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Application of deep eutectic solvents in sample preparation for analysis (update 2017–2022). Part A: Liquid phase microextraction

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Abstract

Sustainable development in all branches of human activity has become an unequivocal necessity in the last two decades, and green chemistry goes hand in hand with it. Various ways have been proposed in analytical chemistry to meet the current requirements of green chemistry. One such approach is the research of new reagents and solvents for analytical purposes. Deep eutectic solvents (DESs) began being investigated and used in analytical chemistry in the middle of the last decade; since then, we can observe a sharp increase in published works in this area. This paper focuses on liquid-liquid (micro)extraction (LLME) procedures and describes the applications of DESs for the determination of organic and inorganic analytes in various matrices. The use of DESs in sorbent-based procedures will be discussed in a separate paper.

Keywords: deep eutectic solvent; sample pretreatment; liquid phase microextraction

1 Introduction

Usunięto: ,

Nearly 20 years ago the pioneering work of the Abbott group initiated research in a new area, namely that of new solvents, which were later termed deep eutectic solvents (DESs) [1, 2]. These solvents have several interesting properties, which is why they immediately attracted the attention of researchers, as evidenced by the constantly growing number of publications devoted to them (**Fig. 1**). Several physical properties and application areas of DESs are close to those of ionic liquids (ILs), which is why some researchers, especially at the beginning of studies on DESs, considered them to be a subclass of ILs. However, from the chemical point of view, the starting compounds used and the mechanism of their synthesis, we can consider DESs to be a separate and distinct group [3]. A deep eutectic solvent is a mixture of two or more compounds – a combination of a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA) – that has a lower melting point than those of their individual components [4]. Some authors are of the opinion that these conditions are insufficient and consider it necessary to distinguish between a DES and an ES, and only mixtures whose eutectic point temperature is below that of an ideal liquid mixture can be considered as a DES [5, 6].

Since the number of suitable starting compounds is huge, the physicochemical properties of DESs can be tailored by choosing suitable HBAs and HBDs, adjusting their molar ratio or by adding water. It is probably this feature that makes DESs such an interesting subject of research. The first publications dedicated to the use of DESs in analytical chemistry appeared sometime in the middle of the last decade. Some six years ago we published in this journal a mini-review, "*Application of deep eutectic solvents in analytical chemistry*", in which we briefly discussed the articles that were available at the time [7]. Since then, a number of new works devoted to this topic have appeared (**Fig. 2**). Although there are many possibilities for the use of DESs in analytical chemistry, the area of sample pretreatment is probably the most studied. We can distinguish two main directions, namely procedures based on liquid–liquid (micro)extraction (LLE/LLME) and procedures based on the use of sorbents. Given that the number of published works devoted to this subject matter is too large, we have divided our review into two separate papers, each of which is focused on one of the main directions mentioned above. We hope that this review will interest and motivate readers and will be useful for their further research.

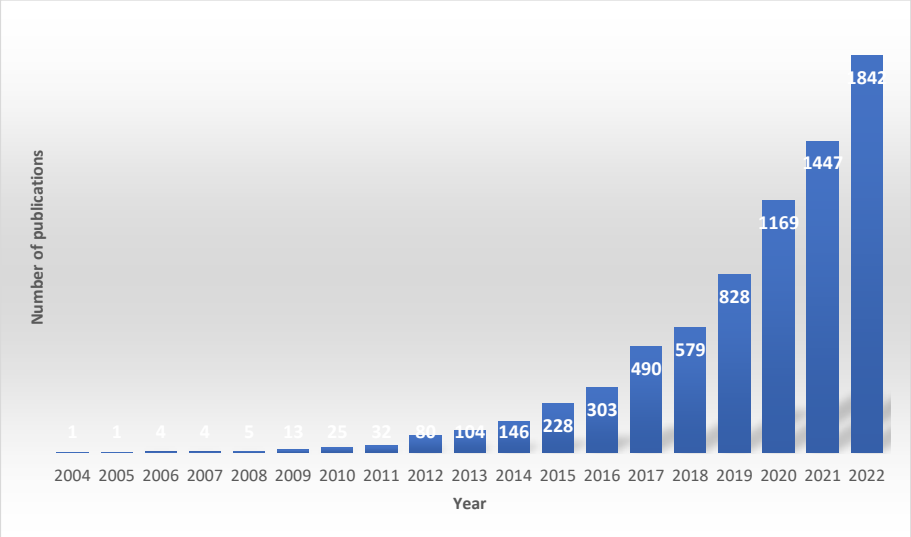

Fig. 1. Evolution in the number of publications devoted to deep eutectic solvents (based on Scopus; accessed on December 2022) [8].

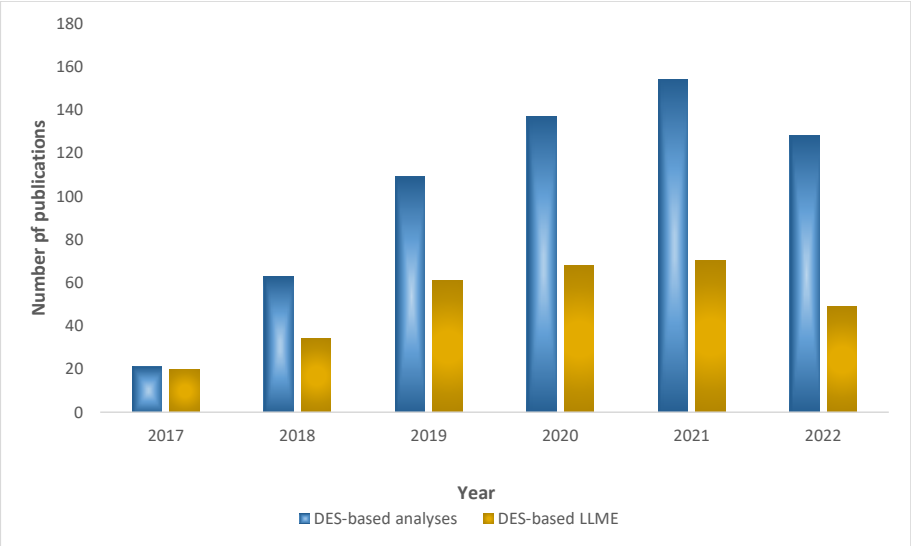

Fig. 2. Evolution in the number of publications devoted to the topic published during 2017–2022 (based on Scopus [8] and data included in Tables 1 and 2).

2 Determination of organics

As was previously mentioned, DESs have been investigated in a wide range of areas, including analytical chemistry, as many of them have unique properties and are considered to be green solvents. They also have tunable physicochemical properties and a great ability to extract organic and inorganic compounds. Therefore, they are often used in sample preparation processes, including LLE/LLME. The vast majority of works in this field (77% of the total number of reviewed papers) have dealt with organic analysis [9-241], with various drugs, plant bioactive compounds, pesticides and dyes most often determined. Other analytes, such as nitrogen-containing organic compounds, phenols, polycyclic aromatic hydrocarbons, phthalates, parabens and endocrine-disrupting compounds, have been determined less often (**Fig. 3**). Regarding the samples, the most frequently analysed are various water samples, as well as other aqueous samples, such as beverages and juices. Articles focusing on the analysis of samples with a complex matrix, such as biological samples or samples of certain foods, are also not uncommon, as evidenced in **Fig. 4**. It should be emphasised that for some samples pretreatment is necessary prior to DES extraction. When analysing water samples, no or minimal pre-treatment, such as centrifugation and/or filtration, is required to remove solid particles. For simple aqueous samples, such as beverages and juices, dilution of the sample is also often used to reduce the influence of the matrix. More complex matrices, such as food or biological samples, require additional pretreatment steps before DES preconcentration. For example, protein precipitation is usually required for blood samples. The applications of DES-based liquid–liquid extraction procedures for the determination of organic analytes are summarised in **Table 1**. The vast majority of papers deal with various modalities of LLME, and only few papers are focused on single-drop microextraction (SDME) or hollow-fibre liquid-phase microextraction (HF-LPME) approaches. As for detection, liquid chromatography (LC) is most often used (66%), followed by gas chromatography (GC) with 20% representation and spectrophotometry with 14% representation. Instrumental analysis techniques are associated with different detectors, as is shown in more detail in **Fig. 5**. Examples of the determination of organic compounds in various matrices using DES-based procedures will be discussed below.

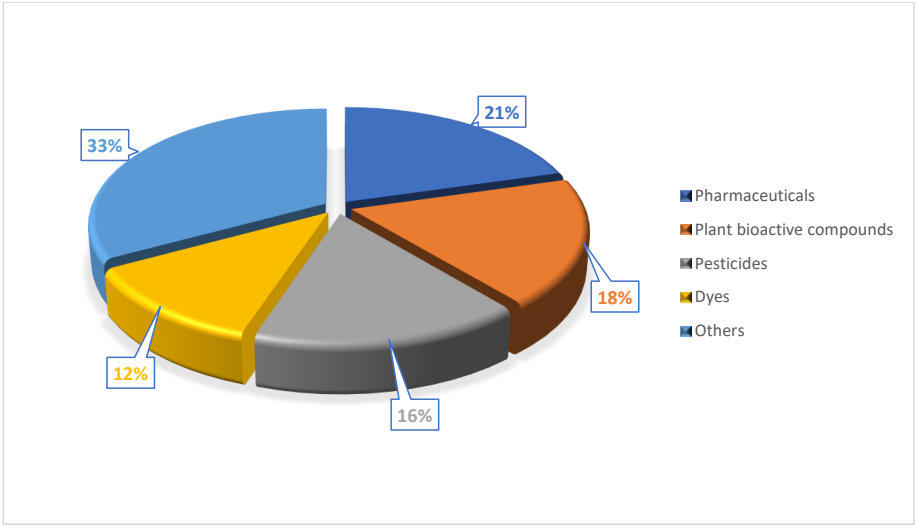

Fig. 3. Types of analytes determined using DES-based procedures. Data extracted from Table 1.

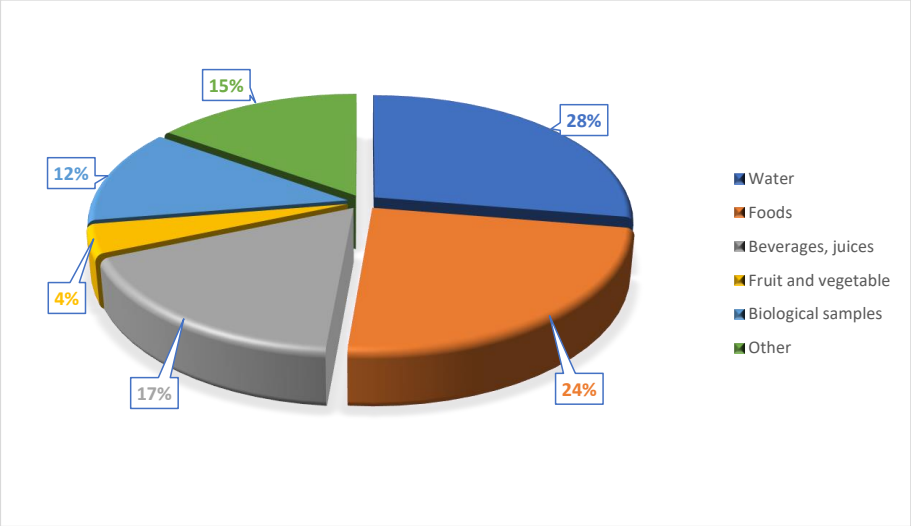

Fig. 4. Types of samples pretreated using DES-based procedures. Data extracted from Table 1.

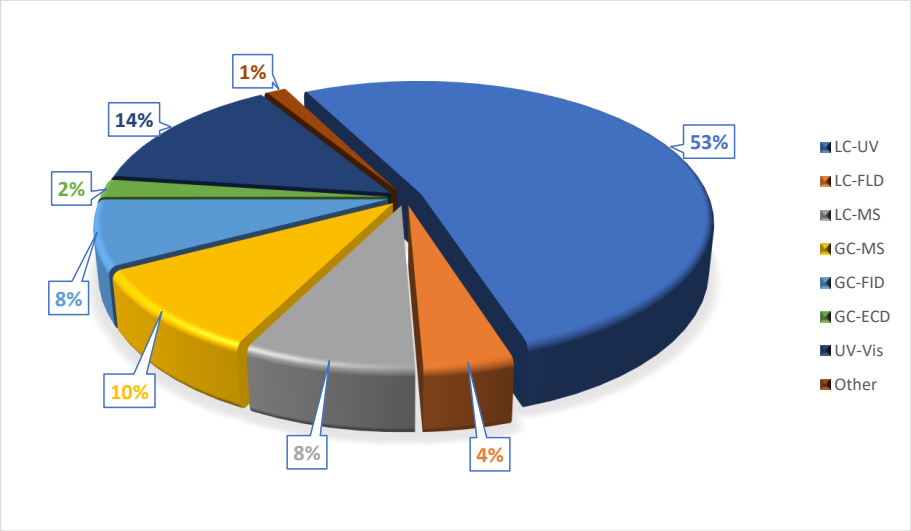

Fig. 5. Types of analytical techniques used. Data extracted from Table 1.

Some researchers have proposed using temperature control of the aqueous phase to ensure the dissolution of the DES, its dispersion and subsequent acceleration of phase separation. Farajzadeh et al. developed a temperature-controlled LPME method employing a DES for the extraction and preconcentration of some pesticides from aqueous samples [139]. The dispersion of the extraction

solvent is performed by changing the aqueous phase temperature and without the use of a disperser solvent. Briefly, the sample solution in a test tube with a conical bottom was placed in a water bath (70 °C for 1 min); an appropriate volume of DES was then added, and the solution was shaken manually. The elevated temperature enables the dissolution of the DES in the aqueous phase. The decrease in DES solubility during the 5 min ice bath cooling step led to the formation of a turbid solution and extraction of the target analytes into the DES phase. The developed method was applied for for extraction and preconcentration of pesticides from fruit juice and vegetable samples, followed by GC with a flame ionization detector (FID), resulting in the limits of detection (LOD) ranging from 0.13 to 0.31 ng mL^{-1} [139]. A procedure for simultaneous extraction/preconcentration of diazinon and fenitrothion, followed by HPLC with an ultraviolet (UV) detector, was also presented [70]. A water-immiscible DES consisting of choline chloride and 4-chlorophenol was added to the aqueous sample and followed by heating the mixture in a water bath (75 °C) until the solvent was completely dissolved. The solution was then cooled in an ice bath, and the resulting cloudy solution was centrifuged. The LODs were 0.15–0.3 μg L^{-1}. The method was applied to the analysis of water and fruit juice samples [70]. Zhang et al. prepared a hydrophobic DES composed of menthol and myristic acid with a melting point only slightly higher than room temperature by choosing a suitable HBA and HBD, as well as their appropriate molar ratio [235]. They then applied it for the extraction of triclosan and alkylphenols in environmental water samples using a temperature-controlled air-assisted LLME based on the solidification of a floating DES. In addition, the greenness of the method was evaluated using the analytical Eco-Scale and the Complex Green Analytical Procedure Index [235].

Procedures based on both *in situ* DES formation and *in situ* DES decomposition were reported. Li et al. developed an LLME procedure based on *in situ* formation of a hydrophobic DES that allows direct application of solid DES components into samples without their time-consuming preparation [83]. The authors investigated several combinations of monoterpenes and fatty acids and selected a DES comprising thymol and heptanoic acid (2:1) due to its highest extraction efficiency. The procedure can be briefly described as follows. Specified amounts of the individual DES components were added separately to a glass centrifuge tube containing the sample solution. After a short shaking, the tube was incubated at 52°C for 5 minutes without mixing and then vortexed for 1 min. The collected DES phase was diluted and subjected to HPLC-UV analysis. The method, which showed good linearity in the range of 15–3000 ng mL^{-1} with an LOD of 3.0 ng mL^{-1}, was applied for the quantification of fluoroquinolone antibiotics (ofloxacin, norfloxacin, ciprofloxacin and enrofloxacin) in real surface water samples [83].

Methods based on DES decomposition during extraction were also presented. Niroumandpassand et al. developed a pH-induced solidification of floating organic droplet homogenous liquid–liquid extraction (HLLE) procedure for the extraction of pyrethroid insecticides from milk samples prior to GC-FID quantification. A DES consisting of menthol and *p*-aminophenol was dissolved in the sample solution to form a homogeneous solution. The addition of several microlitres of ammonia solution and sonication caused the DES to decompose, leading to the formation of tiny droplets of menthol into which the target analytes were extracted. The extraction phase was solidified by cooling in an ice bath; it was then collected and melted at room temperature, and an aliquot was analysed. The method's LODs were found to be 1.1–2.4 ng mL^{-1} [190]. An air-assisted *in situ* DES decomposition followed by the solidification of floating organic droplets LLME for simultaneous determination of three azole antifungal agents in biological samples was presented [33]. The dispersion of the extraction solvent in the sample solution as a result of the *in situ* decomposition of a

DES consisting of tetrabutylammonium bromide and 1-dodecanol (1:2) was also supported by air mixing. Under optimal conditions, the LODs were in the range of 0.5–2.8 μg L^{-1} [33].

Several studies employing two DESs, one hydrophobic and the other hydrophilic, have been published. The analytes are first extracted into the hydrophilic DES and then preconcentrated into several microlitres of the hydrophobic DES [72, 228]. A microwave-assisted LLE combined with a DES-based in-syringe DLLME for extraction and preconcentration of seven herbicides from wheat samples was developed [91]. The analytes are extracted into 1.2 mL of water-miscible choline chloride–phenol DES under microwave irradiation. After extraction, 1.0 mL of supernatant (as a dispersive solvent) was mixed with 180 μL of choline chloride–butyric acid DES (as the extraction solvent) and rapidly injected into 5 mL of deionized water. The water-insoluble DES was dispersed into the solution and the analytes were extracted into the extraction solvent droplets. The demulsifier solvent consisted of 250 μL of acetonitrile. The extraction solvent collected on top of the solution was then used for determination using a GC-MS system. Low LODs in the range of 1.6–12 ng kg^{-1} were obtained [91].

The use of homemade devices sometimes allows the dispersing solvent or the centrifugation step to be omitted, thus improving the extraction procedure. Jouyban et al. reported a glass-filter-based dispersive liquid phase microextraction (DLPME) using a lighter-than-water DES for the extraction and preconcentration of different classes of pesticides from fruit juice and vegetable samples. A U-shaped tube containing a glass filter was used as the extraction device. The aqueous sample solution was placed on top of the glass filter, while the choline chloride–pivalic acid DES was placed below the glass filter. The extraction solvent was forced through the glass filter using air flow and dispersed in the aqueous solution, allowing the analytes to be extracted into the fine droplets of the extraction solvent. The extraction phase was then separated without using centrifugation [141]. Later, the authors took a very similar approach for the extraction of pesticides from plasma and urine samples of farmers using a DLLME procedure based on the solidification of floating organic droplets. The lighter-than-water DES used, which had a melting point near room temperature, was dispersed into the solution by passing through the glass filter under nitrogen gas stream, and then the solvent droplets were solidified using cool water and collected at the top of the solution. The procedure does not require the use of a dispersion solvent, centrifugation or cooling in an ice bath [138]. Nezami et al. reported a gas flow-assisted DES-based DLPME procedure for the determination of parabens in personal care products. A flow of inert gas was employed to disperse the extraction solvent in the sample solution, leading to the accumulation of the DES on the sample surface. The extraction phase was then collected in the narrow neck of the homemade extraction device. The LODs were in the range of 0.2–0.3 μg L^{-1}. According to the authors, the advantages of the procedure are that it eliminates the use of a dispersion solvent as well as the centrifugation step while reducing the consumption of the extraction phase; the extraction efficiency was also improved by applying only a thin layer of the extraction phase on the surface of the gas bubbles [131]. Mehravar et al. reported a DES-based headspace single-drop microextraction (HS-SDME) procedure for GC-MS analysis of polycyclic aromatic hydrocarbons in aqueous samples. To increase the stability of the microdroplet at higher stirring rates, a microsyringe with a bell-shaped tube was used as a carrier [181].

Automation is an integral part of current analytical chemistry, as it enables the reduction of risk for laboratory workers, eliminates operator errors and thus increases the accuracy of determinations as well as productivity. Unfortunately, the automation of liquid–liquid microextraction is quite a complex and demanding issue for various reasons, the main one likely being the necessity of centrifugation to separate the aqueous and organic phases after extraction [242]. Nevertheless, this remains an interesting task, which is why researchers have proposed various solutions. Similar works

on the automation of DES-based extraction are thus far rare. Yıldırım et al. reported an automated direct immersion single-drop microextraction (DI-SDME) procedure based on the Lab-in-Syringe concept. Only 60 µL of hexanoic acid-thymol DES was used for analysis. The samples were mixed with a magnetic stir bar placed inside the syringe. The system was coupled online to HPLC with fluorescence detection and was applied to the determination of fluoroquinolones in water samples, with LOD values in the range of 6–9 ng L^{-1} [85].

Table 1 Examples of DES-based liquid-liquid extraction procedures for the determination of organic analytes

Analyte	Matrix	Detection	Selected DES / Procedure	LOD	Refs
Acaricides (*clofentezine, fenpyroximate, pyridaben*)	Fruit juices (*apple, orange, sour cherry, grape, peach, apricot*)	HPLC-UV	methyltrioctylammonium chloride and *n*-butanol (1:3) / DES-based vortex-assisted LPME	0.5–1 μg L^{-1}	[9]
Aflatoxin M_1	Cheese samples	HPLC-FLD	*N,N*-diethanol ammonium chloride and carvacrol (1:2) / combination of solvent extraction with DES-based DLLME	0.74 ng kg^{-1}	[10]
Aflatoxin M_1	Milk samples	UV-Vis	betaine chloride and maltose (1:3) / DES-based ultrasound-assisted DLLME	6.1 ng L^{-1}	[11]
Aflatoxins (G_1, B_1, G_2, B_2)	Rice samples	HPLC-FLD	tetramethylammonium chloride and malonic acid (1:2) / DES-based UAE	0.01–0.06 μg kg^{-1}	[12]
Alkyl gallates (*propyl gallate, octyl gallate*)	Vegetable oils (*sunflower oil, corn oil, hazelnut oil*)	HPLC-UV	choline chloride and ethylene glycol (1:2) / DES-based vortex-assisted LLME	2.1–4.6 μg kg^{-1}	[13]
Alkylphenols, bisphenols and alkylphenol ethoxylates	Microbial-fermented functional beverages and bottled water samples	UHPLC-MS	DL-menthol and octanoic acid (1:1) / DES-based vortex-assisted DLLME	0.10 ng L^{-1} – 2.99 μg L^{-1}	[14]
Allura Red	Tap water, detergent samples, chocolate samples	UV-Vis	tetrabutylammonium bromide and decanoic acid (1:5) / DES-based (ultrasound-assisted) LPME	3.92 μg L^{-1}	[15]
Allura Red AC and tartrazine	Food products (*powder juice, candies*)	UV-Vis	tetrabutylammonium bromide and octanoic acid (1:2) / DES-based LPME	0.004–0.005 mg L^{-1}	[16]
Amaranth (E123)	Water samples (*tap water, lake water*) and food samples (*cherry fruit juice, red tea, powdered drink*)	UV-Vis	tetrabutylammonium bromide and decanoic acid (1:1) / DES-based ultrasound-assisted LPME	23 μg L^{-1}	[17]
Amoxicillin and ceftriaxone	Hospital sewage	HPLC-UV	1-decyl-3-methylimidazolium chloride and *n*-butanoic acid (1:2) / vortex-assisted LPME based on SDES	0.005–0.10 μg L^{-1}	[18]
Amphetamine and methamphetamine	Human plasma, pharmaceutical wastewater	HPLC-UV	choline chloride and phenylethanol (1:4) / DES-based air-agitated EME	2.0–5.0 ng mL^{-1}	[19]
Antiarrhythmic agents (*propranolol, carvedilol, verapamil, amlodipine*)	Urine, plasma, pharmaceutical wastewater	HPLC-UV	choline chloride and 1-phenylethanol (1:4) / carrier less three-phase HF-LPME	0.3–0.8 ng mL^{-1}	[20]
Antibiotics (*penicillin G, dihydrostreptomycin, enrofloxacin, ciprofloxacin*)	Honey samples	HPLC-MS/MS	tetrabutylammonium chloride and *p*-cresol (1:2) / LLME based on *in situ* formation/decomposition of DES with SFOD	0.55–0.79 ng g^{-1}	[21]
Antibiotics (*oxytetracycline, doxycycline, penicillin G, chloramphenicol*)	Milk samples	HPLC-UV	phosphocholine chloride, dichloroacetic acid and dodecanoic acid (1:1:1) / HLLE combined with DES-based DLLME	2.0–2.8 μg L^{-1}	[22]
Antibiotics (*levofloxacin, ciprofloxacin*)	Water samples (*feed water, tap water, wastewater*)	HPLC-UV	thymol and hexanoic acid (2:1) / DES-based HLLME	0.018–0.027 μg mL^{-1}	[23]
Antibiotics (*levofloxacin, ciprofloxacin*)	Water samples (*tap water, wastewater, seafood market water*)	HPLC-UV	tricaprylylmethylammonium chloride and 1-octanol (1:1) / vortex-assisted LLME	0.016–0.024 μg mL^{-1}	[24]
Antibiotic residues (*oxytetracycline, penicillin G, tilmicosin*)	Sausage samples	IMS	phosphocholine chloride, dichloroacetic acid, and dodecanoic acid (1:1:1) / HLLE combined with DLLME based on solidification of DES	1.52–2.73 ng g^{-1}	[25]
Anti-depressant drugs (*escitalopram, desipramine, imipramine*)	Human plasma and wastewater samples	HPLC-UV	choline chloride and phenol (1:4) / DES-based air-agitated EME	3.0–4.5 ng mL^{-1}	[26]
Anti-seizures (*carbamazepine, diazepam, chlordiazepoxide*)	Urine samples	GC-FID	choline chloride and benzyl ethylenediamine (1:2) / LLE combined with DES-based DLLME	3.4–6.9 ng mL^{-1}	[27]

Aromatic amines	Simulant of kitchenware samples	HPLC-UV	bis(2-ethylhexyl) phosphoric acid and thymol (1:2) / DES-based vortex-assisted DLLME	1.5–3.0 μg L^{-1}	[28]
Aromatic amines	Water samples (*lake water, river water, seawater, melted snow water*)	HPLC-UV	trihexyl(tetradecyl)phosphonium chloride and decanol (1:2) / DES-based ultrasound-assisted DLLME with solidification of the aqueous phase	0.07−0.11 ng m L^{-1}	[29]
Aromatic amines	Water samples (*lake water, fish-pond water, tap water*)	HPLC-UV	bis(2-ethylhexyl) phosphate and phenol (1:2) / DES-based DLLME	0.07–0.17 μg L^{-1}	[30]
Aromatic amines	Water samples (*tap water, surface water, river water, municipal wastewater, leather processing unit wastewater*)	GC-MS	choline chloride and *n*-butyric acid (1:2) / air-assisted LLME based on SDES	1.8–6.0 ng L^{-1}	[31]
Auxins	Water samples (*tap water*) and fruit juices (*apple, orange, apple, banana*)	HPLC-UV	trioctylmethylammonium chloride and isoamyl alcohol (1:4) / DES-based vortex-assisted DLLME	0.2–0.3 μg L^{-1}	[32]
Azole antifungal drugs (*ketoconazole, clotrimazole, miconazole*)	Tap water, plasma, urine samples	HPLC-UV	tetrabutylammonium bromide and 1-dodecanol (1:2) / air-assisted LLME using DES decomposition followed by SFOD	0.5–2.8 μg L^{-1}	[33]
Benzoylurea insecticides (*diflubenzuron, triflumuron, hexaflumuron, lufenuron, chlorfluazuron*)	Olive oil	HPLC-UV	octyltributylphosphonium bromide and ethylene glycol (1:1) / DES-based vortex-assisted LLME	1.5–7.5 μg L^{-1}	[34]
Benzoylureas (*triflumuron, hexaflumuron, flufenoxuron, lufenuron*)	Water samples (*river water, well water, swimming pool water*)	HPLC-UV	tricaprylmethylammonium chloride and 1-dodecanol (1:2.5) / DES-based DLLME based on SFOD	0.11–0.35 μg L^{-1}	[35]
Benzotriazole and benzothiazole derivatives	Surface water samples (*campus ditch water, river water, reservoir water*)	UHPLC-MS	choline chloride and phenol (1:2) / DES-based USAEME	0.02−0.5 μg L^{-1}	[36]
Benzotriazole and benzothiazole derivatives	Tea beverages	UHPLC-MS	choline chloride and 4-chlorophenol (1:3) / DES-based ultrasound-assisted LPME	0.5–4 ng mL^{-1}	[37]
β-blockers (*atenolol, propranolol, metoprolol*)	Plasma samples	GC-MS	tetramethylammonium chloride and alpha terpineol (1:2) / LLME based on *in situ* formation of DES	0.130–0.205 ng mL^{-1}	[38]
Beta-blockers (*metoprolol, propranolol*)	Water samples (*river water, lake water, tap water*)	HPLC-UV	azelaic acid and thymol (1:17) / vortex-assisted LLME based on *in situ* formation of DES	0.1–0.2 μg L^{-1}	[39]
β-carotene and lycopene	Fruit juices (*watermelon juice, grapefruit juice, tomato juice, guava juice*)	HPLC-UV	C_9:C_{10}:C_{11} fatty acids (2:1:1) / DES-based acid–base-induced LLME	0.002–0.05 μg mL^{-1}	[40]
β-lactam antibiotics residues (*penicillin G, ampicillin, amoxicillin*)	Food samples (*chicken meat, honey, egg*)	HPLC-UV	benzyltriethylammonium chloride and decanoic acid (1:3) / DES-based ultrasound-assisted DLLME based on SFOD	1.16–5.08 μg kg^{-1}	[41]
Bicalutamide	Water samples (*river water, tap water*) and human plasma	UV-Vis	borneol and capric acid (1:2) (extraction solvent) and tetrabutylammonium bromide and acetic acid (1:2) (dispersive solvent) / DES-based DLLME	0.022–0.048 μg mL^{-1}	[42]
Biogenic amines	Tuna fish samples	HPLC-UV	choline chloride and hexanedioic acid (1:1) / MAE combined with DLLME based on *in situ* formation of DES	0.25–0.50 ng g^{-1}	[43]
Bisphenol A and 4-nonylphenol	Canned tuna and marine fish tissues	HPLC-FLD	choline chloride and urea (1:2) / DES-based extraction	0.021 and 0.015 μg g^{-1}	[44]
Bisphenols (*BPS, BPA, BPB*)	Canned fruits	UPLC-MS/MS	menthol and undecanol (1:2) / DES-based DLLME based on SFOD	1.5−3.0 ng g^{-1}	[45]
Bisphenols (*BPA, BPB, BPAP, BPZ*)	Food-contacted plastics (*fresh-keeping film, pipette, disposable plastic cup, plastic cup, baby bottle nipple*)	HPLC-FLD	trioctylmethylammonium chloride and decanoic acid (1:2) / DES-based vortex-assisted LLME	0.3–0.5 μg L^{-1}	[46]

Bisphenols and polycyclic aromatic hydrocarbons	Tea infusions	HPLC-UV	DL-menthol and dodecanoic acid (3:1) / air-assisted LLME based on SDES	0.16–0.75 μg L^{-1}	[47]
Brominated flame retardants and organochlorine pollutants	Fish oil samples for animal feed and fish oil supplements for human consumption	GC-MS/MS	choline chloride and phenol (1:2) / DES-based vortex-assisted LLME	0.2–0.7 ng g^{-1}	[48]
Brown HT (E155)	Artificial urine and water samples	UV-Vis	tetrabutylammonium bromide and decanoic acid (1:2) / DES-based LPME	0.23 μg mL^{-1}	[49]
tert-Butylhydroquinone	Edible oils (*soybean oil, sunflower seed oil, blend oil*)	HPLC-UV	choline chloride and ascorbic acid (2:1) / DES-based ultrasound-assisted LLME	0.02 mg kg^{-1}	[50]
tert-Butylhydroquinone	Edible oils (*soybean oil, sunflower seed oil, blend oil*)	HPLC-UV	choline chloride and ethylene glycol (1:2) / DES-based ultrasound-assisted LLME	0.02 μg mL^{-1}	[51]
tert-Butylhydroquinone	Edible oils (*soybean oil, sunflower oil, blend vegetable oil*)	HPLC-UV	choline chloride and sesamol (1:3) / DES-based vortex-assisted LLME	0.02 mg kg^{-1}	[52]
tert-Butylhydroquinone	Soybean oils	HPLC-UV	choline chloride and sesamol (1:3) / DES-based ultrasound-assisted LLME	0.02 μg mL^{-1}	[53]
Caffeic acid	Coffee, green tea and tomato samples	HPLC-UV	serine and lactic acid (1:4) / DES-based HF-LPME and 30% MeOH (as acceptor phase)	0.3 ng mL^{-1}	[54]
Caffeine	Food samples (*dry coffee, chocolate, ice cream*) and beverage samples (*cola, energy drink, ice tea, nescafé, espresso*)	UV-Vis	choline chloride and urea (1:2) / DES-based (ultrasound-assisted) microextraction	7.5 μg L^{-1}	[55]
Calcium dobesilate	Water samples (*tap water, river water, outlet water of sewage treatment plant*) and urine	UV-Vis	methyltrioctylammonium chloride and bromoacetic acid (1:1) / DES-based vortex-assisted LLME	0.05–0.50 μg L^{-1}	[56]
Carbamazepine	Plasma	HPLC-UV	choline chloride and phenol (1:2) / DES-based ultrasound-assisted LPME	1.17 ng mL^{-1}	[57]
Carboxylic acids	Aqueous matrices	GC-MS	choline chloride and 4-methylphenol (1:2) / ultrasound-assisted DLLME	1.7–8.3 μg L^{-1}	[58]
Chlorobenzenes	Toilet air freshener and car perfume	GC-MS	monoethanolamine and 4-methoxyphenol (1:1) / DES-based HLLME	0.01–0.15 μg L^{-1}	[59]
Chlorophenols (*4-CP, 2,4-DCP, 2,4,6-TCP*)	Wastewater	HPLC-UV	methyltrioctylammonium chloride and octanoic acid (1:2) / DES-based DLLME	0.03–0.05 μg mL^{-1}	[60]
Chlorophenols	Water samples	GC-ECD	*o*-cresol and acetic acid (1:3) / DES-based DLLME	0.015–1.0 μg L^{-1}	[61]
Cinnamic acid derivatives (*caffeic acid, p-hydroxycinnamic acid, ferulic acid, cinnamic acid*)	Traditional Chinese medicines (*Chuanxiong Rhizoma, Mai-luo-ning injection*)	HPLC-UV	tetrabutylammonium chloride and hexanoic acid (1:3) / DES-based HF-LPME	0.1–0.3 ng mL^{-1}	[62]
Cortisol and cortisone	Saliva samples	LC-UV	trioctylmethylammonium chloride and pentafluorophenol (1:2) / DES extraction (ultrasound-assisted)	1.8–2.1 pmol mL^{-1}	[63]
Coumarins (*aesculetin, aesculin, fraxetin, fraxin*)	*Cortex Fraxini*	HPLC-UV	betaine and glycerin (1:3) / ultrasound-assisted DES extraction	0.2–0.7 μg mL^{-1}	[64]
Curcumin	Food samples (*cinnamon tea, anti-parasite herbal tea, herbal tea, mixed herbal tea with turmeric, turmeric, curry, cinnamon, sesame*)	UV-Vis	betaine hydrochloride and glycerol (1:3) / DES-based vortex-assisted microextraction	1.5 μg L^{-1}	[65]
Curcumin	Tea (*herbal tea, black tea, green tea*), honey (*flower honey, pine honey, chestnut honey*), and spices (*thyme, turmeric, cinnamon, curry*)	UV-Vis	choline chloride and maltose (1:3) / DES-based ELLME	0.1 ng mL^{-1}	[66]
Curcuminoids	*Curcumae longae* Rhizoma and turmeric tea	HPLC-UV	L-menthol and lactic acid (1:2) / solvent terminated DES-based microextraction	0.1–0.4 ng mL^{-1}	[67]

Curcuminoids	*Curcumae longae* Rhizoma and turmeric tea	HPLC-UV	tetrabutylammonium chloride and decanoic acid (1:1) / DES-based DLLME based on SFOD	7.0×10^{-5} – 9.0×10^{-5} mg L^{-1}	[68]
Daclatasvir and sofosbuvir	Urine samples	HPLC-UV	tetrabutylammonium chloride and *p*-aminophenol (1:2) / DES-based ultrasound-assisted HLLME	1.0–1.3 μg L^{-1}	[69]
Diazinon and fenitrothion	Water samples (*tap water, well water*) and fruit juices (*apple, pear, orange*)	HPLC-UV	choline chloride and 4-chlorophenol (1:2.5) / DES-based temperature-controlled LLME	0.15–0.3 μg L^{-1}	[70]
Diphenylamine	Fruits (*apple, pear, orange*)	HPLC-FLD	menthol and n-octanoic acid (1:4) / DES-based ultrasound-assisted LLME	0.05 μg L^{-1}	[71]
Endocrine disrupting compounds and hydroxymethylfurfural	Honey samples	GC-MS	[tetrabutylammonium chloride : dichloroacetic acid : ethylene glycol] (hydrophilic) and [tetrabutylammonium chloride : dichloroacetic acid : decanoic acid] (hydrophobic) / HLLE combined with DES-based DLLME	0.21–0.50 ng g^{-1}	[72]
Endocrine-disrupting compounds	Polyethylene packed injection solutions	GC-MS	menthol and decanoic acid (1:2) / air-assisted LLME based on SDES	14–33 ng L^{-1}	[73]
Endocrine-disrupting compounds	Water samples (*tap water, river water*)	HPLC-UV	C_9:C_{10}:C_{12} fatty acids (1:1:1) / air-assisted DLLME based on SFOD	0.96–2.30 μg L^{-1}	[74]
Endocrine-disrupting chemicals	Sewage	HPLC-FLD	octanoic acid and 1-dodecanol (1:3) / vortex-assisted DLLME based on SDES	1.33–2.92 ng L^{-1}	[75]
Endocrine-disrupting phenols	Water, milk and beverage	HPLC-UV	tetrabutylammonium chloride and methyl salicylate (1:1) / DES-based ultrasound-assisted DLLME	0.25–1.0 μg L^{-1}	[76]
Erythrosine	Biological samples (*blood, urine*) and pharmaceutical samples (*pharmaceutical tablet, syrup*)	UV-Vis	tetrabuthylammonium bromide and 1-octanol (1:2) / DES-based ultrasound-assisted LLME	3.75 μg L^{-1}	[77]
Erythrosine	Drug, water and powdered fruit juice	UV-Vis	tertbutylammonium bromide and decanoic acid (1:2) / DES-based LPME	0.53 μg L^{-1}	[78]
Flavonoids (*quercetin 3-O-rhamnoside, kaempferol 3-O-rhamnoside and their aglycones*)	*Camellia oleifera* flowers	HPLC-UV	choline chloride and lactic acid (1:2) / DES-based UAE	0.04–0.07 μg mL^{-1}	[79]
Flavonoids (*myricetin, morin, rutin, luteolin, hyperoside, quercitin, apigenin*)	*Lycium barbarum* L. fruits	HPLC-UV	choline chloride and *p*-toluene sulfonic acid (1:2) / DES-based UAE	0.11–0.89 μg g^{-1}	[80]
Flavonoids (*quercetin, naringenin, kaempferol, isorhamnetin*)	*Pollen Typhae*	HPLC-UV	choline chloride and 1,2-propanediol (1:4) / DES-based UAE	0.05–0.14 μg mL^{-1}	[81]
Flavonoids (*morin, quercetin*)	Vegetable and fruit samples (*apple, orange, pineapple, onion*)	HPLC-UV	tetramethylammonium chloride and ethylene glycol (1:3) / three-phase solvent bar microextraction based on DES	0.2–2.6 ng mL^{-1}	[82]
Fluoroquinolone antibiotics (*ofloxacin, norfloxacin, ciprofloxacin, enrofloxacin*)	Water samples (*reservoir water, pond water, tap water*)	HPLC-UV	thymol and heptanoic acid (2:1) / shaker-assisted LLME based on *in situ* formation of DES	3.0 ng mL^{-1}	[83]
Fluoroquinolones (*sparfloxacin, gatifloxacin, enrofloxacin, ciprofloxacin, lomefloxacin, levofloxacin*)	Milk, honey and water samples	MECC-UV	methyltrioctylammonium bromide and *n*-decanoic acid (1:2) / DES-based salting out-assisted DLLME combined with back-extraction	0.010 μg mL^{-1}	[84]
Fluoroquinolones *(levofloxacin hemihydrate, moxifloxacin hydrochloride, ciprofloxacin*	Water *(river water, lake water, wastewater treatment plant)*	HPLC-UV	thymol and hexanoic acid (1:3) / Lab-In-Syringe DES-based DI-SDME	6–9 ng L^{-1}	[85]

hydrochloride, lomefloxacin, enrofloxacin)					
Folic acid	Wheat flour	HPLC-UV	trioctylmethylammmonium chloride and isoamyl alcohol (1:4) / DES-based vortex-assisted DLLME	1.0 ng g^{-1}	[86]
Formaldehyde	Biological samples (*duck and pig blood*) and indoor air samples	HPLC-UV	trioctylmethylammonium chloride and 4-cyanophenol (1:1) / DES-based vortex-assisted LLME	0.2 µg L^{-1}	[87]
Free seleno-amino acids	Powdered and lyophilized milk samples	LC-ICP MS	lactic acid and glucose (5:1) / DES-based UAE	7.37–9.64 µg kg^{-1}	[88]
Fungicides (*azoxystrobin, fludioxonil, epoxiconazole, cyprodinil, prochloraz*)	Fruit juices (*peach, apple, grape, pear, orange, mango, banana*), and tea samples (*black, green, jasmine*)	HPLC-UV	L-menthol and decanoic acid (1:1) / ultrasound-assisted DLPME based on solidification of DES	0.75–8.45 µg L^{-1}	[89]
Ginsenosides	Traditional Chinese medicine (*Kang'ai injection*)	HPLC-UV	choline chloride and 1,4-butanediol (1:1) / aqueous two-phase extraction with DES	0.3–1.5 µg mL^{-1}	[90]
Herbicides (*simazine, prometryn, ametryn, metribuzin, sethoxydim, oxadiazon, diclofob–methyl*)	Wheat	GC-MS	[choline chloride and phenol (1:3)] (first step) and [choline chloride and butyric acid (1:2)] (second step) / microwave-assisted LLE combined with in syringe DLLME using DES	1.6–12 ng kg^{-1}	[91]
Herbicides (*bentazone, pyrazosulfuron-ethyl, pyribenzoxim, fenoxaprop-P-ethyl, anilofos*)	Water samples	HPLC-UV	thymol and *n*-butyric acid (1:1) / DES-based DLLME	20–80 µg L^{-1}	[92]
Icarrin and icarisid II	Rat plasma	UPLC-MS/MS	L-proline and ethylene glycol (1:4) / DES-based extraction	LOQ: 0.32–0.43 ng m L^{-1}	[93]
Illicit drugs	Urine samples	HPLC-MS	choline chloride and sesamol (1:3) / DLLME	0.042–0.072 µg L^{-1}	[94]
Indigo-carmine	Food samples (*energy drink, fruit yoghurt, ice cream, fruit juice, cake, gelatin candies, marshmallows, powdered drinks, biscuit, strawberry milk, liquid candy, chilli sauce, fruit jelly, red wine*)	UV-Vis	citric acid and glucose (1:3) / DES-based vortex-assisted LPME	3.3 ng mL^{-1}	[95]
Irgaphos 168 and irganox 1010	Polypropylene packed drinks	HPLC-UV	choline chloride (0.69 g) and oleic acid (2.8 mL) / HLLME based on *in situ* formation of DES	0.03–0.09 ng mL^{-1}	[96]
Isoflavones (*genistein, daidzein, genistin, daidzin*)	Soy-containing food samples (*soybeans, flour, pasta, breakfast cereals, cutlets, tripe, soy drink, soy nuts, soy cubes, dietary supplements*)	UHPLC-UV	choline chloride and citric acid (1:1) / DES-based UAE	0.06–0.14 µg g^{-1}	[97]
Lamotrigine	Plasma	UV-Vis	choline chloride and 1-phenylethanol (1:4) / DES-based USAEME followed by back-extraction	0.15 µg mL^{-1}	[98]
Lamotrigine	Plasma	HPLC-UV	choline chloride and ethylene glycol (1:2) / DES-based vortex-assisted microextraction	LOQ: 0.1 µg mL^{-1}	[99]
Lignans (*sesamol, sesamin, sesamolin*)	Edible oil samples (*sesame oil, blend oil*)	HPLC-UV	choline chloride and *p*-cresol (1:2) / DES-based ultrasound-assisted LLME	0.3–0.5 mg kg^{-1}	[100]
Liposoluble constituents	*Salvia Miltiorrhiza*	HPLC-UV	diethanolamine and hexanoic acid (1:1) / DES-based LPME	0.5–0.7 ng mL^{-1}	[101]
Lobetyolin and atractylenolide III	*Codonopsis* Radix	HPLC-UV	methyltrioctylammonium chloride and *n*-butanol (1:4) / DES-based DLLME	6×10^{-4} µg mL^{-1} (lobetyolin) and 3×10^{-3} µg mL^{-1}	[102]

				(atractylenolide III)	
Main active compounds	Zi-Cao-Cheng-Qi decoction	HPLC-UV	tetrabutylammonium chloride and hexanoic acid (1:1) / DES-based vortex-assisted DLPME	0.3–0.9 ng mL^{-1}	[103]
Malachite green	Farmed and ornamental aquarium fish water samples	UV-Vis	choline chloride and phenol (1:4) / DES-based ultrasound-assisted ELPME	3.6 µg L^{-1}	[104]
Malachite Green and Crystal Violet	Water (*tap water, fish-pond water, lake water*)	HPLC-UV	benzyltriethylammonium chloride and thymol (1:4) / DES-based DLLME	0.03–0.05 µg L^{-1}	[105]
Malondialdehyde and formaldehyde	Human urine, apple juice and rainwater	HPLC-UV	methyltrioctylammonium bromide and decanoic acid (1:2) / DES-based vortex-assisted LLME	2.0–10.0 ng mL^{-1}	[106]
Methadone	Biological samples (*blood, urine, saliva*)	GC-FID	salol and thymol (1:1) / ultrasonic-air-assisted based on solidification of settled DES	0.3–1.5 µg L^{-1}	[107]
Methadone	Biological samples (*urine, plasma*)	GC-FID	choline chloride and 5,6,7,8-tetrahydro-5,5,8,8-tetramethylnaphthalen-2-ol (1:2) / DES-based air-assisted ELLME	0.7 µg L^{-1}	[108]
Methyl red	Wastewater samples	UV-Vis	choline chloride and phenol (1:3) / DES-based vortex-assisted liquid phase extraction	2.3 µg L^{-1}	[109]
Methylene blue	Water samples (*wastewater, river water*)	UV-Vis	methyltrioctylammonium bromide and decanoic acid (2:1) / DES-based shaker-assisted LLME followed by back-extraction	0.5 ng mL^{-1}	[110]
Methylparaben	Cosmetic samples (*shampoo, shower gel, hair cream, moisturizing cream, suntan cream, hand cream, anti-acne cream, face care gel, liquid soap, face moisturizing gel, gel soap, toothpaste, eye area care cream, argan extract hair mask, face clay mask, hemp oil foot mask, facial cleansing gel, firming body lotion, antibacterial liquid soap, hair care mask, solid soap, clay hand mask*)	UV-Vis	proline, malic acid and water (1:2:3) / DES-based sonication-assisted DLLME	4.5 µg L^{-1}	[111]
Microcystins	Surface water samples	UHPLC-MS	choline chloride and phenol (1:2) / DES-based vortex-assisted LLME	0.14–0.16 ng mL^{-1}	[112]
3-Monochloropropane-1,2-diol	Refined edible oils	GC-MS	choline chloride and acetic acid (1:2) / DES-based air-assisted LLME	0.26 ng g^{-1}	[113]
Morphine and oxymorphone	Exhaled breath condensate samples	GC-MS	choline chloride, menthol, and phenylacetic acid / microwave enhanced DES-based air-assisted LLME	1.5−2.1 ng mL^{-1}	[114]
Mycotoxins	Edible insects (*cricket flour, silkworm pupae powder, black cricket powder*)	UHPLC-MS/MS	choline chloride and urea (1:2) / DES-based extraction	10–110 µg kg^{-1}	[115]
Natamycin	Fruit juices (*mango, apricot, pomegranate, grape, orange, sour cherry, apple*)	HPLC-UV	choline chloride, acetic acid and butanol (1:1:1) / DES-based surfactant-assisted salting-out HLLE	0.78 ng mL^{-1}	[116]
Neonicotinoid insecticide residues (*thiamethoxam, clothianidin, acetamiprid, thiacloprid*)	Water, soil and egg yolk samples	HPLC-UV	tetrabutylammonium bromide and decanoic acid (1:3) / DES-based DLLME	0.001–0.003 µg mL^{-1}	[117]
Niacinamide	Pharmaceutical and cosmetic samples	UV-VIS	sorbitol and glycerol / DES-based ultrasound-assisted DLLME	0.33 ng mL^{-1}	[118]
Niclosamide	Pharmaceutical and wastewater samples	UV-Vis	choline chloride and phenol (1:2) / DES-based LPME	0.112 µg L^{-1}	[119]

Nitroaromatic pollutants	Water samples (*well water, surface water, tap water*)	HPLC-UV	salol and DL-menthol (1:1) / effervescent-assisted EME based on solidification of settled DES	0.03–0.05 μg L^{-1}	[120]
Nitrophenols (*4-NP and 2,4-DNP*)	Water samples (*tap water, lake water fish-pond water*)	HPLC-UV	tetrabutylammonium bromide, thymol and octanoic acid (1:1:3) / DES-based DLLME	0.2–0.3 μg L^{-1}	[121]
Non-steroidal anti-inflammatory drugs (NSAIDs) (*salicylic acid, oxaprozin, diclofenac, ibuprofen*)	Water samples (*sea water, lake water, tap water*) and milk samples	HPLC-UV	1,1,3,3-tetramethylguanidine chloride and thymol (1:2) / DES-based ultrasound-assisted DLLME	0.5–1 μg L^{-1}	[122]
Nutraceutical compounds (*chlorogenic acids*)	Spent coffee grounds	HPLC-UV/MS	betaine and triethylene glycol (1:2) / DES-based UAE	0.04–0.10 ng mL^{-1}	[123]
Organochlorine pesticides	Cocoa powder	GC-ECD	*N,N*-diethanol ammonium chloride and pivalic acid (2:1) / solvent extraction combined with DES-based DLLME	0.011–0.031 ng g^{-1}	[124]
Organophosphorus pesticides (*phosalone, chlorpyrifos*)	Fruit juices (*red grape, sour cherry*)	HPLC-UV	choline chloride and phenol (1:2) / DES-based ultrasound-assisted LLME	0.070 and 0.096 ng mL^{-1}	[125]
Oxyprenylated phenylpropanoids (*ferulic acid, umbelliferone, boropinic acid, 7-isopentenyloxycoumarin, 4'-geranyloxyferulic acid (GOFA), auraptene*)	Vegetable oils (*olive, soy, peanuts, corn, sunflower*)	UHPLC-UV	phenylacetic acid and betaine (2:1) / DES-based DLLME	0.007–0.02 μg mL^{-1}	[126]
Parabens (*methyl paraben, ethlyparaben, propylparaben, butylparaben*)	Cosmetic oil products (*message, body, nail, hair, eyelash, sun oils*)	HPLC-UV	choline chloride and ethylene glycol (1:2) / DES-based vortex-assisted LPME	0.049–0.061 μg mL^{-1}	[127]
Parabens (*methylparaben, ethylparaben, propylparaben, butylparaben*)	Foods, cosmetics and pharmaceutical products	HPLC-UV	DL-menthol and polyethylene glycol 400 (1:1) / vortex-assisted DLLME	0.3–2 ng mL^{-1}	[128]
Parabens (*methylparaben, ethylparaben, propylparaben, butylparaben*)	Mouthwashes	HPLC-UV	DL-menthol and decanoic acid (4:1) / DES-based vortex-assisted LLME	4.6–6.1 μg L^{-1}	[129]
Parabens (*methylparaben, ethylparaben, propylparaben, butylparaben*)	Water (*tap water, river water, lake water, wastewater*)	HPLC-UV	DL-menthol and decanoic acid (2:1) / LLME based on *in situ* formation of DES	0.6–0.8 ng mL^{-1}	[130]
Parabens (*methylparaben, ethylparaben, propyl paraben, butylparaben*)	Personal care products (*mouthwash, lidocaine gel, aloe vera gel, skin tonic*)	HPLC-UV	thymol and enanthic acid (2:1) / gas flow-assisted DLPME	0.2–0.3 μg L^{-1}	[131]
Paracetamol	Synthetic urea and pharmaceutical samples	UV-Vis	betaine and oxalic acid (1:2) / shaker-assisted DES microextraction	14.9 μg L^{-1}	[132]
Patent Blue V	Syrup and water samples	UV-Vis	choline chloride and phenol (1:4) DES-based ultrasound-assisted ELPME	0.37 μg L^{-1}	[133]
Patulin	Fruit juices (*apple, orange, peach, apricot, grape, kiwi, cherry, mango*)	UV-Vis	tetrabutylammonium chloride and 2,3-butanediol (1:3) / DES based ultrasound-assisted ELPME	2.2 μg L^{-1}	[134]
Patulin	Fruit juices (*pear juice, mango juice, cider, apple juice, orange juice*) and dried fruits (*apple, fig, prune*)	UV-Vis	L-proline and glycerol (3:1) / air-assisted DES-based solidified homogeneous LPME	3.5 μg L^{-1}	[135]
Pesticides	Cucumbers	GC-FID	choline chloride, acetic acid, and 4-chlorophenol (1:1:1) / HLLE combined with DES-based DLLME	0.42–0.88 ng g^{-1}	[136]

Pesticides (*fipronil, fipronil-sulfide, fipronil-sulfone, boscalid*)	Environmental water and white wine samples	HPLC-UV	lactose, glucose, and water (5:1:3) / DLLME based on SFOD	0.8–1.3 μg L^{-1}	[137]
Pesticides (*diazinon, prometryn, terbutryn, bifenthrin, fenpropathrin, bromopropylate, fenamiphos-sulfone, phosalone, fenvalerate, deltamethrin*)	Farmer urine and plasma	GC-MS	menthol and phenylacetic acid (4.68 g:1.36 g) / DLLME based on SDES	2–17 ng L^{-1} (urine) and 4–36 ng L^{-1} (plasma)	[138]
Pesticides (*diazinon, metalaxyl, bromopropylate, oxadiazon, fenazaquin*)	Fruit juice (*grape, apple, sour cherry*), and vegetable samples (*fresh beet, cucumber, tomato, potato*)	GC-FID	choline chloride and *p*-chlorophenol / DES-based temperature-controlled LPME	0.13–0.31 ng mL^{-1}	[139]
Pesticides (*penconazole, cyproconazole, diniconazole, propiconazole, hexaconazole, triticonazole, difenconazole*)	Fruit juice (*orange*), and vegetable samples (*cucumber, tomato*)	GC-FID	choline chloride and 4-chlorophenol (1:2) / DES-based HS-SDME	0.82−1.0 μg L^{-1}	[140]
Pesticides (*dichlorvos, diazinon, simazine, prometryn, terbutryn, bifenthrin, fenpropathrin, bromopropylate, phosalone, deltamethrin*)	Fruit juices (*apple, grape, sour cherry, and apricot*), and vegetable samples (*cucumber, beet, potato, tomato*)	GC-MS	choline chloride and pivalic acid (1:2) / glass-filter-based DLPME using DES	3–26 ng L^{-1} (fruit juices) and 10.0–16.9 ng kg^{-1} (vegetable samples)	[141]
Pesticides (*penconazole, hexaconazole, diniconazole, tebuconazole, diazinon, fenazaquin, clodinafop-propargyl, haloxyfop-R-methyl*)	Fruit and vegetable samples (*grape juice, fresh apple, onion, cucumber, tomato*)	GC-FID	choline chloride and 4-chlorophenol (1:2) / DES-based gas-assisted DLPME	0.24–1.4 μg L^{-1}	[142]
Pesticides (*metalaxyl, penconazole, chlorpyrifos, haloxyfop-R-methyl, oxadiazon, clodinafop-propargyl, diniconazole, fenazaquin, fenpropathrin, fenoxaprop-P-ethyl*)	Green tea and herbal distillates	GC-FID	dichloroacetic acid, L-menthol and *n*-butanol (4:1:1) / DES-based DLLME	0.11–0.23 μg L^{-1}	[143]
Pesticides (*diazinon, ametryn, chlorpyrifos, penconazole, oxadiazon, diniconazole, fenazaquin*)	Honey	GC-FID	menthol and dichloroacetic acid (1:2) / DES-based DLLME	0.32–1.2 ng g^{-1}	[144]
Pesticides	Surface water	HPLC-MS/MS	choline chloride and acetylsalicylic acid (1:2) / DLLME	0.002−2.3 μg L^{-1}	[145]
Pesticides (*fipronil, triadimenol, tebuconazole, hexaconazole, diniconazole*)	Traditional Chinese medicine	HPLC-UV	choline chloride and phenol (1:4) / DES-based ultrasound-assisted ELPME	0.02–0.2 μg mL^{-1}	[146]
Pesticides	Urine samples	HPLC-MS	choline chloride and sesamol (1:3) / DLLME	LOQ: 0.02–0.76 μg L^{-1}	[147]
Pesticides	Water samples (*tap water, seawater, river water, underground water*)	GC-μECD	polyethylene glycol and thymol (2:1) / DES-based DLLME	0.001–0.02 μg L^{-1}	[148]
Pesticides	Water samples (*river water, seawater, tap water, groundwater*)	GC-μECD	[thymol and myristyl alcohol] (2:1) (extraction solvent) and [alanine, kojic acid, and water] (1:2:5) (as disperser solvent) / hydrophobic and hydrophilic DES-based DLLME	0.001–0.030 μg L^{-1}	[149]

Pesticides (*triadimefon, bifenthrin, bromopropylate, permethrin*)	Water samples	GC-ECD	DL-menthol and citric acid (1:2) / DES-based air-assisted LLME	0.34–3.3 μg L^{-1}	[150]
Pharmaceuticals and personal care products (*sulfamethazine, sulfamethoxazole, triclocarban, carbamazepine*)	Fish oil	UHPLC-MS/MS	choline chloride and glycerol (1:2) / DES-based ultrasound-assisted LPME	16.7–33.0 ng L^{-1}	[151]
Phenolic acids (*gallic, ferulic, syringic acids*)	Vegetable oils (*soybean, peanut, blending oils*)	HPLC-UV	choline chloride and urea (1:2) / DES-based vortex-assisted DLLME	0.010–0.021 μg g^{-1}	[152]
Phenolic antioxidants	Edible oil samples (*corn, sunflower, olive, canola, grape seed*)	GC-FID	tetrabutylammonium chloride and hydroquinone (1:2) / elevated temperature LLE combined with DES-based DLLME	0.13–0.42 ng mL^{-1}	[153]
Phenolic compounds (*3-hydroxytyrosol, p-coumaric acid, apigenin, oleuropein, cinnamic acid, gallic acid, (±)catechin hydrate, naringenin, caffeic acid, quercetin dihydrate*)	Agro-food industrial by-products (*olive cake, pear waste, onion, tomato waste*)	HPLC-UV	lactic acid and glucose (5:1), 15% water / DES-based UAE	0.0006–0.0891 μg g^{-1}	[154]
Phenolic compounds (*phenol, p-chlorophenol, 2,4-dichlorophenol, 2-nitrophenol, α-naphthol, bisphenol A*)	Beverage samples packed in plastics (*mango juice, sour cherry juice, orange juice, soda, mineral water*)	GC-MS	8-hydroxyquinoline and pivalic acid (1:2) / stir bar HF-LPME	9–22 ng L^{-1}	[155]
Phenolic compounds	Extra-virgin olive oil (*EVOO*)	HPLC-UV/MS	betaine and glycerol (1:2) / DES-based extraction	0.1–1.0 μg mL^{-1}	[156]
Phenolic compounds	Medicinal plants (*Larrea cuneifolia*)	HPLC-UV	lactic acid and dextrose (5:1) with 15% of H_2O / DES-based UAE	0.004–0.098 μg mL^{-1}	[157]
Phenolics (*chlorophenol, 2,3-dihydroxybenzoic acid, p-cresol, 4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol*)	Vegetable oil	HPLC-UV	choline chloride and 1,6-hexanediol (1:2) / DES-based DLLME	0.05–0.1 μg mL^{-1}	[158]
Phenolic compounds (*bisphenol-A, bisphenol-AF, tetrabromobisphenol-A, 4-tert-octylphenol*)	Water samples (*tap water, lake water, river water*)	HPLC-UV	C_8:C_9:C_{12} fatty acids (3:2:1) / DES-based gas-assisted LLME	0.22–0.53 μg L^{-1}	[159]
Phenolic compounds (*phenol, m-cresol, 2, 4-dichlorophenol, 2, 4, 6-trichlorophenol*)	Water samples (*tap water, lake water, wastewater*)	HPLC-UV	α-terpineol and 1-octanoic acid (1:2) / DES-based DLLME	0.15–0.38 μg L^{-1}	[160]
Phenoxy acid herbicides	Paddy field water samples	HPLC-UV	choline chloride and 2-chlorophenol (1:2) / DES-based ELLME	1.66 μg L^{-1}	[161]
Phthalate esters	Food-contacted plastics	GC-FID	*n*-hexyl alcohol and tetrabutylammonium bromide (4:1) / DES-based vortex-assisted LLME	1 μg L^{-1}	[162]
Phthalate esters	Packed milk samples	HPLC-UV	menthol and lauric acid (1:1) / DES-based vortex-assisted LLME	1.06–4.55 ng mL^{-1}	[163]
Phthalate esters	Soft drinks	UPLC-MS/MS	thymol and octanoic acid (2:1) / DES-based vortex-assisted DLLME	-	[164]
Phthalate esters	White wines and grape-based beverages	Nano-LC-UV	choline chloride and acetic acid (1:2) / vortex-assisted emulsification DLLME	2–17 ng mL^{-1}	[165]

Phthalates (*benzylbutyl phthalate, diisobutyl phthalate, diisopentyl phthalate, di-n-pentyl phthalate, di-(2-ethylhexyl) phthalate, di-n-octyl phthalate, diisononyl phthalate, diisodecyl phthalate*)	Beverages (*tea, apple-based beverage, pineapple juice*)	HPLC-UV	choline chloride and phenol (1:2) / DES-based vortex-assisted emulsification DLLME	5.1–17.8 μg L^{-1}	[166]
Phthalic acid esters	Soft drinks bottled in plastics *(green tea)* and cans *(tonic, lime, lemon soft drinks*), and infusions (*camomile, pennyroyal mint, linden teas*)	HPLC-UV	L-menthol and acetic acid (1:1) / DES-based DLLME based on SFOD	LOQ: 3.5–51.1 μg L^{-1}	[167]
Phthalic acid esters	Water samples (*tap water, mineral water*) and beverages (*apple juice drink*)	HPLC-UV	menthol and acetic acid (1:1) / DES-based DLLME	1.1–7.6 μg L^{-1}	[168]
Phytosterols	Animal based butter and oil samples	GC-FID	ethyl (methyl) ammonium chloride and pivalic acid / LLE combined with air-assisted LLME	0.73–1.5 ng mL^{-1}	[169]
Phytosterols (*lupeol, β-sitosterol, stigmasterol, campesterol, brassicasterol*)	Cow cream samples	GC-MS	[tetrabutylammonium bromide and ethylene glycol] and [tetrabutylammonium bromide, dichloroacetic acid, and octanoic acid] / HLLE combined with DES-based effervescent-assisted DLLME	0.06–0.26 μg kg^{-1}	[170]
Phytosterols	Cow milk	HPLC-UV	choline chloride and *p*-chlorophenol / DES-based DLLME	0.09–0.32 ng mL^{-1}	[171]
Phytosterols	Cow milk and cream samples	GC-FID	ethyl (methyl) ammonium chloride and pivalic acid / HLLE combined with DES-based DLLME	1.6–4.1 μg L^{-1}	[172]
Phytosterols	Cow milk butter samples	GC-FID	ethyl (methyl) ammonium chloride and pivalic acid / ultrasound and heat-assisted LLE combined with DES-based DLLME	0.51–1.3 ng g^{-1}	[173]
Plastic migrants	Plastic migrants from kombuchas	UHPLC-MS	thymol and octanoic acid (2:1) / DES-based vortex-assisted LLME	0.07–5.45 μg L^{-1}	[174]
Plastic migrants	Water samples (*treated wastewater, runoff water, pond water*)	UHPLC-MS/MS	thymol and menthol (2:1) DES-based LLME	LOQ: 0.013–0.425 μg L^{-1}	[175]
Polyphenols (*resveratrol, oxyresveratrol, piceatannol*)	Wine samples	HPLC-UV	tributylmethylammonium chloride and decanoic acid (1:3) / DES-based DLLME	1.69–2.53 μg L^{-1}	[176]
Polycyclic aromatic hydrocarbons	Aqueous samples (*industrial effluents from the production of bitumens*)	GC-MS	thymol and camphor (1:1) / ultrasound-assisted DLLME	0.0039–0.0098 μg L^{-1}	[177]
Polycyclic aromatic hydrocarbons	Honey samples	GC-MS	menthol and decanoic acid (1:2) / DES-based DLLME based on SFOD	14–52 ng kg^{-1}	[178]
Polycyclic aromatic hydrocarbons	Soft drinks	GC-MS/MS	camphor and hexanoic acid (1:1) / DES-based DLLME	0.01 μg L^{-1}	[179]
Polycyclic aromatic hydrocarbons	Tea, medicinal herbs and liquid foods	HPLC-FLD	choline chloride and hexafluoroisopropanol / DES-based LPME	0.6–4.2 ng L^{-1} (liquid foods) and 0.05–0.35 ng g^{-1} (solid foods)	[180]
Polycyclic aromatic hydrocarbons	Water samples (*tap water, well water, river water, wastewater*)	GC-MS	choline chloride and oxalic acid (1:2) / DES-based HS-SDME	0.003–0.012 μg L^{-1}	[181]
Polycyclic aromatic hydrocarbons	Water samples (*river water, lagoon water, lake water, well water*)	HPLC-FLD	tetrabutyl ammonium bromide and decanoic acid (1:2) / DLLME based on SDES	0.7–6.6 ng L^{-1}	[182]
Ponceau 4R	Water and cosmetic samples	UV-Vis	tetrabutylammonium bromide and decanoic acid (1:5) / DES-based ultrasound-assisted LPME	5.97 μg L^{-1}	[183]

Preservatives (*benzoic acid, sorbic acid, methyl paraben, ethyl paraben, propyl paraben, butyl paraben*)	Beverages	HPLC-UV	tetrabutylammonium bromide and acetic acid (1:2) (as disperser) / DLLME based on SFOD	0.02–0.05 mg L^{-1}	[184]
Primary aromatic amines (*total PAAs as aniline*)	Food contact materials (*polyamide cooking utensils, coloured kitchenware samples*)	UV-Vis	bis(2-ethylhexyl) phosphate and butylparaben (1:3) / DES-based vortex-assisted DLLME followed by back-extraction	1.5 µg L^{-1}	[185]
Pyrethroids pesticides (*transfluthrin, fenpropathrin, fenvalerate, ethofenprox, bifenthrin*)	Tea beverages (*green tea, red tea, oolong tea*) and fruit juices (*apple, red grape, purple grape*)	HPLC-UV	L-carnitine and hexafluoroisopropanol (1:2) / DES-based DLLME	0.06–0.17 ng mL^{-1}	[186]
Pyrethroid pesticides	Soil samples	UHPLC-MS	ethanolamine and *o*-cresol (1:1) / temperature-responsive DES-based UAE	0.1–0.6 µg kg^{-1}	[187]
Pyrethroid pesticides	Fruit juices	GC-MS	choline chloride and butyric acid (1:2) / gas-controlled DES-based evaporation-assisted DLLME	9–21 ng L^{-1}	[188]
Pyrethroid pesticides (*deltamethrin, etofenprox, fenpropathrin, bifenthrin*)	Juices (*litchi, lemon, grapefruit, pear, pineapple, grape*) and tea beverages (*green tea, flower tea, oolong tea, black tea*)	HPLC-UV	tetraoctylammonium bromide, 1-dodecanol and phenol (1:2:2) / DES-based film emulsification LPME	0.45–1.30 µg L^{-1}	[189]
Pyrethroid pesticides (*deltamethrin, cypermethrin, bifenthrin, cyhalothrin, permethrin*)	Milk samples	GC-FID	menthol and *p*-aminophenol (1:2) / pH-induced HLLME based on SFOD using DES decomposition	1.1–2.4 ng mL^{-1}	[190]
Pyrethroids (*bifenthrin, ß-cypermethrin, deltamethrin*)	Cereals (*corn, wheat, barley, oats*)	HPLC-UV	thymol and octanoic acid (1:4) / DES-based DLLME based on SFOD	2.0–2.7 mg kg^{-1}	[191]
Quercetin	Vegetable and fruit samples (*onion, grape, apple, tomato*)	UV-Vis	tetrabutylammonium chloride and decanoic acid (1:3) / DES-based USAEME	18.8 µg L^{-1}	[192]
Quercetin	Wine and food samples (*apricot, onion, celery, green tea, herbal tea, fig, dill weed, tomato, honey, apple juice, orange juice, red wine*)	UV-Vis	tetrabutylammonium chloride and ethyl glycol (1:2) / DES-based ultrasound-assisted DLPME	6.1 µg L^{-1}	[193]
Raloxifene and ethinylestradiol	Pharmaceutical wastewater	HPLC-UV	choline chloride and ethylene glycol (1:1) / DES-based carrier-mediated HF-LPME	5.0–10 ng mL^{-1}	[194]
Red dyes (*amaranth, ponceau 4R, allura red, azorubine, erythrosine*)	Food samples (*beverage, jelly, chocolate dragee*)	HPLC-UV	benzyltriethylammonium chloride and thymol (1:4) / DES-based vortex-assisted DLLME	0.01–0.08 µg L^{-1}	[195]
Rhodamine B	Chilli oil	UPLC-FLD	choline chloride and ethylene glycol (1:3) / DES-based extraction	1.67 µg kg^{-1}	[196]
Rhodamine B	Cosmetic products and water samples (*river water, seawater, cologne, nail polish cleaner, lipstick samples*)	UV-Vis	tetrabutylammonium chloride and decanoic acid (1:2) / DES-based LPME	2.2 µg L^{-1}	[197]
Salbutamol	Exhaled breath condensate samples	GC-MS	*N,N*-diethylethanolammonium chloride, dichloroacetic acid, and octanoic acid (1:1:1) / DES-based air-assisted LLME	0.370 µg L^{-1}	[198]
Sesamol	Sesame oil	HPLC-UV	choline chloride and ethylene glycol (1:2) / DES-based ultrasound-assisted LLME	0.02 mg kg^{-1}	[199]
Short-chain fatty acids	Beverages (*yoghurt-based carbonated drink, non-alcoholic beer, fruit juices: apple, orange, grape, mango*)	GC-FID	ethyl methyl ammonium chloride and carvacrol (2:1) / DES-based DLLME	0.89–6.6 µg L^{-1}	[200]

Steroidal hormones (*dydrogesterone, cyproterone acetate*)	Urine, plasma samples	HPLC-UV	methyltriphenylphosphonium iodide and ethylene glycol (1:4) / DES-based three-phase HF-LPME	0.5–2 μg L^{-1}	[201]
Steroid hormones (*estrone, 17β-estradiol, 17β-ethinylestradiol, estriol*)	Water samples (*tap water, agricultural well water, river water and wastewater*)	GC-MS	L-menthol and (1S)-(+)-camphor-10-sulfonic acid (5:1) / DES-based LPME	0.2–1.0 ng L^{-1}	[202]
Steroids (*prednisolone, cortisone, dexamethasone, triamcinolone acetonide, hydrocortisone acetate, 1,4-androstadiene-3,17-dione, testosterone, finasteride, 4-androstene-3,17-dione*)	Water samples (*tap water, river water*)	HPLC-UV	tetrabutylammonium bromide and acetic acid (1:2) / DLLME based on SFOD	1.0–9.7 ng mL^{-1}	[203]
Strobilurin fungicides (*azoxystrobin, pyrimethanil, kresoxim-methyl*)	Apple samples	HPLC-UV	methyltrioctylammonium chloride and *n*-butanol (1:3) / DES-based ultrasound-assisted DLLME	1.5−2 μg kg^{-1}	[204]
Strobilurin fungicides (*picoxystrobin, pyraclostrobin, trifloxystrobin*)	Water, juice, wine and vinegar samples	HPLC-UV	thymol and octanoic acid (1:5) / effervescence tablet-assisted microextraction based on SDES	0.15–0.38 μg L^{-1}	[205]
Sudan dyes	Food samples (*chilli sauce, chilli powder, ketchup*)	HPLC-UV	benzyltriethylammonium bromide and eugenol (1:2) / DES-based vortex-assisted DLLME	0.5−1 ng mL^{-1}	[206]
Sudan dyes	Spice samples (*chilli peppers, paprika, cumin, sumac*)	HPLC-UV	thymol and coumarin (1:1) / DES-based ultrasound-assisted solid-liquid microextraction	0.25−0.35 μg g^{-1}	[207]
Sudan dyes	Tomato chilli sauces	HPLC-UV	Brij-35 and hexafluoroisopropanol (1:20) / DES-based vortex-assisted LLME	0.0045–0.0118 μg g^{-1}	[208]
Sudan I	Food samples (*chilli oil, chilli sauce, duck egg yolk*)	HPLC-UV	choline chloride and sesamol (1:3) / DES-based vortex-assisted LLME	0.02 mg kg^{-1}	[209]
Sudan I	Food samples (*duck blood, chilli powder*)	HPLC-UV	trioctylmethylammonium chloride and oleic acid (1:2) / DES-based vortex-assisted LLME	0.3 μg kg^{-1}	[210]
Sulfonamides (*sulfapyridine, sulfamethazine, sulfamethoxine*)	Fruit juices (*apple juice, grape juice, peach juice, pear juice*) and black tea	HPLC-UV	trioctylmethylammonium chloride and 2-octanol (1:2) / DES-based ultrasound-assisted LLME	0.02–0.05 μg mL^{-1}	[211]
Sulfonamides (*sulfadiazine, sulfamerazine, sulfametoxydiazine, sulfamethoxazole*)	Water samples (*river water*)	HPLC-UV	choline chloride and phenol (1:2) / DES-based ELLME	1.2–2.3 μg L^{-1}	[212]
Sulfonamides (*sulfapyridine, sulfamethazine, sulfamethoxazole, sulfaphenazole*)	Water samples (*mineral water, sea water, tap water*)	UHPLC-UV	thymol and acetic acid (1:1) / DES-based vortex-assisted DLLME	0.78–3.42 ng mL^{-1}	[213]
Sunset Yellow dye	Effervescent vitamin C tablets	UV-Vis	menthol and decanoic acid (2:1) / DES-based ultrasound-assisted LLME	0.32 μg mL^{-1}	[214]
Sunset yellow FCF	Food and pharmaceutical products	UV-Vis	tetrabutylammonium bromide and decanoic acid (1:2) / DES-based ultrasound-assisted DLLME	0.05 μg L^{-1}	[215]
Surfactants	Exhaled breath condensate samples	HPLC-MS/MS	phosphocholine chloride and fatty acids (1:3) / DES-based air-assisted LLME	0.12–0.23 ng mL^{-1}	[216]
Synthetic colorants (*Amaranth, Carmine, Allura red, Brilliant blue*)	Beverages (*energy drinks, fruit juices, carbonated drinks*)	HPLC-UV	choline chloride and phenol (1:4) / DES-based effervescence-assisted DLLME	0.6−3.0 ng mL^{-1}	[217]
Synthetic dyes (*tartrazine, quinoline yellow, sunset yellow,*	Jellies and drinks	HPLC-UV	benzyltriethylammonium chloride and thymol (1: 4) / DES-based vortex-assisted DLLME	0.02−0.05 μg L^{-1}	[218]

brilliant blue, ponceau 4R, indigo carmine, allura red, carmoisine)					
Synthetic pigments (*Lemon yellow, Carmine, Sunset yellow, Allura red, Brilliant blue, Erythrosine, Indigo, Amaranth*)	Beverages	HPLC-UV	tetrabutylammonium chloride and octanoic acid (1:2) / DES-based LLME	0.016–1.12 ng mL^{-1}	[219]
Tamoxifen and its metabolites	Plasma samples	HPLC-UV	thymol and nonanoic acid (1:1) / DES-based vortex-assisted DLLME	0.3–3.2 μg L^{-1}	[220]
Tartrazine	Water, drug and beverage samples	UV-Vis	tetrabutylammonium bromide and decanoic acid (1:3) / DES-based ultrasound-assisted microextraction	0.084 mg L^{-1}	[221]
Terpenes	Spices (*cinnamon, cumin, fennel, clove, thyme, nutmeg*)	GC-MS	tetrabutylammonium bromide and dodecanol (1:2) / DES-based HS-SDME	LOQ: 0.47–86.40 μg g^{-1}	[222]
Testosterone and methyltestosterone	Milk	HPLC-UV	menthol, lauric acid, and decanoic acid (3:1:1) / DES-based LLME	0.067–0.2 μg mL^{-1}	[223]
Tetracyclines (*oxytetracycline, tetracycline, doxycycline*)	Milk samples	HPLC-UV	octanoic acid and thymol (1:1) / DES-based DLLME	1.5–8.5 μg L^{-1}	[224]
Tetracyclines (*oxytetracycline, tetracycline, doxycycline*)	Infant formulas	HPLC-UV	thymol, ethylene glycol, and benzyl alcohol (2:2:1) / DES-based vortex-assisted ELLME	0.88–2.74 μg kg^{-1}	[225]
Tetracyclines (*tetracycline, doxycycline, oxytetracycline*)	Water samples (*seawater, agriculture water, river water, underground water, tap water*)	HPLC-UV	choline chloride, thymol, and nonanoic acid (1:2:2) / DES-based air-bubble-assisted DLLME	1.2–8.0 μg L^{-1}	[226]
Tetracyclines (*tetracycline, oxytetracycline, chlortetracycline*)	Water samples (*tap water, lake water, reservoir water, drinking water*)	HPLC-UV	methyltrioctylammonium chloride and nonanoic acid (1:2) / DES-based LLME	0.5–2.0 ng mL^{-1}	[227]
Tetracyclines (*oxytetracycline, doxycycline, tetracycline*)	Water samples (*well water, rainforest water, coastal seawater, gardening water, mineral water*)	HPLC-UV	[thymol and octanoic acid (1:1)] (hydrophobic) and [choline chloride and ethylene glycol (1:2)] (hydrophilic) / hydrophobic and hydrophilic DES-based DLLME	1.37–4.38 μg L^{-1}	[228]
Thiabendazole	Fruit samples (*orange, apple, grapefruit, peach, lemon, kumquat, mandarin, nectarines, strawberry, bitter orange quince, apricot, pineapple*)	UV-Vis	glycolic acid and betaine (1:2) / DES-based vortex-assisted DLLME	0.1 μg L^{-1}	[229]
Thiophanate-methyl and carbendazim	Water samples (*lake water, tap water*)	HPLC-UV	menthol and 1-ctanol (1:3) / DES-based vortex-assisted LLME	0.007–0.053 μg mL^{-1}	[230]
Thiophenols (*thiophenol, 4-methylthiophenol, 4-aminothiophenol, 4-bromothiophenol*)	Water samples (*tap water, wastewater*)	GC-FID	choline chloride and *p*-cresol (1:2) / DES-based ELLME	10–15 μg L^{-1}	[231]
Triarylmethane dyes (*malachite green, crystal violet*)	Shrimp water samples	HPLC-UV	thymol and camphor (1:1) / DES-based ELLME	0.09–0.13 μg L^{-1}	[232]
Triazine herbicides (*simazine, ametryn, prometryn, terbuthylazine*)	Vegetable oils (*soybean oil, maize oil, sunflower seed oil, peanut oil*)	HPLC-UV	tetrabutylammonium chloride and ethylene glycol (1:2) / DES-based vortex-assisted reversed-phase LLME	0.60–1.50 μg L^{-1}	[233]
Triclosan	Personal care products (*facial cleanser, soap, toothpaste, hand sanitizer*) and environmental water samples (*tap water, surface water, rainwater, lake water, wastewater from a sewage treatment plant*)	HPLC-UV	triclosan and 2,2,4-trimethyl-1,3-pentanediol / LLME based on *in situ* formation of DES	0.5 μg L^{-1}	[234]

Triclosan and alkylphenols	Water samples (*lake water, river water, well water, tap water, rainwater*)	HPLC-UV	menthol and myristic acid (3:1) / temperature-controlled air-assisted LLME based on the solidification of floating DES	0.1–0.5 μg L^{-1}	[235]
UV filters (*2,4-dihydroxybenzophenone, benzophenone, 2-hydroxy-4-methoxybenzophenone*)	Water samples (*swimming pool water, river water*)	HPLC-UV	trioctylmethylammonium chloride and decanoic acid (1:3) / DES-based ultrasound-assisted DLLME	0.15–0.30 ng mL^{-1}	[236]
UV filters (*benzophenone-type*)	Water samples (*swimming pool water, river water, wastewater*)	HPLC-UV	DL-menthol and decanoic acid mixture (1:1) / DES-based air-assisted DLLME	0.05–0.2 ng mL^{-1}	[237]
UV filters (*benzophenone, salicylate*)	Water samples (*swimming pool water, well water, river water*)	HPLC-UV	C_{10}:C_{12} fatty acids (2:1) / air-assisted LLME based on SDES	0.045–0.54 μg L^{-1}	[238]
Vincristine	Plasma	HPLC-UV	methyltrioctylammonium chloride and *n*-butanol (1:3) / DES-based vortex-assisted DLLME	0.02 μg L^{-1}	[239]
Volatile aromatic hydrocarbons (*benzene, toluene, ethylbenzene, xylene isomers*)	Water (*well water, surface water*) and urine samples	GC-FID	choline chloride and chlorophenol (1:2) / DES-based HS-SDME	0.05–0.90 ng mL^{-1}	[240]
Warfarin	Water, plasma and urine samples	HPLC-UV	borneol and decanoic acid (1:3) / DES-based air-assisted LLME	0.5−2.7 μg L^{-1}	[241]

3 Determination of inorganics

Although the majority of the described procedures are devoted to the determination of organic compounds, articles focused on the determination of inorganic analytes are also significantly represented (23% of the total number of reviewed papers) [243-311]. The applications of DES-based liquid–liquid extraction procedures for the determination of inorganic analytes are summarised in **Table 2**. Most of these articles (58%) are devoted to the determination of a single element [243-282], while 17% and 12% of the articles present the determination of two [283-294] or more elements [295-302], respectively. Only a few articles describe speciation analysis of elements, such as arsenic [303], chromium [304, 305], iron [306] and selenium [307-309], and only 2 articles are devoted to the determination of anions. One reported a DES-based vortex-assisted DLLME combined with HPLC for the determination of nitrite in water and biological samples [310], and another described a DES-based vortex-assisted microextraction for the determination of orthophosphate in water samples by the molybdenum blue method [311]. Examples of the determination of inorganic compounds in various matrices using DES-based procedures will be discussed below.

In regard to the determination of inorganic analytes, various atomic absorption techniques, such as flame atomic absorption spectrometry (FAAS) and electrothermal atomic absorption spectrometry (ETAAS), were most often used for detection, with 46% and 26% representation, respectively, while techniques such as ICP-OES [255, 264, 300-302] or UV-Vis spectrophotometry [251, 254, 261, 279, 306, 307, 311] have been reported less frequently. The determination of metals using a DES-based preconcentration followed by AAS detection was covered in detail in our previous review, published early last year [312]; we will therefore limit ourselves to a brief discussion of the issue here. Spectrophotometric detection was mainly used in the analysis of water samples [251, 254, 261, 279, 306, 307], as well as food samples (tomato sauce, green and black tea, and dark chocolate) [251], (apple, banana, carrot and potato) [261]. A remarkable method based on the use of digital image colorimetry detection was proposed by Lemos et al. [280]. The DES-based ultrasound-assisted LPME was based on the extraction of V complex with Br-PADAP into choline chloride-phenol (1:2) DES. The addition of tetrahydrofuran and ultrasonic energy were used to promote the dispersion of the extraction solvent in the aqueous solution. After centrifugation and removal of the enriched phase, detection was carried out directly in the solvent by digital image colorimetry, with an LOD of 0.3 μg L^{-1}. The procedure was applied to the determination of V(V) and V(IV) species in water samples and total vanadium in food samples [280].

Regarding samples, the most frequently analysed were water (37%) and food (34%), followed by fruit and vegetable samples (12%), while others, such as biological or environmental samples (soils, sediments, cosmetics, rocks, etc.), were analysed less frequently. It should be noted that with the analysis of solid samples, a sample pretreatment step consisting of either sample decomposition/digestion [244, 247-249, 258, 259, 272, 274, 275] or the extraction/leaching of the analytes into a suitable solvent [265] is usually necessary. Unfortunately, authors quite often pay only minimal attention to the sample pretreatment step and focus only on the DES-based extraction step. Procedures using a DES for direct extraction of the analytes from solid samples have also been reported. Kanberoglu et al., for example, reported a DES-based digestion followed by a DES-based ultrasound-assisted LPME procedure for copper determination [256]. The liver samples were first digested using a DES consisting of lactic acid and choline chloride; then the residue was dissolved in distilled water, and the Cu(II) ions were complexed with sodium dimethyl dithiocarbamate and extracted into tetrabuthylamonium chloride–decanoic acid DES. The quantification of copper was performed using FAAS technique with an LOD of 4 μg L^{-1} [256]. A DES-based procedure was applied for

the extraction of manganese from vegetable samples, such as basil herb, spinach, dill and cucumber peels, prior to ICP-OES analysis [264]. The method is based on the solubilisation of manganese in a choline chloride-based DES medium. The LODs were found to be in the range of 0.34–1.23 μg L^{-1} depending on the acid component of the DES (tartaric acid, oxalic acid and citric acid) [264]. Rastegarifard et al. described a DES-based extraction method for the determination of total Hg in marine fish samples using cold vapor atomic absorption spectrometry. The method is based on the complete dissolution of samples in a choline chloride–oxalic acid DES without additional microwave or pressure processing. The remaining small particles were digested quickly after adding 7 mol L^{-1} HNO_3. Since a clear, residue-free solution was obtained, further steps, such as centrifugation and filtration, are not necessary. The LOD of the method was found to be 0.03 μg g^{-1}. In addition, several fish samples were analysed using a DES-based method and a conventional acid digestion method, with no significant difference found between the results of the proposed method and the reference method [262]. Oil samples can also be pretreated using some well-known digestion procedure and subsequently analysed using DES microextraction [257]. However, a simpler method based on diluting the sample with ethyl acetate followed by reversed-phase DLLME has also been reported [285].

As for microextraction procedures, we can state that various modalities of the LLME technique have been used, often aided by the use of auxiliary energy such as ultrasound [243, 246, 247, 251-253, 256, 257, 272, 278, 280, 281, 283, 284, 288-290, 292, 295, 298, 303, 305, 306, 308, 309], vortex [244, 258, 261], microwave [301], or both ultrasound and vortex [249]. Air-assisted [270, 275, 277, 286] and effervescence-assisted [260] procedures have also been described. In the majority of cases, a DES was used as the extraction solvent. However, Sorouraddin et al. reported a procedure in which a DES miscible with both aqueous and organic phases, prepared by mixing glycolic acid and mandelic acid at a molar ratio of 2:1, was applied as a dispersive solvent in a reversed-phase DLLME for the extraction of Cd(II) and Zn(II) ions from oil samples prior to FAAS quantification. The procedure shows good detection limits of 0.12 μg L^{-1} and 0.18 μg L^{-1} for Cd(II) and Zn(II), respectively, and was applied for the analysis of fish oil, butter and margarine samples [285].

Table 2 Examples of DES-based liquid-liquid extraction procedures for the determination of inorganic analytes

Analyte	Matrix	Detection	Selected DES / Procedure	LOD	Refs
Al	Water samples (*river, drinking, mineral, seawater, spring water*) and food samples (*rice, cultivated mushroom, chicken meat*)	ETAAS	choline chloride and phenol (1:4) / DES-based ultrasound-assisted LPME	0.032 μg L^{-1}	[243]
As	Water (*wastewater, well water, bottled water*), rice and honey samples	HG-AAS	benzyltriphenylphosphonium chloride and ethylene glycol (1:1) / DES-based vortex-assisted LPME	6.5 ng L^{-1}	[244]
Au	Plating bath solution	SQT-FAAS	choline chloride and phenol (1:2) / DES-based LPME	5.1 μg L^{-1}	[245]
Cd	Celery and apple samples	SQT-FAAS	chloline chloride and phenol (1:2) / DES-based ultrasound-assisted LPME	0.35 μg L^{-1}	[246]
Cd	Food samples (*bean stew, black tea, chicken shawarma, canned corn, corn, canned mushroom, cheese, mushroom, fish tissue, tomato, meat, canned fish, rice and spinach*) and water samples (*tap water, wastewater, ice tea*)	ETAAS	choline chloride and phenol (1:4) / DES-based ultrasound-assisted LPME	0.023 ng L^{-1}	[247]
Cd	Food samples (*cow and goat cheese, goat milk*) and water samples (*wastewater, snow water, rainwater, tap water*)	FAAS	trihexyltetradecylphosphonium chloride and pivalic acid (1:4) / DES-based LPME	1.6 μg L^{-1}	[248]
Cd	Water samples (*drinking water*) and some food samples (*rice, wheat, watermelon*)	GFAAS	L-menthol and salicylic acid (4:1) / DES-based ultrasound-vortex-assisted DLLME	0.37×10^{-4} μg L^{-1}	[249]
Co	Linden tea samples	SQT-FAAS	choline chloride and phenol (1:2) / DES-based LPME	2.0 μg L^{-1}	[250]
Co	Water samples (*tap water, river water*) and food samples (*tomato sauce, green and black tea, dark chocolate*)	UV-Vis	*n*-phenyliminodiacetic acid and choline chloride (2:1) / DES-based ligandless ultrasound-assisted LPME	5.23 μg L^{-1}	[251]
Cr	Urine samples	ETAAS	benzyltriphenylphosphonium bromide and phenol (1:7) / ultrasound assisted DLLME followed by SFOD	2.0 ng L^{-1}	[252]
Cr	Water samples (*wastewater, groundwater, seawater, canal water, mineral water, tap water*)	GFAAS	$ZnCl_2$ and acetamide (1:3) / DES-based ultrasound-assisted DLLME	6.0 ng L^{-1}	[253]
Cr	Water samples (*tap water, wastewater, mineral water, fish pool, well water*)	UV-Vis	benzyltriethylammonium chloride and phenol (1:4) / DES-based DLLME	1.5 μg L^{-1}	[254]
Cu	Lake and river sediment samples	ICP-OES	choline chloride and oxalic acid (1.5:1) / DES-based extraction	1.2 μg L^{-1}	[255]
Cu	Liver samples	MS-FAAS	[choline chloride and lactic acid (1:2)] and [tetrabuthylamonium chloride and decanoic acid (1:2)] DES-based digestion and ultrasound-assisted ELPME	4.00 μg L^{-1}	[256]
Cu	Olive oil and water samples (*lake water, wastewater*)	FAAS	choline chloride and phenol (1:4) / DES-based ultrasound-assisted LPME	6.6 μg L^{-1}	[257]
Cu	Quince samples	SQT-FAAS	choline chloride and phenol (1:2) / DES-based vortex-assisted ELPME	0.5 μg L^{-1}	[258]
Cu	Vegetable samples (*spinach, lettuce, broccoli, potato, carrot, parsley*)	FAAS	benzyltriphenylphosphonium bromide and ethylene glycol (1:8) / DES-based HLLME	0.13 μg L^{-1}	[259]
Cu	Water samples (*tap water, lake water*)	FAAS	choline chloride and phenol (1:3) / DES-based effervescence-assisted DLLME	2.9 μg L^{-1}	[260]

Fe	Water samples (*bottled water, tap water, lake water, river water, well water*) and food samples (*apple, banana, carrot, potato*) samples	UV-Vis	thymol and lauric acid (2:1) / temperature-controlled vortex-assisted LLME based on SDES	1.5 μg L^{-1}	[261]
Hg	Fish samples	CVAAS	choline chloride and oxalic acid (1:2) / DES-based extraction	0.03 μg g^{-1}	[262]
Mn	Blood samples	FAAS	zinc chloride and acetamide (1:2) / DES-based extraction	0.29 μg L^{-1}	[263]
Mn	Vegetable samples (*basil herb, spinach, dill, cucumber peel*)	ICP-OES	choline chloride and tartaric acid, or oxalic acid, or citric acid (1:1) / DES-based extraction	0.34–1.23 μg L^{-1}	[264]
Mn	Wastewater and coffee samples	FAAS	choline chloride and phenol (1:2) / DES-based LPME	0.52 μg L^{-1}	[265]
Ni	Spinach samples	SQT-FAAS	choline chloride and phenol / DES-based LPME	3.8 μg L^{-1}	[266]
Ni	Water samples (*tap water, river water, mineral water, seawater*)	FAAS	choline chloride and 4-boromo phenol / DES-based DLLME	1.7 μg L^{-1}	[267]
Ni	Water samples (*waste, sea, mineral, well*) and food samples (*onion, parsley, cigarette*)	MS-FAAS	tetrabutylammonium chloride and decanoic acid (1:3) / DES-based LPME	0.13 μg L^{-1}	[268]
Pb	Blood samples	ETAAS	choline chloride and urea (1:2) / carrier-mediated HF-LPME	0.1 ng mL^{-1}	[269]
Pb	Gasoline samples	GFAAS	menthol, mandelic acid and glycolic acid (2:1:1) / DES-based air-assisted LLME	1.6 ng L^{-1}	[270]
Pb	Milk samples	SQT-FAAS	choline chloride and phenol (1:2) / DES-based LPME	8.7 μg L^{-1}	[271]
Pb	Tobacco and food samples (*cigarette, parsley, onion*)	FAAS	tetrabutylammonium chloride and decanoic acid / DES-based ultrasound-assisted LPME	4.4 μg L^{-1}	[272]
Pb	Water samples (*tap water, river water, seawater*)	FAAS	choline chloride and 2-chlorophenol (1:2) / DES-based ELLME	5.93 μg L^{-1}	[273]
Pb	Water samples (*tap, river, canal, wastewater*) and food samples (*black tea, canned fish, green tea, spinach, boiled wheat, chicken meat, beef meat, canned mushroom*)	FAAS	choline chloride and decanoic acid (1:1) / DES-based microextraction	0.086 μg L^{-1}	[274]
Pb	Water samples (*lake, waste, river, seawater*) and food samples (*black tea, green tea, cumin, cows meat, linseed, canned fish, chicken meat, potato*)	GFAAS	choline chloride and phenol (1:4) / DES-based air-assisted LPME	0.60 ng L^{-1}	[275]
Pd	Catalytic converter and road dust samples	ETAAS	phenyl salicylate (salol) and DL-menthol (1:1) / DES-based temperature-controlled LLME	0.03 μg L^{-1}	[276]
Pd	Water samples (*tap, mineral, sea, river water*) and acid-digested environmental samples	FAAS	choline chloride and phenol (1:4) / DES-based air-assisted ELLME	1.2 μg L^{-1}	[277]
Se	Water samples (*tap water, river water, mineral water, well water*) and food samples (*rice flour, mushroom, soya, corn flour, broccoli, pumpkin, buckwheat flour, oat flour, egg, tomato, brown rice, green tea, canned tuna, canned shrimp, chicken liver*)	HG-AAS	menthol and lauric acid (1:3) / DES-based ultrasound-assisted LLME	0.25 ng L^{-1}	[278]
Th	Water samples (*river water and seawater*) and rock sample	UV-Vis	1-hexyl-3-methylimidazolium and salicylic acid (1:1) / DES-based DLLME	2.1 ng mL^{-1}	[279]

V	Food samples (*beetroot, passion fruit, eggplant, plum, spinach*) and water samples (*river water and well water*)	Digital image colorimetry	choline chloride and phenol (1:2) / DES-based ultrasound-assisted LPME	0.3 μg L^{-1}	[280]
V	Foodstuffs (*tomato, cucumber, banana, black tea, apple, cabbage, egg, chicken meat, cultivated mushroom, spinach, honey, canned fish, cow meat, bean, coffee, cheese, red wine, white wine, cow milk, ice tea*)	ETAAS	choline chloride and phenol (1:4) / DES-based ultrasound-assisted DLLME	0.025 μg L^{-1}	[281]
Zn	Fish and eel samples	FAAS	choline chloride and phenol (1:2) / DES-based extraction	0.041 μg kg^{-1}	[282]
As and Se	Rice samples	HG-AAS	proline and malic acid (2:1) / DES-based ultrasound-assisted microextraction	3.0 ng L^{-1} (Se) and 1.7 ng L^{-1} (As)	[283]
Cd and As	Wine samples	FAAS	trioctylmethylammonium chloride and DL-lactic acid (1:3) / DES-based ultrasound-assisted DLLME	0.080 μg L^{-1} (Cd) and 0.30 μg L^{-1} (As)	[284]
Cd and Zn	Oil samples	FAAS	glycolic acid and mandelic acid (2:1) / DES as a disperser in reversed-phase DLLME	0.12 μg L^{-1} (Cd) and 0.18 μg L^{-1} (Zn)	[285]
Cd and Zn	Water samples (*surface water, tap water*) and juices (*cherry juice, peach juice*)	FAAS	menthol, sorbitol, and mandelic acid (1:2:1) / DES-based air-assisted LLME based on SDES	0.15 μg L^{-1} (Cd) and 0.12 μg L^{-1} (Zn)	[286]
Co and Ni	Water samples (*river water, well water, urban water*) and juices (*grape juice, peach juice*)	FAAS	choline chloride and 4-aminophenol (1:1) / DES-based DLLME	0.30 μg L^{-1} (Ni) and 0.22 μg L^{-1} (Co)	[287]
Ni and Co	Food samples (*broccoli, spinach*) and water samples (*tap, mineral, sea, river*)	FAAS	DL-menthol: decanoic acid (1:1) / DES-based ultrasound-assisted DLLME based on SFOD	0.3 μg L^{-1} (Ni) and 0.4 μg L^{-1} (Co)	[288]
Ni and Zn	Food samples (*hydrogenated edible oil, milk, fish samples*)	FAAS	tetrabutylammonium chloride and decanoic acid (1:2) / DES-based ultrasound-assisted LLME	0.029 μg kg^{-1} (Ni) and 1.5 μg kg^{-1} (Zn)	[289]
Pb and Cd	Cosmetic samples (*lipstick, eye shadow*)	FAAS	$ZnCl_2$ and acetamide (1:2) / DES-based ultrasound-assisted microextraction	0.86 μg L^{-1} (Cd) and 0.66 μg L^{-1} (Pb)	[290]
Pb and Cd	Vegetable samples (*leek, spinach, dill, parsley, mint, arugula, eggplant, dry tea*)	FAAS	citric acid and sucrose (1:3) / DES-based microextraction	0.17 ng mL^{-1} (Pb) and 0.35 ng mL^{-1} (Cd)	[291]
Pb and Cd	Water samples (*tap water, mineral water, river water, well water*) and food samples (*sesame, peanut, eggplant, corn, wheat, soy, cucumber*)	FAAS	L-menthol and dodecanoic acid (3:1) / DES-based ultrasound-assisted LPME	0.24 μg L^{-1} (Pb) and 0.46 μg L^{-1} (Cd)	[292]
Se and As	Edible mushroom	GFAAS	choline chloride and oxalic acid (1:2) / DES-based extraction	0.32 μg L^{-1} (Se) and 0.50 μg L^{-1} (As)	[293]

Se and As	Fish samples	ETAAS	choline chloride and oxalic acid (1:2) / DES-based digestion (extraction)	0.75 μg kg^{-1} (Se) and 0.46 μg kg^{-1} (As)	[294]
Cu, Cd, and Pb	Honey	FAAS	citric acid and sucrose (3:2) / DES-based ultrasound-assisted DLLME	0.23–0.87 μg kg^{-1}	[295]
Cd, Pb, and Cu	Milk samples (*milk, honey milkshake, babana milkshake*)	FAAS	menthol, sorbitol and mandelic acid (1:2:1) / DES-based DLLME	0.38–0.42 μg L^{-1}	[296]
Hg, Pb, and Cd	Soil and vegetables irrigated with treated municipal wastewater	GFAAS	1-decyl-3-methylimidazolium chloride and 1-undecanol (1:2) / DLLME based on SDES	0.01–0.03 μg kg^{-1}	[297]
Pb, Cd, Co, and Ni	Water samples (*lake water, river water, well water*)	HPLC-UV	trihexyl(tetradecyl)phosphonium chloride and thiosalicylic acid (1:2) / DES-based ultrasound-assisted DLLME with solidification of the aqueous phase	0.05–0.13 μg $^{-1}$L	[298]
Pb, Co, Ni, and Mn	Edible oils (*sunflower oil, baby oil, trout oil, waste frying oil and syrup-soaked pastry oil*)	MS-FAAS	choline chloride and urea (1:2) / DES-based LPME	2.4 μg L^{-1} (Pb) , 4.6 μg L^{-1} (Co), 7.5 μg L^{-1} (Ni), and 1.0 μg L^{-1} (Mn)	[299]
Cd, Co, Hg, Ni, Pb, and V	Oral and parenteral drugs	ICP-OES	DL-menthol and decanoic acid (2:1) / DES-based DLLME	0.05–1.2 μg L^{-1}	[300]
Cd, Cu, Fe, Mn, and Zn	Medicinal herb samples	ICP-OES	choline chloride, oxalic acid and water (1:1:1) / DES-based microwave-assisted extraction (MAE)	0.008–0.36 mg kg^{-1}	[301]
As, Cr, Mo, Sb, Se, and V	Soil samples	ICP-OES	choline chloride and oxalic acid (1:2) / DES-based UAE	0.009–0.1 μg g^{-1}	[302]
Speciation of arsenic (*water samples*) and total arsenic (*food and environmental samples*)	Water samples (*lake water, mineral water, tap water, river water*), foods (*edible mushrooms, fish, green tea, black tea, rice*) and sediment, soil, cigarette samples	ETAAS	choline chloride and phenol (1:3) / DES-based ultrasound-assisted LPME	10 ng L^{-1}	[303]
Speciation of chromium	Water samples (*river water, well water, tap water, wastewater*) and urine	GFAAS	choline chloride and phenol (2:3) / DES-based microextraction	0.096 μg L^{-1}	[304]
Speciation of chromium (*water samples*) and total chromium (*food samples*)	Water samples (*bottled mineral water, tap water, seawater, wastewater*) and food samples (*fish, mushroom*) samples	ETAAS	choline chloride and ethylene glycol (1:3) DES-based ultrasound-assisted LPME	4.3 ng L^{-1}	[305]
Speciation of iron	Water samples (*steam water, drum water, tap water*)	UV-Vis	choline chloride and 4-chlorophenol (1:3) / DES-based ultrasound-assisted temperature-controlled DLPME	1.2 μg L^{-1}	[306]
Speciation of selenium	Water samples (*tap water, river water, well water, wastewater, mineral water*)	UV-Vis	benzyltriphenylphosphonium bromide and 1-undecanol (1:4) / DLLME based on the SDES	0.76 μg L^{-1}	[307]
Speciation of selenium (*water and ice tea samples*) and total selenium (*food samples*)	Water samples (*tap water, mineral water*), ice tea and food samples (*sheep milk, cow's milk, yoghurt, mixed fruit juice, egg, orange juice, grape fruit, honey, canned fish, edible mushroom*)	ETAAS	choline chloride and phenol (1:3) / DES-based ultrasound-assisted LPME	4.61 ng L^{-1}	[308]
Speciation of selenium (*water samples*) and its total content (*milk formula and cereals*)	Water, milk formula and cereals	GFAAS	choline chloride and phenol (1:3) / DES-based ultrasound-assisted DLLME	0.029 μg L^{-1}	[309]

Nitrite	Water samples (*well water, tap water, lake water*) and biological samples (*saliva, human urine*)	HPLC-UV	trioctylmethylammonium chloride and oleic acid (1:2) / DES-based vortex-assisted DLLME	0.2 µg L^{-1}	[310]
Orthophosphate	Water samples (*tap water, river water*)	UV-Vis	glucose and choline chloride / DES-based vortex-assisted microextraction	0.2 µg L^{-1}	[311]

Concluding remarks and future trends

The unique physicochemical properties of DESs as well as the simplicity of the combination of DES-based extraction techniques with the main chromatographic and spectroscopic methods allow their use in the analysis of various samples. As we have seen, DESs have been used for liquid–liquid (micro)extraction of both organic and inorganic analytes. The wide range of organic compounds separated and pre-concentrated with their use include pharmaceuticals, plant bioactive compounds, pesticides, dyes, polycyclic aromatic hydrocarbons, phthalates, parabens, endocrine disrupting compounds as well as others. In the case of inorganic analysis, the fact that a very narrow range of DES-LLME applications is devoted to speciation analysis of elements as well as for determination of anions is worth mentioning. The application of DESs in LLE/LLME offers many advantages compared to classical organic solvents. In addition, their preparation is simple, and they are generally considered to be green solvents. Therefore, DESs attract and motivate researchers to look for new possibilities of their use. However, DESs are currently not widely available, which limits their application in routine analyses in commercial laboratories. The first attempts to automate analytical methods using DESs have been published, and this will contribute to the development of new analytical methods. We hope to see more publications in this area in the near future.

CRediT authorship contribution statement

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Abbreviations

DES, Deep eutectic solvent;

DI-SDME, Direct immersion single-drop microextraction; DLLME, Dispersive liquid–liquid microextraction; DLPME, Dispersive liquid-phase microextraction; ELLME, Emulsification liquid–liquid microextraction; ELPME, Emulsification liquid-phase microextraction; EME, Emulsification microextraction; HF-, Hollow-fibre; HF-LPME, Hollow-fibre liquid-phase microextraction; HLLME,

Homogeneous liquid–liquid microextraction extraction; HLLE, Homogeneous liquid–liquid extraction; HS-SDME, Headspace single-drop microextraction; LLE, liquid–liquid extraction; LLME, Liquid–liquid microextraction; LPME, Liquid-phase microextraction; MAE, Microwave-assisted extraction; SDES, Solidification of DES; SDME, single-drop microextraction; SFOD, Solidification of floating organic droplet; UAE, Ultrasound-assisted extraction; USAEME, Ultrasound-assisted emulsification microextraction.

CVAAS, Cold vapor atomic absorption spectrometry; ETAAS, Electrothermal atomic absorption spectrometry; FAAS, Flame atomic absorption spectrometry; GC-μECD, Gas chromatography–micro electron capture detector; GC-ECD, Gas chromatography–electron capture detector; GC-FID, Gas chromatography–flame ionization detector; GC-MS, Gas chromatography–mass spectrometry; GC-MS/MS, Gas chromatography–tandem mass spectrometry; GFAAS, Graphite furnace atomic absorption spectrometry; HG-AAS, Hydride generation–atomic absorption spectrometry; HPLC-FLD, High-performance liquid chromatography–fluorescence detector; HPLC-MS, High-performance liquid chromatography–mass spectrometry; HPLC-MS/MS, High-performance liquid chromatography–tandem mass spectrometry; HPLC-UV, High-performance liquid chromatography–ultraviolet detection; ICP MS, Inductively coupled plasma mass spectrometry; ICP-OES, Inductively coupled plasma optical emission spectrometry; IMS, Ion mobility spectrometry; LC-, Liquid chromatography; LC-ICP MS, Liquid chromatography–inductively coupled plasma mass spectrometry; LC-UV, Liquid chromatography–ultraviolet detection; MECC-UV, micellar electrokinetic capillary chromatography–ultraviolet detection; MS-FAAS, Micro-sample injection flame atomic absorption spectrometry; SQT-FAAS, Slotted quartz tube–flame atomic absorption spectrometry; UHPLC-MS, Ultra-high-performance liquid chromatography–mass spectrometry; UHPLC-MS, Ultra-high performance liquid chromatography–mass spectrometry; UHPLC-MS/MS, Ultra-high performance liquid chromatography–tandem mass spectrometry; UHPLC-QTOF-MS, Ultra-high performance liquid chromatography–quadrupole time-of-flight mass spectrometry; UHPLC-UV, Ultra-high performance liquid chromatography–ultraviolet detection; UPLC-FLD, Ultra-high-performance liquid chromatograph–fluorescence detector; UPLC-MS/MS, Ultra performance liquid chromatography–tandem mass spectrometry; UV-Vis, UV-Vis spectrometry;

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