mixture containing butyl methacrylate (as a functional monomer), ethylene glycol dimethacrylate (as a cross-linking agent) and consisting of an ionic liquid (methylimidazolium 3-hexyl-1-tetrafluoroborate) and a deep eutectic solvent (ChCl:ethylene glycol) added as a binary porogen. Another hybrid material was proposed by Zhang et al. [69], who prepared an organic-inorganic hybrid monolith with nanotubes of titanium dioxide (TNT) and a deep eutectic solvent (composed of ChCl and methacrylic acid), which they then used for the isolation and preconcentration of selected rat liver proteins using the SPME technique. According to the test results, the synergistic effect of the TNT and DES significantly improved the extraction efficiency with this type of sorbent compared to the monolith without the addition of the TNT and DES; the recovery of analytes increased to almost 99%, i.e. with an improvement of over 60%.

A DES-based monolithic polymer column was proposed by Wang et al. [70]. This column was prepared for the *in-tube* SPME technique, in which the sorbent is placed inside the tube instead of on the support. A DES composed of ChCl and itaconic acid was used as a functional monomer for the preparation of a polymer monolith inside a poly(ether-ether-ketone) tube functionalized with polydopamine. The proposed *in-tube* SPME-HPLC method showed almost 100% extraction efficiency and very good precision (RDS < 4.3%) to non-steroidal anti-inflammatory drugs, which were determined in samples of lake water and human plasma.

Asghari et al. [71] proposed an efficient sorbent consisting of calcium alginate (CA) aerogel beads modified with a DES composed of ChCl and polyethylene glycol. The proposed sorbent was used in SPME for the preconcentration of 5-hydroxymethylfurfural from coffee samples, obtaining much higher recovery values than with the aerogel without the use of a DES. In addition, it can be assumed that the combination of the CA and DES aerogel allows a very “environmentally friendly” sorption material to be obtained.

A new solution for SPME was also proposed by Karimi et al. [72]. The authors immobilized a DES composed of ChCl and thiourea on the surface of graphene oxide (GO) nanosheets, reinforcing it inside the pores of a hollow fiber. The resulting hybrid DES/GO sorbent was then used in SPME-FAAS for determination of trace amounts of Ag(I) in wastewater, ore and hair samples with good precision (better than 3.5%) and significant recovery.

Another SPME sorbent based on graphene oxide was developed by Wang et al. [73]. The thermostable graphene aerogel was prepared by modifying graphene oxide with natural DES (ChCl:glucose). A three-dimensional aerogel with a very porous structure was obtained that was used as a coating for the SPME fiber, leading to efficient adsorption of polychlorinated naphthalenes from shrimps.

Li and Row [69] proposed the use of a ternary DES (ChCl, 3,4-dihydroxybenzoic acid and ethylene glycol in a molar ratio of 1:1:2) as a matrix and functional monomer in the preparation of molecularly imprinted polymers, so-called TDES-MIP. The obtained sorbent was used for preconcentration and determination of DHBA in *Ilex chinensis*. Using TDES-MIP as a sorbent in a miniaturized version of the SPME technique, a precision better than 4.2% and a very good recovery in the range of 87–102% were obtained. Another attempt to combine a DES with an MIP was proposed by Mirzajani et al. [75], who developed hollow fibers and monolithic fibers, which they produced based on metal-organic framework deep eutectic solvents (ChCl and glycol in a molar ratio of 2:1)/molecularly imprinted polymers (MOF-DES/MIP). The fibers were used for preconcentration of phthalate esters in a solid-phase microextraction by a liquid capillary membrane (HFLMP-SPME).

Recently, Kardani et al. [77] proposed a multiple monolithic fiber solid-phase microextraction (MMF-SPME) instead of using a single fiber. The authors produced the MMF using metal-organic framework deep eutectic solvents and molecularly imprinted polymers (DES@UMCM-1MOF/MIP), which they then used to enrich and quantify 39 antibiotics in meat and dairy products, with recoveries ranging from 95% to 100% .

Werner et al. proposed the direct application of a DES in thin-film solid-phase microextraction (TF-SPME) [78–81]. The authors designed and synthesized a large group of DESs, several of which turned out to be solids at room temperature, with properties that allow them to be used in SPME, i.e. insolubility in water and organic solvents as well as mechanical stability on a stainless steel mesh support. The DESs were applied to the support by immersion in a DES heated to 80–90°C, and after removing the support from the solution, a thin film of the DES solidified within a few seconds and guaranteed a large sorption area. For example, a DES synthesized from trihexyltetradecylphosphonium chloride and n-docosanol in a molar ratio of 1:2 was deposited on a grid and used to extract parabens from aqueous environmental samples with a good precision (3.6–6.5%) and recovery in the range of 68.1–91.4%. However, after cleaning and conditioning the DES-support system, it was possible to use it with repeatable recovery only twice [78]. Therefore, in order to increase the stability of this sorbent, hybrid materials of the same DES with PDMS were produced in further studies using the sol-gel method. This process had practically no effect on the precision and recovery but significantly improved the possibilities of sorbent application, as the tests confirmed that more than 10 repetitions of the analytical procedure can be performed on one hybrid material

[81]. In addition to the DESs discussed above, a DES composed of benzyldimethylhexadecyl ammonium chloride (BDMHACl) and dodecanoic acid (DDA) in a molar ratio of 1:3 [79] and a DES synthesized from trihexyl(tetradecyl)phosphonium chloride and octadecanoic acid (ODA) in a molar ratio of 1:2 were used directly as sorbents in TF-SPME [80].

Li et al. [82] proposed using a DES (obtained by mixing ethylparaben with methyltrioctylammonium chloride) as an additive to the sol-gel coating of a PDMS fiber. They found that the addition of a hydrophobic DES created many pores on the surface of the PDMS fiber, thereby significantly improving the coating performance of the PDMS fiber. A fiber prepared in this way was used for the extraction of volatile organic compounds. A comparison of the DES/PDMS sorbent with the PDMS sorbent only showed a 3-times greater analytical signal obtained using the newly synthesized material.

Asiabi et al. [83] described a new coating material for use in electrochemically controlled in-tube solid-phase microextraction (EC-IT-SPME). The proposed material consists of a nanocomposite obtained from polypyrrole and a popular DES (consisting of ChCl and urea in a 1:2 molar ratio) by electrochemical deposition on the inner walls of a stainless-steel capillary that served as the working electrode. The extraction efficiency, mechanical stability and chemical stability of the coating material were tested and found to be quite stable in relatively acidic and alkaline media and were reusable more than 450 times without a decrease in extraction efficiency. Its extraction capacity compared to a commercial polypyrrole coating is 1.5-times better.

Table 3. Summary of studies using deep eutectic solvents as a part of hybrid sorbents or as sorbents in SPME techniques

Analytes	Samples	Extraction method	Support coating	DES (molar ratio)	Detection	LOD [ng mL^{-1}]	EF	RSD [%]	Ref.
DESs as a part of hybrid sorbents									
PAHs QNs	Lake waters	SPME	SMSN/BMA/ EGDMA/DES	ChCl:EG (1:2)	CEC	10	-*	<3.0	[68]
Proteins	Rat liver	SPME	TNT-poly(GMA-DES-EGDMA)	ChCl:MAA (1:2)	SP	-*	22–28	2.2–3.1	[69]
Anti-inflammatory drugs	Plasma, water	in tube SPME	poly(DES-EGDMA)	ChCl:IA (1:1.5)	HPLC-UV	0.01-0.05	98–103	1.89–4.32	[70]
HMF	Coffee	SPME	CA/DES	ChCl:PEG (1:1)	HPLC-UV	2.25 µg kg^{-1}	-*	<4.7	[71]
Silver	Water, ore, hair	HF-SPME	GO/DES	ChCl:urea (1:2)	FAAS	0.20	200	3.5	[72]
PCNs	Shrimp	SPME	GO/DES	ChCl:glucose (1:2)	GC-MS	9.8–66 µg kg^{-1}	410–1553	5.8–20.5	[73]
3,4-DHBA	*Ilex chinensis* Sims	mini-SPME	TDES-MIPs	ChCl:3,4-DHBA:EG (1:1:2)	HPLC-UV	310	-*	<4.2	[76]
Phthalate esters	Yogurt, water, edible oil	HFLMP-SPME	MOF-DES/MIPs	ChCl:EG (2:1)	GC-FID	0.008	441–446	2.6–3.4	[75]
Antibiotics	Meat and dairy products	MMF-SPME	DES/UMCM-1 MOF/MIP	ChCl:EG (2:1)	HPLC-UV	1.0–2.2	-*	2.8–5.6	[77]
Chlorophenols	Honey, tea, wastewater	TF-SPME	ACGO/DES	ChCl:TEACl (1:2)	HPLC-UV	0.03–0.13	33.4–35.8	<6.1	[74]
Parabens	Lake and river waters	TF-SPME	PDMS/DES	THTDPCl:BA (1:2) +PDMS	HPLC-UV	0.023–0.062	174–186	≤4.5	[81]

Toluene Ethylbenzene o-Xylene	Waters	gel-sol SPME	gel-sol PDMS-HDES	EP:MTOACl (2:1)	GC-FID	0.025 0.005 0.005	7.6 20.4 17.1	6.7 4.5 4.2	[82]
Losartan	Water, urine, plasma	EC-IT-SPME	PPy/DES	ChCl:urea (1:2)	HPLC-UV	0.05	-*	<4.9	[83]
DESs as sorbents									
Parabens	Lake and river waters	TF-SPME	DES	THTDPCl:BA (1:2)	HPLC-UV	0.018–0.055	166–183	≤6.5	[78]
Formaldehyde	Lake and river waters	TF-SPME	DES	BDMHACl:DDA (1:3)	HPLC-UV	0.150	178	4.8	[79]
Chlorophenoxy acid herbicides	River waters, drainage ditches	TF-SPME	DES	THTDPCl:ODA (1:2)	HPLC-UV	0.148–0.165	65–71	≤8.1	[80]

* – not given; PAHs – polycyclic aromatic hydrocarbons; QNs – quinolones; SMSN – stellated mesoporous silica nanoparticles; EG – ethylene glycol; EGDMA – ethyl dimethylacrylate; BMA – butyl methacrylate; ChCl – choline chloride; PEG – poly(ethylene glycol); CEC – capillary electrochromatography; GMA – glycidyl methacrylate; MMA – methylmetacrylate; SP – spectrophotometry; EGDMA – ethylene glycol dimethylacrylate; IA – itaconic acid; HMF – 5-hydroxymethylfurfural; CA – calcium alginate; PEG – polyethylene glycol; HF – hollow fiber; GO – graphene oxide; PCNs – polychlorinated naphthalenes; GA – graphene aerogel; 3,4-DHBA – 3,4-dihydroxybenzoic acid; TDES – ternary deep eutectic solvent; MOF – metal-organic framework; MIPs – molecularly imprinted polymers; THTDPCl – trihexyltetradecylphosphonium chloride; BA – behenyl alcohol; BDMHACl – benzyldimethylhexadecylammonium chloride; DDA – dodecanoic acid; ODA – octadecanoic acid; PDMS – polydimethylsiloxane; MTOACl – methyltrioctylammonium chloride; CPs – chlorophenols; EC-IT – electrochemically controlled in tube; PPy – polypyrrole; MMF – multiple monolithic fiber; ACGO – graphene oxide coated agarose/chitosan

6. Use of deep eutectic solvents in hyphenated liquid-liquid and solid-phase extraction

Hyphenated extraction techniques using a combination of liquid-phase microextraction (LPME) with different variants of SPE have recently become increasingly popular, as they not only allow the extraction of compounds from complex matrices but also provide very high enrichment factors. In combined techniques, DESs are used as extractants (in LLME, DLLME techniques) or as sorbents (in SPE, d-µSPE, M-µSPE, SPME techniques), as presented in Table 4.

An example is the research by Davoodi et al. [84], who developed a highly sensitive method for the extraction of endocrine compounds from wastewater using the SPE technique in combination with dispersive liquid-liquid microextraction (DES-DLLME). In the role of the extractant they used a DES composed of citric acid monohydrate and 1-octyl-3-methylimidazolium chloride in a molar ratio of 1:1. The synthesized DES has a lower density than water and its melting point is higher than that of water; therefore, after extraction from the surface of the aqueous phase, it can be collected and analyzed after melting. The two-step preconcentration of SPE/DES-DLLME showed impressive EF values in the range of 33,000 to 41,000, but a relatively low extraction yield in the range of 55–68% of enriched estrogenic compounds.

Mogaddam et al. [85,86] presented an interesting solution of combining d-µSPE and DLLME-SFO techniques (with solidification of a floating organic droplet) using a DES synthesized *in situ*. The proposed preconcentration method was used to extract some phytosterols [85] and pesticides [86] from edible oil samples. The first step in the preparation of the oil samples was their saponification; then the analytes were adsorbed on an octadecylsilane (C18) [85] or on a primary-secondary amine (PSA) [86] sorbent. The analytes were desorbed from the sorbent with ethanol as the elution solvent, and the eluent was diluted with water. Choline chloride and N,N-dimethylammonium chloride were dissolved in this solution. The resulting DES was dispersed in the solution. The mixture was then cooled in a water bath, and the solidified extractant (lighter than water) was collected from the surface. The EF values and recoveries ranged from 312 to 375 and 75–90% for phytosterols [85] and from 170 to 192 and 68 to 77% for pesticides, respectively [86].

Mohebbi et al. used another solution in a similar extraction system [87], where the solvent extraction step was supported with air. The authors used the developed d-uSPE/DES-AA-DLLME method to extract and pre-concentrate selected tricyclic antidepressants from human urine and plasma samples. In this method, they used the popular C18 sorbent, on which the analytes were adsorbed. After the sorbent was centrifuged, a deep eutectic solvent prepared from ChCl and 4-chlorophenol was added to the aqueous solution. The resulting mixture was quickly aspirated into a glass syringe and then injected into the tube. This procedure was repeated several times, and a cloudy solution was formed consisting of fine droplets of DES dispersed in the aqueous phase. After centrifugation of the obtained cloudy solution, droplets of extractant with analytes were collected from the bottom of the test tube. However, for the above method, recoveries were obtained in the range of 62–77%.

Yang et al. [88] proposed a method using hyphenated magnetic-SPE and LLME techniques. Magnetic nanoparticles coated with magnesium and aluminum layered double hydroxides (MgAl-LDHs) were selected for the extraction of phenolic compounds from beverage samples. A DES composed of “environmentally friendly” substrates – undecanoic acid and menthol – was used as the extractant in LLME. In the proposed method, so-called acid-base induction was used, which significantly improved the extraction efficiency, with obtained recoveries ranging from 84.4 to 101.3%.

Ragheb et al. [89] proposed an innovative magnetic biosorbent prepared for initial Hg(II) concentration. Functionalized magnetic nanoparticles ($Fe_3O_4@SiO_2\text{-}NH_2$) were deposited on an organometallic structure (HKUST-1), and the sorbent served as a platform for the immobilization of the aptamer (Apt-$Fe_3O_4@SiO_2\text{-}NH_2$@HKUST-1). Mixing the biosorbent with the sample solution allowed for selective Hg(II) adsorption. Preconcentration was then performed using the DLLME technique, where a DES of low density (menthol with salicylic acid in a molar ratio of 4:1) was used as an extractant, and an ultrasonic bath was used for effective dispersion of the sample-extractant system. The proposed procedure resulted in a very high EF of about 2400.

Monajemzadeh et al. [90] proposed a method based on a magnetic effervescent tablet in which d-µSPE was combined with in-syringe DLLME. The method was used for the preconcentration of selected pesticides and metabolites from egg samples. The authors for the first time made and used an effervescent tablet from Fe_3O_4@MWCNT. The tablet was dropped into the sample solution, and produced carbon dioxide, which dispersed the nanoparticles into the analyzed sample solution. The nanoparticles were collected using a magnet, and the adsorbed analytes were eluted with a water-miscible DES (ethyldimethylammonium chloride:propionic acid), which was used as a dispersive solvent, while another DES (ethyldimethylammonium chloride:menthol:carvacrol) was used as an extraction solvent. The proposed method enables high enrichment factors in the range of 219–276 and satisfactory extraction recoveries in the range from 73 to 92%.

Sereshti et al. [91] developed a hyphenated solid and liquid extraction method based on a new sorbent prepared from magnetic graphene oxide functionalized by (3-glycidyloxypropyl)-trimethoxysilane and a new extractant – a DES prepared from ChCl:4-chlorophenol in a molar ratio equal to 1:2. The proposed method was used for the preconcentration of pesticides in fruit juice samples, with high EFs in the range of 210–540 and recoveries in the range of 71–115%.

An interesting application of a DES in extraction techniques was proposed by Nie et al. [92] who developed a microwave-assisted sample preparation method based on a DES that acted as a medium absorbing microwave radiation, destroying cell walls and dissolving compounds released from cells. The analytes were then extracted and concentrated using the SPME technique on a fiber coated with a mixture of commercial DVB/CAR/PDMS polymers.

Shahi et al. [93] synthesized multi-walled carbon nanotubes/formaldehyde urea nanocomposite by co-precipitation polymerization, and the sorbent thus obtained was then packed into an SPE syringe cylinder and used to extract antibiotics from honey samples. The analytes adsorbed at this stage were then eluted from the sorbent using a water-miscible organic solvent. The collected eluate was mixed with a DES (tetrabutylammonium chloride:butanol), and the mixture was subjected to the DLLME procedure. The proposed method yielded high EF values in the range of 830–910.

Dilmaghani et al. [94] proposed a magnetic dispersive µSPE in combination with DLLME. Interestingly, the authors used a new sorbent synthesized from iron nanoparticles and coated with a DES using ultrasonic energy. Analytes were extracted from mascara into a methanol/water solution, after which the previously prepared sorbent was added and the mixture vortexed. After separating the sorbent from the aqueous solution, the analytes were desorbed with methanol. The eluate was collected, and CCl_4 was added as an extractant and dispersed. The above method was used to determine PAHs in mascara samples, with extraction recovery in the range of 80–95%.

Table 4. Summary of studies using DESs in hyphenated liquid-liquid and solid-phase extraction techniques

Analytes	Samples	Extraction method	Sorbent SPE	Extractant (molar ratio)	Detection	LOD [ng mL^{-1}]	EF	RSD [%]	Ref.
DESs as extractants									
Estrogenic compounds	Wastewater	SPE/ DES-DLLME	C18	CA:OMIMCl (1:1)	GC-MS	10–50	33000–41000	1.5–3.8	[84]
Phytosterols	Edible oils	d-SPE/ DES-DLLME-SFO	C18	ChCl:DMBA (1:1)	GC-MS	0.52–3.60	312–375	3.9–8.2	[85]
Pesticides	Edible oils	d-SPE/ DES-DLLME-SFO	PSA	ChCl:DMBA (1:1)	GC-NPD	0.06–0.19	170–192	<9.2	[86]
Antidepressant drugs	Urine, plasma	d-SPE/ DES-AA-LLME	C18	ChCl:4-CP (1:1)	GC-MS	0.5–2.0	64–385	3.0–5.0	[87]
PAHs	Urine	d-SPE/ DES-DLLME	PS	ChCl:DCA (1:2)	GC-MS	3.6–7.2 μg mL^{-1}	435–475	<8.6	[95]
Hormones	Milk	M-SPE/ VA-LLME	Magnetic MWCNT	ChCl:Urea (1:2)	HPLC-DAD	1.0–1.3	-*	<13.9	[96]
Phenolic compounds	Beverages	M-SPE/ DES-LLME	F_3O_4@MgAl-LDHs	Menthol:UDA (3:1)	HPLC-UV	0.006–0.011	86–91	3.8–5.0	[88]
Mercury(II)	Waters, hair, nail, butterfish	M-SPE/ DES-UA-DLLME	F_3O_4@SiO_2-NH_2@MOF	Menthol:SA (4:1)	ET-AAS	0.34	2400	3.68–3.80	[89]
DES as dispersive solvent									
Pesticides	Eggs	M-ET-d-SPE/ in syringe DES-DLLME	F_3O_4@MWCNT	EDMAC:PrA (1:1)	GC-MS	0.03–0.24 μg kg^{-1}	219–276	<10.2	[90]
DES as solvent for analytes									
65 volatile compounds	Tobacco	MADESE-SPME	DVB /CAR/PDMS	ChCl:EG$^{\#}$ (1:3)	GC-MS	-*	-*	7.8–11.2	[92]

DESs as a part of sorbents and as extractants									
Valproic acid	Exhaled breath condensate	SPE/ DES-DLLME	MIP DMACl:PA	HQ:DCA:PVA (1:1:1)	GC-MS	0.04	164	4.9–18	[97]
Antibiotics	Honey	SPE/ DES-DLLME	MWCNT@Urea-FA	TBACl:BuOH (1:1)	IMS	0.32–0.86 $\mu g\ kg^{-1}$	830–910	6.8–9.1	[93]
DESs as part of sorbents									
PAHs	Mascara	M-d-µSPE/ DLLME	$ChCl:DA/Fe(CO)_5$	CCl_4	GC-FID	0.33–0.57 $\mu g\ kg^{-1}$	-*	<8.6	[94]

* – not given; # - used both to destroy cell walls and dissolve analytes; DMACl – N,N-dimethylammonium chloride; PA – propionic acid; ChCl – choline chloride; 4ClPh – 4-chlorophenol; UDA – undecanoic acid; MgAl-LDHs – Mg(II)-Al(III) layered double hydroxide; GPTMS – (3-glycidyloxypropyl)trimethoxysilane; MGO – magnetic graphene oxide; CA – citric acid; OMIMCl – 1-octyl-3-methylimidazolium chloride; SFO – solidification of floating organic drop; PSA – primary secondary amine; DMBA – 3,3-dimethylbutyric acid; NPD – nitrogen phosphorus detector; $N_{4444}Cl$ – tetrabutylammonium chloride; BuOH – butanol; MWCNT – multiwall carbon nanotubes; FA – formaldehyde; IMS – ion mobility spectrometer; MIP – molecularly imprinted polymer; 8-HQ – 8-hydroxyquinoline; DCA – dichloroacetic acid; PVA – pivalic acid; VA – vortex assisted; EDMAC – ethyl dimethylammonium chloride; PrA – propionic acid; SA – salicylic acid; MOF – metal-organic framework; PAHs – polycyclic aromatic hydrocarbons; PS – polystyrene; DA – decanoic acid; MADESE - microwave-assisted deep eutectic solvent extraction; DVB – divinylbenzene; CAR – carboxen; UAE – ultrasound assisted extraction; EG – ethylene glycol; TBACl – tetrabutylammonium chloride; ET – effervescent tablet

7. Conclusions and future trends

The unique physicochemical properties of DESs, the virtually unlimited number of HBA and HBD combinations that allow fine-tuning of their properties and the ease of their synthesis without the need for purification, make DESs interesting solvents for a variety of applications in analytical chemistry. In this review, we have summarized the most important applications of DESs in sorbent-based (micro)extraction techniques published from 2017 to the end of April 2023.

While for liquid-phase microextraction techniques, DES are very popular as extraction or dispersing solvents, for sorbent-based extraction procedures, DESs can perform several different and important functions, such as a modifier of existing commercial sorbents or natural, renewable materials, as a carrier for sorbents, as well as for elution of target analytes from sorbents after extraction. Sorbents modified or synthesized with a DES can be used in various modes of sorbent-based procedures, such as conventional SPE, miniaturized pipette tip SPE, dispersive solid-phase microextraction, matrix dispersion in solid-phase and solid-phase microextraction, as well as combined solid-phase and liquid-liquid extraction techniques.

The review also revealed that there is a clear trend toward the fabrication of natural sorbents and biosorbents as well as a reduction in the amount of sorbent components used and the stages of sample preparation. The changes being made are undoubtedly aimed at making the newly developed methods compatible with the principles of green analytical chemistry.

Abbreviations

AA, air-assisted;
AC, activated carbon;
AcA, acetic acid;
AD, adipic acid;
APTMACl, 3-acrylamidopropyl trimethylammonium chloride;
ATEAB, allyl triethylammonium bromide;
BA, butyric acid;
BDMHACl, benzyldimethylhexadecylammonium chloride;
BMA, butyl methacrylate;
BuOH, butanol;
CA, calcium alginate;
CAR, carboxen;
CEC, capillary electrochromatography;

Chal, chalcone;
ChCl, choline chloride;
CPs, chlorophenols;
DC, 3,6-dichloro-2-methoxybenzoic acid;
DCA, dichloroacetic acid;
DDA, dodecanoic acid;
DDAC, dimethyldioctadecylammonium chloride;
DES, deep eutectic solvents;
DES-M, DES-modified monolithic polymer;
DHBA, 3,4-dihydroxybenzoic acid;
DLLME, dispersive liquid–liquid microextraction;
DMACl, N,N-dimethylammonium chloride;
DMBA, 3,3-dimethylbutyric acid;
DVB, divinylbenzene;
d-μSPE, dispersive micro solid-phase extraction;
EC-IT-SPME, electrochemically controlled in-tube solid-phase microextraction;
EDMA, ethylene glycol dimethacrylate;
EF, enrichment factor;
EG, ethylene glycol;
EGDMA, ethylene glycol dimethacrylate;
ES, ethyl silicate;
FA, formic acid;
FAAS, flame atomic absorption spectrometry;
F-d-μSPE, floating dispersive solid-phase extraction;
GA, graphene aerogel;
GAC, green analytical chemistry;
GC, gas chromatography;
Gly, glycerol;
GMA, glycidyl methacrylate;
GO, graphene oxide;
GPTMS, (3-glycidyloxypropyl)trimethoxysilane;
HA, hexanoic acid;
HBD, hydrogen bond donor;
HF, hollow fiber;
HFLMP-SPME, hollow fiber liquid membrane-protected solid-phase microextraction;
HMF, 5-hydroxymethylfurfural;
HPLC, high-performance liquid chromatography;
IA, itaconic acid;
ICP-OES, inductively coupled plasma optical emission spectrometry;
IMS, ion mobility spectrometer;
LA, lactic acid;
LLME, liquid–liquid microextraction methods;
LPME, liquid-phase microextraction;
MAA, methacrylic acid;
MAC, magnetic-activated carbon;
MADESE, microwave-assisted deep eutectic solvent extraction;
MCPA, 2-methyl-4-chlorophenoxyacetic acid;

MCPP, 2-methyl-4-chlorophenoxypropionic acid;
M-d-µSPE, magnetic dispersive micro solid-phase extraction;
MgAl-LDHs, Mg(II)-Al(III) layered double hydroxide;
Mgel-d-µSPE, magnetic gel dispersive solid-phase extraction;
MGO, magnetic graphene oxide;
MIP, molecularly imprinted polymers;
MMA, methylmetacrylate;
MMC, magnetic mesoporous carbon;
MOF, metal-organic framework;
MS, mass spectrometry;
MSM, mesoporous siliceous material;
MS/MS, tandem mass spectrometry;
MSPD, matrix solid-phase dispersion;
Mtpp, methyltriphenylphosphonium bromide;
MWCNT, multi-walled carbon nanotubes;
NPD, nitrogen phosphorus detector;
$N_{4444}Cl$, tetrabutylammonium chloride;
OA, oxalic acid;
ODA, octadecanoic acid;
OMIMCl, 1-octyl-3-methylimidazolium chloride;
QNs, quinolones;
P123, polyethylene-polypropylene-polyglycol triblock copolymer;
PA, propionic acid;
PAHs, polycyclic aromatic hydrocarbons;
pAS-COOH-GO, carboxylated graphene oxide modified with p-aminostyrene;
PCN, polychlorinated naphthalenes;
PDA, polydopamine;
PDES, polymerized DES;
PDMS, polydimethylsiloxane;
PEG, polyethylene glycol;
PG, propylene glycol;
Ph, phenol;
poly(APTES-MAA-co-DES-co-EDMA), 3-aminopropyl triethoxysilane-methacrylic acid with DES and ethylene glycol dimethacrylate;
PPy, polypyrrole;
PrA, propionic acid;
PS, polystyrene;
PSA, primary secondary amine;
PT-SPE, Pipette-tip solid-phase extraction;
PVA, pivalic acid;
PVP, polyvinylpyrrolidone;
SA, salicylic acid;
SFME, solvent-free microwave extraction;
SFO, solidification of a floating organic drop;
SG, silica gel;
SMSN, stellate mesoporous silica nanoparticle;
SP, spectrophotometry;

SPE, solid-phase extraction;
SPME, solid-phase microextraction;
SQT-FAAS, slotted quartz tube-flame atomic absorption spectrophotometry;
SS, silicone surfactant;
TBAC, tetrabutyl ammonium chloride;
TDES, ternary deep eutectic solvent;
TEAC, tetraethylammonium chloride;
THTDPCl, trihexyltetradecylphosphonium chloride;
TMAC, tetramethylammonium chloride;
TNT, titanium dioxide nanotubes;
UAE, ultrasound assisted extraction;
UDA, undecanoic acid;
UV, ultraviolet detection;
VA, vortex assisted;
VALLME, vortex-assisted liquid–liquid microextraction;
1,3,5-TMB, 1,3,5-trimethylbenzene;
3,4-DHBA, 3,4-dihydroxybenzoic acid;
4ClPh, 4-chlorophenol;
8-HQ, 8-hydroxyquinoline

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