

Review

# Application of Extraction and Determination Based on Deep Eutectic Solvents in Different Types of Environmental Samples

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**Abstract:** Water sources are an indispensable resource for human survival. Monitoring the pollution status of the surrounding environment is necessary to protect water sources. Research on the environmental matrix of deep eutectic solvents (DESs) has expanded rapidly because of their high extraction efficiency for various target analytes, controllable synthesis, and versatile structure. Following the synthesis of hydrophobic deep eutectic solvents (HDESs), their application in aqueous matrices broadened greatly. The present review conducted a survey on the pollutant extraction methods based DESs in environmental matrices from two aspects, application methods and matrix types; discussed the potential risk of DESs to the environment and future development trends; and provided some references for researchers to choose DES-based extraction methods for environmental research.

**Keywords:** deep eutectic solvents; drinking water; environmental analysis; sample preparation; green solvents



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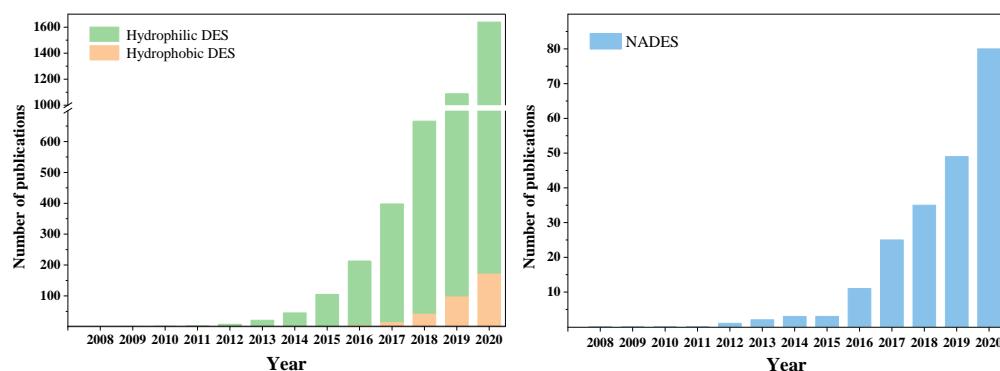
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## 1. Introduction

New pollutants continue to appear with the development of society, many of which cannot be decomposed in natural water as a source of drinking water [1]. The pollution process of these pollutants in water sources is slow and hidden. They enter the human body through drinking water and pose a threat to human health. In addition to the production and life of human beings, pollutants in water sources migrate from contaminated soil and the atmosphere into water bodies [2,3]. These pollutants have now been detected in environmental matrices, such as surface water, sewage/sludge, soil/sediments, and indoor air/dust. In order to further study their potential threat, the first step is to understand their occurrence in environmental samples. However, the matrices are complex, and the organic pollutant concentration is usually low to the nanogram level. Therefore, it is urgent to explore an effective pretreatment method.

At present, the main pretreatment method is SPE, but it has disadvantages such as high cost, complicated operation, and poor repeatability. Although LPME overcomes the shortcomings of traditional pretreatment technologies, these methods have disadvantages such as toxic and harmful solvents and poor biodegradability. Based on the concept of green chemistry, Abbott et al. proposed a new type of green solvent called DES [4]. According to the definition, DES is a liquid, and its melting point is lower than all its components. The reason is that hydrogen bonds are formed between the components. Due to their noteworthy properties, such as negligible vapor pressure, large polarity range, and high thermal stability, DESs have been applied in separation processes, analytical chemistry, synthesis, electrochemistry, etc. [5–8]. DES synthesis methods include heating, evaporation, and freeze-drying. The heating method is currently the most commonly used method due to its easy operation [9]. Some authors have developed alternative synthesis methods to make DESs greener. For example, Gomez et al. [10] developed an MA method with a short synthesis time (20 s) and low energy consumption.

Analytical sample pretreatment is one of the emerging applications of DESs. Due to their properties such as low cost, easy preparation and restructuring, and low toxicity and biodegradability, DESs are preferable over conventional solvents. Additionally, interactions between DESs and target analytes, including electrostatic,  $\pi-\pi$ , van der Waals (dispersion), hydrogen bonding, hydrophobic, and dipole–dipole and ion–dipole forces, provide DESs with high solubility to pollutants during pretreatment [11]. In addition, the density of DESs is usually higher than water, which helps them separate from the water phase during the extraction process. Thus, the number of reports on using DESs as extractants to concentrate analytes has increased rapidly since 2012 (Figure 1) [5]. DESs have been applied in various pretreatment techniques to extract different kinds of analytes (such as metal ions, fatty and organic acids, volatile organic compounds, dyes and pigments, pesticides, peptides and proteins, plant compounds) in real matrices, including water, air, soil, and biological samples [9].



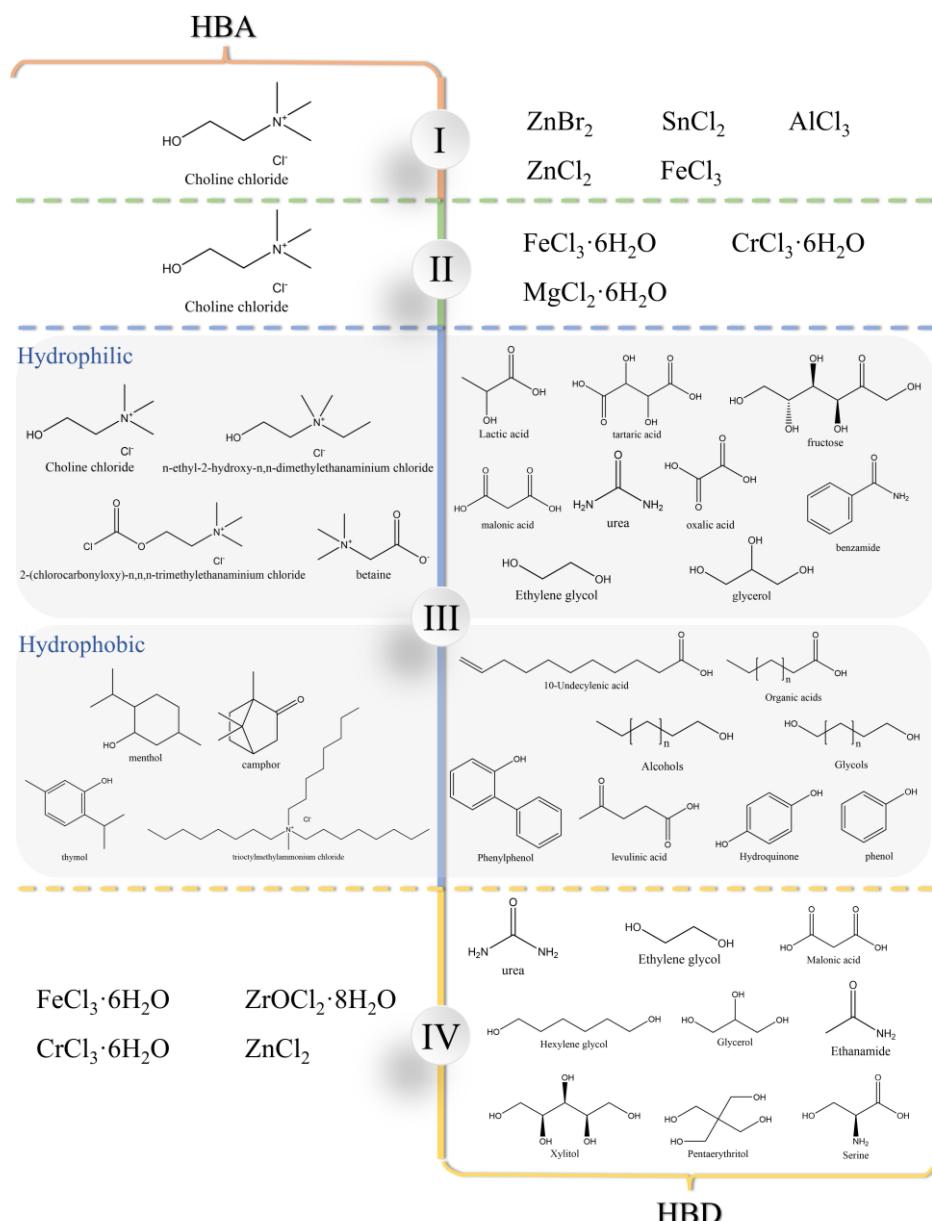
**Figure 1.** Number of papers published during 2008–2020 in Web of Science (Keywords: “deep eutectic solvents”, “hydrophobic deep eutectic solvents”, and “nature deep eutectic solvents” with “extraction”).

With the increasing application of DESs in the analytical field, many review articles have been published. For example, the review article by Makoś et al. [12] focused on HDESs used in the microextraction method. The review article by Santana et al. [9] compiled two aspects, sample preparation and analytical techniques, related to the application of DESs in analytical chemistry in 2016–2020. A recent review by Tang et al. [13] paid attention to the development of DES-based microextraction procedures. Some recent papers gave a focused and comprehensive review of the applications of DESs during DLLME of pesticides in food samples [14] and coastal zone environmental samples [15]. This review systematically focused on recent applications of DESs in different environmental matrices to improve the general understanding of the use of DESs in analytical chemistry.

## 2. Deep Eutectic Solvents

### 2.1. Classification of DESs

DESs are commonly classified into four types: Type I (quaternary salt and metal halide), Type II (quaternary salt and hydrated metal halide), Type III (quaternary salt, terpene, and hydrogen bond donor), and Type IV (metal halide and HBD) (Figure 2).



**Figure 2.** Classification of DESs according to their composition.

Type I DESs are formed by quaternary ammonium salts and nonhydrated metal halides. Although the types of nonhydrated metal halides that can form type I DESs are limited, DESs vary with the molar fraction of nonhydrated metal halides, which is different from ionic liquids consisting of independent anions such as  $\text{BF}_4^-$  and  $\text{PF}_6^-$ . This kind of ionic DES is mainly used as a catalyst or to synthesize catalysts in the organic field [16].

Type II DESs are formed by quaternary salt and hydrated metal halide. Due to their low cost and insensitivity to components, they are easy to synthesize. However, only a few applications in extraction are available because of the toxicity of metal halide. Choi et al. [17] developed an efficient lipid extraction method from *Chlorella vulgaris* using a DES composed of [EMIM][OAc] and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ .

Type III DESs formed by quaternary salt or terpene with HBD are fundamentally different from the former two types of DES. In type III DESs, the halogen anion  $X^-$  forms a hydrogen bond with ligand Y, which reduces the Coulomb force between the anion and cation. Thus, these DESs possess excellent dissolution properties owing to their ability to donate protons or accept electrons to form hydrogen bonds [18]. Regarding

environmental analysis, it has been successfully applied to extract and isolate organic compounds, inorganic analytes, pharmaceuticals, pesticides, and so on [9].

Moreover, DESs prepared from a combination of metal halide, generally with transition metals, and organic ligands (HBD) are classified as Type IV [19]. This kind of DES is usually used as an electroplating solution [20] in metal electroplating and a catalyst [21] in organic reactions. Liu et al. [22] used a DES catalyst to convert cellulose into gluconic acid.

## 2.2. *Hydrophilic and Hydrophobic DESs*

The presence of hydrophilic functional groups in the components, such as hydroxyl, carboxyl, or amino groups, will cause DESs to become hydrophilic (namely hydrophilic DESs), such as Type I, II, IV, and some Type III hydrophilic DESs. The application range of hydrophilic DESs is limited due to their instability in water. Conversely, hydrophilic DESs have great advantages in the extraction of hydrophilic analytes from nonaqueous samples. For example, phenolic compounds are extracted from a variety of plant samples [23–27], and bioactive carbohydrates, such as polysaccharides [28,29] and pectin [30], are extracted from plants. Although most bioactive compounds are hydrophilic, some lipid-soluble bioactive compounds are hydrophobic. Hydrophobic solvents can enhance the extraction efficiency of lipid-soluble bioactive compounds.

To expand the application of DESs, especially in aqueous samples, van Osch et al. [31] proposed the first HDESs in 2015, which consisted of decanoic acid and long-chain quaternary ammonium salt. Later, a series of HDESs composed of a variety of fatty alcohols and long-chain fatty acids combined with long-alkyl-chain quaternary ammonium salts were synthesized [31]. Ribeiro et al. [32] proposed another type of hydrophobic deep eutectic solvent consisting of DL-menthol as the HBA, which is a natural monoterpenes, and several short-chain acids (i.e., acetic, lactic, and pyruvic acids) as the HBD. Other terpenes can also be used to synthesize HDESs, such as thymol [33], camphor [34], and lidocaine [35]. However, the presence of hydrophilic components will reduce the stability of HDESs. The extent of influence on stability depends on the hydrophilicity of the components. It is worth highlighting that although there is a leaching loss, the HDES-rich phase still exists independently [12]. HDESs can be used to extract compounds in various matrices, such as artemisinin from leaves [36], cannabinoids from raw cannabis plant [37], pesticides [38] and antibiotics from water [39], drugs from human urine [40], and endocrine disruptor compounds from water [41].

## 2.3. *Toxicity of DES*

Few reports on the potential toxicity of DESs are available. Generally, DESs synthesized from sugars, alcohols, sugar alcohols, and amides are more eco-friendly, while, in contrast, DESs synthesized from metal ions and organic acids are not “green” [42]. Studies have shown that ChCl-based DESs combined with urea, glycerine, triethylene glycol, and ethylene glycol have no toxic effect, but they do have cytotoxicity. The cytotoxicity of these DESs is higher than their components [43]. Recently, different test organisms were used to test the toxicity of ChCl-based DESs composed of organic acid and sugar. DESs combined with organic acid and sugar had higher cytotoxicity than those combined with organic alcohol. However, the cytotoxicity of the components of the tested DESs was higher than that of DESs [44]. In addition, the molar ratio of HBA and HBD, lipophilicity, and the Hofmeister effect can also affect the toxicity of DESs [45]. Recently, Torregrosa-Crespo et al. [46] proposed that it is more accurate to confine the discussion to a certain concentration range for the toxicity of DESs. Some studies used predictive computational models to evaluate the cytotoxicity of DESs [42,47,48]. However, the results from toxicity tests are even more convincing, and more factors need to be considered, including culture conditions, type of culture media, and sterilization methods [46]. In future research avenues, more types of test organisms should be considered to represent different functional levels. It can help us fully understand how aquatic ecosystems are affected by DESs. Moreover, in order to have

a more comprehensive understanding of the environmental sustainability of DESs, more studies focusing on bioaccumulation and biodegradability are required.

### 3. Application Forms in Environmental Analysis

LLE is the process of separating and extracting components of liquid mixtures with solvents. The volume of the extractant is usually the same as the volume of the water sample. The type of DES used is determined based on the nature of the sample and analyte. Some studies have applied this method to the extraction of volatile organic acids, metal ions, and organic pollutants in environmental water samples. However, LLE is gradually replaced by LPME due to the large volume of organic solvents and poor enrichment effect (Table 1).

LPME is an extraction technology that greatly reduces the volume of the extractant compared with LLE. Many methods have been developed to assist the extraction process, such as vortex, heating, microwave, and ultrasonic. Some studies made the methods more convenient and faster by reducing the number of steps, such as the synthesis of DESs [49,50]. At the same time, in order to more thoroughly separate the organic phase and the water sample, researchers made the extractant magnetic and combined it with LPME [51]. The analyte selectivity of DESs is higher than ordinary organic solvents such as methanol, acetonitrile, and dichloromethane because of the special structure of DESs. Combined with LPME, the method not only has the advantages of extraction technology but also reduces costs and improves environmental friendliness. In general, LPME can be divided into three categories: DLLME, SDME, and HF-LPME.

**Table 1.** Extraction technique combined with DESs in environmental analysis.

Techniques	DES			Sample			Other Features	Analytes	Instrumental Analysis	LOD (ug/L,g)
	HBA	HBD	Molar Ratio	Volume	Type	Volume				
SLLE [52]	N8881-Cl	Octanol/octanoic acid	1:2:3	2 mL	Plant leaves	0.2 g	Two DES phases were involved	Flavonoids Terpene trilactones Procyanidin Polyprenyl acetates Lower alcohols Ethanol 1-Propanol 1-Butanol	HPLC-UV	
LLE [53]	Menthol	Dodecanoic acid	2:1		Water				NMR	
LLE [54]	Dodecanoic acid	Octanoic acid Nonanoic acid Decanoic acid	1:3 1:3 1:2	2 mL	Water	2 mL		Bisphenol A	UV-vis	
DLLME [55]	N8881-Cl	Oleic acid	1:2	20 uL	Water and biological samples	5 mL	Vortex assisted	Nitrite	HPLC-UV	0.2
DLLME [56]	Quaternary ammonium salt	DL-menthol			Aqueous samples		Air assisted	Benzophenone	HPLC-UV	
DLLME [57]	ChCl	Triethylamine	1:1		Biological and environmental samples	20 mL	Air assisted Volume of DES/triethylamine (TEA) (1:1) is 100 uL.	Heavy Metals	FAAS	0.31–0.99
DLLME [58]	ChCl	Phenol	1:3	450 uL	Lake water	10 mL	Ultrasound assisted	Chromium (III/VI)	FAAS	5.5
DLLME [59]	ChCl	Phenol	1:3	1000 uL	Soil, sediment, and water	25 mL	Ultrasound assisted	Arsenic	ETAAS	0.01
DLLME [60]	N4444-Cl	Decanoic acid	1:2	200 uL	Liver samples	10 mL	Ultrasound assisted DES (ChCl-lactic acid) is digestion solution	Copper	MS-FAAS	4.00
HS-SDME [61]	N4444-Br	Dodecanol	1:2	1.5 uL	Plant samples	50 mg		Terpenes	GC-MS	0.87–86.40
HF-LPME [62]	ChCl	Phenylethanol	1:4	40 uL	Human plasma urine and pharmaceutical wastewater	10 mL	Three-phase (liquid–liquid–liquid) microextraction	Antiarrhythmic agents Propranolol Carvedilol Verapamil Amlodipine	HPLC-UV	

N8881-Cl: trioctylmethylammonium chloride (TAC); MS-FAAS: microsample injection system coupled with flame atomic absorption spectrometer; HS-SDME: headspace single-drop microextraction; SLLE: supported liquid–liquid extraction.

### 3.1. DLLME

In DLLME, the extractant is dispersed by the dispersive solvent or other auxiliary means to form small droplets, which are evenly distributed in the entire solution to increase the contact area. Using DESs as extractants in DLLME can obtain better application prospects [63]. Liu et al. [64] used the DES-DLLME method combined with HPLC-UV to determine SAs in river water. However, hydrophilic DESs cannot exist stably in water, and they can only be used for nonaqueous samples because water can break the hydrogen bond. Therefore, HDESs that use long-chain fatty acids, quaternary amine salts, and terpenes as HBD are applied as extractants for water samples. For example, Werner [65] established the UA-DES-DLLME method for the green and efficient determination of aromatic amines from environmental water samples. El-Deen et al. [66] extracted steroids in a water sample through tetrabutylammonium bromide/acetic acid DES. Wang et al. [67] evaluated the in situ applicability of HDESs for the extraction of UV filters dissolved in raw water samples by DLLME. A new type of DLLME is AA-LLME. By pumping and injecting several times, the extractant and water can be completely mixed. Lamei et al. [68] extracted methadone from biological and water samples using this technique.

### 3.2. SDME

SDME has been recognized as one of the simple miniaturized sample preparation tools for the isolation and preconcentration of several analytes from a complex sample matrix [69]. The application of DESs in SDME is rapidly growing in analytical practice for the extraction and preconcentration of several analytes, owing to their unique physicochemical and mechanical properties [70]. In SDME, droplets are commonly immersed in the sample. In addition, the method of suspending extractant droplets on the tip of a syringe to extract volatile compounds is called HS-SDME.

Yousefi et al. [71] used gel prepared from DES as an extractant in HS-SDME to concentrate volatile hydrocarbons from water and urine samples. Compared with traditional solvents, DESs have higher thermal stability, higher viscosity, lower volatility, and adjustable miscibility and are more capable of forming stable droplets of HS-SDME. A novel DES based on montmorillonite clay, Fe<sub>3</sub>O<sub>4</sub>-DL-menthol, and decanoic acid [51] is highly hydrophobic, with lower viscosity and density than that of water, and can extract explosive compounds from water and soil samples. Deep eutectic solvents were synthesized by mixing tetrabutylammonium bromide (HBA) with various alcoholic molecules and ChCl-urea with ChCl-lactic acid at different molar ratios [72] to analyze terpenes based on the HS-SDME method.

### 3.3. HF-LPME

Pedersen-Bjergaard [73] established a new microextraction method in which the extractant exists in the form of a liquid film. In the HF-LPME system, the extraction phase is usually SLM in the hollow fiber, which separates the target compound from the sample and then enters the acceptor phase in the cavity of the hollow fiber.

In 2018, Khatael et al. reported three-phase HF-LPME based on n-dodecane and DESs, which consisted of ChCl and MTPB as the acceptor phase of steroid hormones from biological fluids [74]. Rajabi et al. first adopted a completely eco-friendly and high solubility HDES (ChCl/1-phenylethanol) for HF-LPME in biological and environmental samples [62]. In 2021, Pedersen-Bjergaard et al. first reported that a hydrophobic NADES (coumarin/thymol) was used as SLM for electromembrane extraction in a biological fluid sample and almost completely extracted different polar compounds [75]. This paper proved that DESs are very suitable for extraction in the form of SLM.

## 4. Applications in Environmental Matrix

When the analyte concentration is very low and the sample matrix is complex, the most important and unavoidable step in the analytical process is extraction. Choosing the right extractant can more efficiently analyze and determine the environmental matrix. DESs

are novel, green, and designable solvents with high degradability and low cost. Therefore, the number of studies on the application of DESs in environmental sample preparation methods is rapidly increasing. As shown in Table 2, most methods using HDESS can be used to detect targets in various types of matrices. Hydrophilic DESs are mainly used for the extraction of active substances from plants and are rarely used for soil samples. The reason is that when detecting the content of organic matter in soil, the target substance is first extracted from the soil into the aqueous solution and then enriched and purified. This will also depend on whether the target is hydrophilic or hydrophobic.

**Table 2.** Compilation of application of DESs in extraction from various types of environmental matrix.

Sample Matrix	Analytes	DES Composition (Mole Ratio)	Method of Extraction	Instrumental Analysis	LODs
Waters (tap, lake, waste) [58]	Cr (III/VI)	ChCl/phenol (1:3)	UALME	FAAS	5.5 ug/L
Switchgrass [76]	Cellulose-rich pulp, lignin, and xylose-rich liquor.	ChCl/glycerol (1:2)		HPLC-RID, NMR, ATR-FTIR, XRD	
Tartary buckwheat Hulls [77]	Flavonoid (rutin)	ChCl/glycerol (1:1)	UAME	HPLC-UV	
Flower petals [78]	Anthocyanins	Lactic acid/glucose 1,2-propanediol/ChCl	UAE	HPLC-DAD	
Soil samples [79]	As, Cr, Mo, Sb, Se and V	ChCl/oxalic acid	UAE	ICP-OES	0.009–0.1 ug/g
Sediment samples [80]	Cu	ChCl/oxalic acid (1.5:1)	SLE	ICP-OES	1.2 ug/L
Wastewater and human plasma [81]	Amphetamine-type stimulants	Hydrophobic deep eutectic solvents ChCl/phenylethanol (1:4)	AA-EME	HPLC-UV	2.0–5.0 ng/mL
Surface water [49]	Fluoroquinolones	Thymol/Heptanoic acid (2:1)	In situ LPME	HPLC-UV	3 ng/mL
Wastewater [82]	Neonicotinoids	DL-menthol/organic acids	LLE	UV-vis	
River water [56]	BP, BP-1, BP-3, BP-6, 4OH-BP	DL-menthol/decanoic acid (1:1)	Air-assisted DLLME	HPLC-DAD	0.05–0.2 ng/mL
Water and soil samples [51]	Explosives	DL-menthol/decanoic acid (1:2)	Ferrofluid-based LPME	HPLC-UV	0.22–0.91, 0.01–0.04 mg/mL
Soil samples [83]	Nitrotoluene	Borneol/menthol	MSPD	HPLC-UV	0.12–0.33 ug/g
Water, soil, egg yolk samples [84]	Insecticide	N4444-Br/decanoic acid	DLLME	HPLC-UV	0.001–0.003 ug/mL
Water, and biological samples [55]	Nitrite	N8851-Cl/oleic acid (1:2)	Vortex-assisted DLLME	HPLC-UV	0.2 ng/mL
Biological and indoor air sample [85]	Formaldehyde	N8851-Cl/4-cyanophenol (1:1)	VA-LLME	HPLC-DAD	0.2 ng/mL

AA-EME: air agitated-emulsification microextraction; MSPD: matrix solid-phase dispersion.

#### 4.1. Extraction from Aqueous Samples

For aqueous applications, HDESS are desirable due to their stability in aqueous solution. HDESS are mainly divided into two categories according to the type of HBA/tetraalkyl-quaternary-ammonium-based HDESS and terpene-based HDESS. Quaternary-ammonium-based HDESS can extract metals. Ruggeri et al. [86] investigated HDESS based on tetrabutylammonium chloride and decanoic acid and their application in the extraction of Cr(VI) species from an aqueous phase. In addition to extracting inorganic metal ions, this type of HDESS can also be used to extract a variety of organic substances. Yousefi et al. [87]

prepared a HDES consisting of TBAB and carboxylic acids and applied the synthesized HDES in the analysis of PAHs in environmental water samples. Terpene-based HDESs have also been applied to extract various organic analytes by liquid–liquid extraction. In 2015, HDESs consisting of DL-menthol (HBA) and various organic acids (HBD) were first reported [32]. Lower alcohols, ethanol, propanol, and butanol could be enriched in menthol-based HDESs [53]. In addition, the extraction of inorganic metals has been reported, and In [88] and Cu [89] can be transferred to menthol and thymol-based HDESs [89].

For aqueous samples, hydrophilic DESs are generally not advisable as the extractant phase for aqueous matrices unless other organic solvents (THF) are added to ensure phase separation. This will reduce the greenness of the method since the volume of organic solvents is increased. However, it should be noted that the efficiency of extracting water-soluble analytes will be significantly improved when a hydrophilic DES is used as the extractant. One of the most widely used hydrophilic DESs for the extraction of contaminants in aqueous samples is formed by ChCl and phenol in different molar ratios. In this case, the mixture of DES and water makes necessary the use of an emulsifier (aprotic solvent) that achieves phase separation because of the self-aggregation phenomenon. Some studies used choline chloride/phenol DES as an extractant and an aprotic solvent THF to separate microcystin [90], BTRs, and BTs [91] from surface water samples. Sometimes, the role of DES in the extraction process is not as an extractant but as an assistant agent to extract steroids from river and tap water [66].

#### 4.2. Extraction from Air Samples and Soil/Sediment Samples

Most applications of DESs in air samples are used as absorption solutions for CO<sub>2</sub>, SO<sub>2</sub>, and NO [92]. However, only a few DESs have been used for the extraction and determination of analytes from air samples up to now. HDESs have been used as extractants using aqueous acid as an absorption solution in the VA-LLME method coupled with HPLC for the selective enrichment and indirect determination of formaldehyde from indoor air samples [85]. In the extraction and separation of analytes from solid samples, the choice of DES is not limited by its own hydrophilicity and hydrophobicity. Therefore, the choice of DES only depends on the solubility of contaminants in the DES when used as an extractant. Following the extraction of solid samples, the suspensions obtained by centrifugation usually need to be filtered before entering the instrument for analysis. The DES composed of choline chloride and oxalic acid was used as a solvent for extraction of As, Cr, Mo, Sb, Se, and V in real soil samples [79] and Cu in sediment samples [80]. Compared with the results determined using the conventional acid digestion method, the method was found to be accurate, precise, and eco-friendly. In addition, it can also be used for the extraction and determination of organic pollutants from soil such as pesticides [84] and nitrotoluene [83]. Furthermore, some studies use DESs to prepare ferrofluid to extract explosives from soil samples by suspended droplet microextraction [51]. The extraction procedure has a high potential for application in complex matrices.

#### 4.3. Extraction from Organism Samples

Compared to environmental water, soil/sediment, and air, the extraction of biological samples based on DES is less explored. In applications related to the field of biological sample analysis, according to the sample classification, it can be divided into three different types: biological fluid, animal, and plant samples. Works related to biological samples mainly focus on digestion methods based on DESs, for example: determination of Cu, Zn, and Fe in fish samples [93]; Cu, Fe, Ni and Zn in marine biological samples [94]; As, Ca, Cd, Cu, Fe, K, Mg, Mn, Na, P, and Zn in plants [95]; and polycyclic aromatic hydrocarbons in biological samples [96]. In general, various methods have been applied in the extraction of biological samples, such as heating [93] and microwave [94].

The air-assisted DLLME method was used to determine trace amphetamine and methamphetamine in human plasma [81]. HDESs consisting of ChCl and phenylethanol were used as the extraction medium during this microextraction process. Rastbood et al. [97]

proposed ChCl:EG@SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub> ferrofluid as a sorbent for the magnetic SPME of the anti-inflammatory drug meloxicam from human plasma and urine samples.

It is interesting to note that the application of DESs in plant samples to extract natural active substances and natural pigments from the herbaceous plant safflower is more stable in NADESs than in water [98]. Recently, Dai et al. [78] employed diverse NADESs to extract anthocyanins from the purple and orange petals of *Catharanthus roseus*. Cao et al. [52] suggested a two-phase DES system to extract and fractionate analytes of diverse polarity, i.e., hydrophobic polyphenyl acetates and partially hydrophilic components (flavonoids, terpene trilactones, and procyanidin) from ginkgo leaves. Compared with the traditional acid digestion method, the reagent consumption of the DES-based extraction method is greatly reduced, the required time is shorter, and the method is safer because neither high pressure nor concentrated acid is involved.

## 5. Concluding Remarks

To control the pollution of drinking water sources, it is necessary not only to conduct real-time detection of water samples in water sources but also to pay certain attention to the nearby soil and atmosphere [99,100]. Extraction is an important and unavoidable step in the environmental analysis process. DESs are ideal as extractants because of their combination of simple and cost-effective preparation and task-specific design to meet the needs of specific processes. Extraction based on DESs is a reliable analytical tool with wide potential applications in environmental analysis. This review summarized recent studies of DESs used in environment samples and briefly discussed the extraction modes and types of environmental matrices, which is beneficial for researchers to understand DES applications in environmental matrices.

Although DESs have been widely applied in the field of extraction and separation, several challenges in DES-based extractants remain. Some DESs are composed of substances with suspicious toxicity. Compared with a single component, the toxicity of the combination of toxic and nontoxic compounds cannot be confirmed [46]. In order to use DESs more safely in extraction technology, toxicity and the environmental impact of more types of DESs need to be further studied. Another problem with HDESSs is that although people are more and more interested in the synthesis of HDESSs, their number is still limited, and further efforts are needed to synthesize new HDESSs as extractants [101]. Furthermore, the study of the physicochemical properties of DESs during the synthesis and extraction mechanism also needs more attention because research on DESs is still at the application level, and the changes in the microstructure and physical and chemical properties are not clear [102]. Structural-related studies need to be designed to be more accurately applied to different environmental samples. In the future, the great interest of many researchers will promote the more sustainable development of extraction technology using DESs.

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## Abbreviations

### Abbreviations

AA	Air assisted
BTRs	Benzotriazole derivatives
BTs	Benzothiazole derivatives
ChCl	Choline chloride
DES	Deep eutectic solvent
DLLME	Dispersive liquid–liquid microextraction
DNA	Deoxyribonucleic acid
[EMIM][OAc]	1-Ethyl-3-methyl imidazolium acetate
HBA	Hydrogen bond acceptor
HBD	Hydrogen bond donor
HDESS	Hydrophobic deep eutectic solvent
HF-LPME	Fiber-based liquid-phase microextraction
HPLC	High-performance liquid chromatography
HS-SDME	Headspace single-drop microextraction
LLE	Liquid-liquid extraction
LPME	Liquid-phase microextraction
MA	Microwave assisted
MTPB	Methyltriphenylphosphonium bromide
NADES	Nature deep eutectic solvent
PAHs	Polycyclic aromatic hydrocarbons
SAs	Sulfonamides
SDME	Single-drop microextraction
SLM	Supported liquid membrane
SPE	Solid-phase extraction
SPME	Solid-phase microextraction
TBAB	Tetrabutylammonium bromide
THF	Tetrahydrofuran
UA	Ultrasound-assisted
VA-LLME	Vortex-assisted liquid–liquid microextraction

### Nomenclature

–	Dipole–dipole forces
$\rho$	Density
–	Ion–dipole forces
$m_p$	Melting point
S	Solubility
–	Polarity
$\eta$	Viscosity
–	van der Waals (dispersion) forces
–	$\pi$ – $\pi$ forces

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