Recent Applications of Deep Eutectic Solvents in Environmental Analysis

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Abstract: The incessant generation of toxic waste and the growing concern over the environment have led the scientific community to delve into the search for more sustainable systems. In this regard, the application of deep eutectic solvents (DESs) has become one of the main strategies in green chemistry. These solvents have emerged as a promising alternative to conventional toxic solvents and even to the well-known ionic liquids. Their unique properties, components availability, and easy preparation, among others, have led to a new trend within the scientific community and industry, based on the use of these up-and-coming solvents not only in science but also in quotidian life. Among the areas that have benefited from the advantages of DESs is analytical chemistry, in which they have been largely used for sample preparation, including the extraction and determination of organic and inorganic compounds from environmental samples. The considerable number of applications developed in the last year in this field and the increasing generation of new data necessitate the continuous updating of the literature. This review pretends to compile the most relevant applications of DESs in environmental analysis and critically discuss them to provide a global vision about the advantages and drawbacks/limitations of these neoteric solvents in the area of environmental analysis.

Keywords: green solvents; sustainability; water; soil; contaminant; environment; green analytical chemistry

1. Introduction

The extensive use of chemicals in the industry and daily life has led to the concerning occurrence of hazardous compounds in the environment which brings about considerable contamination in ecosystems and has a negative effect on the population’s health. In this sense, it is of utmost importance that the development of methodologies enables the reliable remediation and determination of these kinds of substances, especially at the low levels at which they can be harmful for humans [1]. The combinations of efficient sample preparation methods together with the most sensitive and robust analytical techniques are the gold tools to reach suitable determinations in this field, particularly due to the complexity of environmental samples, which usually present a great number of interferences and other components that can hinder the analysis.

However, nowadays, sensitivity, selectivity, and robustness are not enough criteria to define the suitability of an analytical methodology. As part of the current trend to develop more sustainable systems that comply with the goals of green analytical chemistry, the search for environmentally friendly strategies is fundamental to demonstrate the viability of the method and its adequate application. In this sense, it is essential that the development of procedures does not endanger the environment by the generation of...
additional waste, and at the same time, allows to decrease the operator risk during the method performance—thus saving time, cost, and energy [2,3].

Diverse strategies have been tested and successfully applied in the different areas of analytical chemistry to reach these objectives. Among them, the application of direct analyses, the development of miniaturised and automated techniques and the use of novel green materials have been the main lines of research [4]. Great effort has been made by the scientific community to seek new materials such as nanomaterials or alternatives to the use of toxic conventional organic solvents. In this context, in recent years, the application of deep eutectic solvents (DESs) has gained relevance with respect to other previously used solvents such as the generally recognised as safe (GRAS) solvents, supramolecular solvents (SUPRAS), switchable solvents or even ionic liquids (ILs) [5], due to the unique and advantageous properties of these new materials [6].

DESs have been described as mixtures of at least two substances, a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD) interacting by hydrogen bonds, with a freezing point much lower than that of either of each component. However, it is known that other types of interactions such as van der Waals forces or electrostatic interactions could also be established and not all eutectic mixtures present a considerable decrease in the freezing point, which has produced considerable controversy in a large number of works published in recent years, in which diverse mixtures have been used without the clear characterisation and evaluation of the materials used [4,7,8]. For this reason, a stricter definition has been proposed to describe them, namely eutectic mixtures that are liquid at room temperature and whose eutectic point is below that of an ideal liquid mixture [8].

Within the scope of this definition, diverse classifications of DESs have been proposed, as can be seen in different recently published review articles [7–9]. Among them, DESs can be differenced into hydrophilic DESs, when they are soluble in water, hydrophobic DESs (HDESs), exclusively constituted by hydrophobic components, and quasi-HDESs, when at least one component is soluble in water. These two last groups have gained great attention in the field of analytical chemistry since their poor solubility in water simplifies their separation from aqueous samples in analytical applications [7]. Such an aspect is especially important in aqueous environmental matrices, for which those have been used, particularly for the evaluation of organic compounds.

The unique characteristics of DESs make them ideal green solvents with great versatility due to the huge number of possible components and combinations available, as well as the ease of carrying out the synthesis process. In addition, they show non-flammability, low volatility, low cost, and toxicity; good biocompatibility, biodegradation, and reusability capacity, among others [6,10]. In this sense, diverse compounds have been used as HBAs, notably choline chloride (ChCl), one of the most widely used in general but, particularly, in the field of environmental analysis. Nevertheless, other quaternary ammonium salts have also been applied in this field. In addition, as mentioned above, the application of HDESs and quasi-HDESs has recently increased in this area, making use of terpenoids or large chains of quaternary ammonium salts with long-chain fatty acids.

Another remarkable group of DESs is the one constituted by natural components (NaDESs). These solvents are exclusively constituted by primary or secondary metabolites, as well as other compounds presented in cells that make them less- or non-toxic and assure their biocompatibility. These characteristics have enhanced the interest in the application of NaDESs for the evaluation or treatment of environmental matrices due to the low impact of these solvents in such media performing more sustainable procedures [11]. Indeed, a brief evaluation of the recent literature indicates that NaDESs make up the majority of DESs used in the field of environmental analysis for the study of organic and inorganic compounds in liquid and solid matrices. In addition, although not extensively, on some occasions those NaDESs were combined with magnetic nanomaterials in order to harness the advantages of using both kinds of novel materials and developing simpler procedures with better specificity and higher efficiency.
The sharp increase in applications using DESs in recent years necessitates continuous revisions of the literature in which the compilation, description and discussion of the main trends, advantages, and difficulties of the use of these materials are carried out. In fact, in recent years, diverse review articles have been published in this sense [7–9]. However, to the best of our knowledge, a specific study of the use of DESs in the field of environmental analysis has not been carried out up to date. That is why, in this work, we compiled the most remarkable applications of DESs in this area, describing and discussing the main goals and achievements to date, as well as the major difficulties found in the application of these novel materials for the evaluation and treatment of environmental matrices.

2. Recent Applications of DESs in Environmental Analysis

2.1. Analysis of Organic Compounds in Environmental Samples

The unique features of DESs have boosted their applications in analytical chemistry, especially as alternative extraction solvents in sample preparation. In this sense, as can be seen in Table 1 [11–25], these solvents have been successfully employed for the evaluation of plastic migrants [11,16], pharmaceuticals [12,13,17,19], pesticides [14,15,18,25], dyes [15], hormones [16], ultraviolet (UV)-filters [16,21], polycyclic aromatic hydrocarbons (PAHs) [22] and explosives [24] in different environmental matrices, mainly water samples [11–19,21,22,24,25] and to a lesser extent in soil samples [15,24]. Among the types of DESs used with this purpose, HDESs have significantly replaced hydrophilic DESs, since they overcome the limitations for the separation of target analytes from aqueous medium [11–14,17,18,21,24]. Although quasi-HDESs are prepared from medium-chain quaternary ammonium salts and medium-chain fatty acids [15,19,22], combinations of more than two components to form ternary DESs (TDESs) [16], as well as ChCl-based hydrophilic DESs combined with nanomaterials [25] have also been investigated as extractants of organic contaminants from environmental samples. In addition, ChCl-based DESs have also been applied to capture CO\textsubscript{2} from natural gas [20] and biomass delignification [23]. Regarding the extraction procedures, the application of DESs has taken place in various microextraction techniques including liquid–liquid microextraction (LLME) [11,13,15–18,21,22] and its dispersive mode (DLLME) [12,14,19], assisted by vortex (VA) [11,15,19], ultrasounds (UA) [14,18,22], air cycles of pulling in/pushing out [16,21], using a mechanical shaker (SA) [17], controlled by pH changes [13] and solidifying the floating organic droplet (SFOD) after the extraction process [16,22], as well as in solid-phase extraction in its magnetic-micro-dispersive mode (m-μ-dSPE) [24,25]. A heating and stirring extraction has also been developed [23]. Likewise, the in situ formation of DESs has been another strategy used in this field [17].
Table 1. Some examples of the recent applications of DESs to the analysis of organic compounds in environmental samples.

| Sample (Amount) | Analytes | DES (Molar Ratio; Amount) | Extraction Procedure | Analytical Technique | Recovery % | LODs | Comments | Reference |
|----------------|----------|---------------------------|----------------------|----------------------|------------|------|----------|-----------|
| Treated wastewater, runoff, and pond water (10 mL) | 14 PAEs and one adipate | Menthol:thymol (1:2; 100 µL) | VA-LLME | UHPLC-QqQ-MS/MS | 70–127 | 0.013–0.425 µg/L | - Molar ratios of 2:1 and 1:2 were also studied. - Final extract was 20-fold diluted with ACN. - The method was applied to the analysis of real samples. | [11] |
| Well, rainforest, coastal sea, gardening and mineral water (10 mL) | 3 tetracyclines | Thymol:octanoic acid (1:1; 175 µL) | DLLME | HPLC–UV | 74–113 | 1.37–4.38 µg/L | - Nonanoic and decanoic acids were also tested as HBDS. - ChCl:ethylene glycol (1:2) DES was used as disperser (750 µL). - The extraction media was doped with β-CD (5 mg). - The method was applied to the analysis of real samples. - Greenness of the method was assessed using analytical eco-scale and GAPI approaches. | [12] |
| Feed, tap and wastewater (5 mL) | Levofloxacin and ciprofloxacin | Thymol:hexanoic acid (2:1; 100 µL) | Acid-base induced LLME | HPLC–UV | 95–111 | 0.018–0.027 mg/L | - Octanoic, decanoic and dodecanoic acids were also tested as HBDS. - Molar ratios of 1:1, 1:2 and 3:1 were also studied. - KOH (6 M,100 µL) and HCl (6 M, 150 µL) solutions were used to induce pH changes. - Final extract was 10-fold diluted with methanol. | [13] |
| Tap, lake and wastewater (3.2 mL) | 4 phenolic pesticides | α-Terpineol:octanoic acid (1:2; 100 µL) | UA-DLLME | HPLC–DAD | 82–99 | 0.15–0.38 µg/L | - Undecanol and nonanoic acid were also tested as HBDS. - Molar ratios of 1:1 and 2:1 were studied. - ACN was used as disperser (100 µL). - The method was applied to the analysis of real samples. | [14] |
Table 1. Cont.

| Sample (Amount) | Analytes | DES (Molar Ratio; Amount) | Extraction Procedure | Analytical Technique | Recovery % | LODs | Comments | Reference |
|-----------------|----------|---------------------------|----------------------|---------------------|------------|------|----------|-----------|
| Waste and agricultural water (10 mL) Agricultural soil (1 g) | 5 OPPs and 2 dyes | TBAB:decanoic acid (1:3; 200 µL) | VA-LLME in sponge | HPLC–VWD UV–visible | 70–95 | - | - DES was used for pollutants’ removal. - Heptanoic, decanoic and 4-phenylbutyric acids were also tested as HBDs. - Molar ratios of 1:1 and 1:4 were also studied. - Greenness of the method was assessed using analytical eco-scale approach. | [15] |
| River and tap water (5 mL) | 5 EDCs | Nonanoic acid:decanoic acid:dodecanoic acid (1:1:1; 200 µL) | AA-SFOD-LLME | HPLC–PDA | 90–104 | 0.96–2.30 µg/L | - Other binary DESs and TDESs formed by octanoic, nonanoic, decanoic and dodecanoic acids combinations, at different molar ratios, were also investigated. - Six pulling in/pushing out cycles were performed. - Final extract was 2-fold diluted with ACN. - The method was applied to the analysis of real samples. - Greenness of the method was assessed using Raynie pictogram, analytical eco-scale and GAPI approaches. | [16] |
| Surface water (10 mL) | 4 fluoroquinolones | Thymol:heptanoic acid (2:1; 100 µL) | SA-LLME | HPLC–UV | 83–119 | 3 µg/L | - In situ formation of HDESs was carried out. - Other DESs formed by monoterpenes, fatty acids and benzoate ester combinations, at molar ratio of 1:1, were also investigated. - Molar ratios of 1:1, 1:2, 1:3 and 3:1 were also studied. - Final extract was 4-fold diluted with mobile phase. | [17] |
| Sample (Amount) | Analytes | DES (Molar Ratio; Amount) | Extraction Procedure | Analytical Technique | Recovery % | LODs | Comments | Reference |
|----------------|----------|--------------------------|----------------------|---------------------|------------|------|----------|-----------|
| River and lake water (8 mL) | 5 pesticides | THTDPC:dodecanoic acid (1:2; 30 mg) | UA-LLME | HPLC–UV | 81–110 | 0.30–0.60 µg/L | - Octanoic and decanoic acids were also tested as HBDs. - Molar ratios of 1:1, 2:3, 2:5 and 1:3 were also studied. - Final extract was diluted with methanol (50 µL). | [18] |
| Surface and river water (10 mL) | 5 β-agonists | TBAC:octanoic acid (1:3; 500 µL) | VA-DLLME | UHPLC–QqQ-MS/MS | 57–91 | 0.4–0.8 µg/L | - TOMAC, TBAC and DTMAC as HBAs combined with decanoic, octanoic and lauric acids as HBDs were investigated at molar ratio of 1:2. - Molar ratios of 1:4 and 1:5 were also studied. - ACN was used as disperser (1 mL). - Final extract was 1.5-fold diluted with methanol. - The method was applied to the analysis of real samples. | [19] |
| Natural gas (-) | CO₂ | ChCl-based DESs (-; -) | - | - | - | - | - DESs were used for CO₂ capture. - Urea and glycerol were also tested as HBDs. - Energy and exergy analyses were carried out. | [20] |
| Swimming pool, river and wastewater (8 mL) | 6 benzophenone-type UV filters | Menthol:decanoic acid (1:1; 100 µL) | AA-LLME | HPLC–DAD | 89–106 | 0.05–0.20 µg/L | - TBAB, TBAC, and menthol as HBAs combined with octanoic, decanoic and dodecanoic acids as HBDs were investigated at different molar ratios. - Five pulling in/pushing out cycles were performed. - The method was applied to the analysis of real samples. | [21] |
Table 1. Cont.

| Sample (Amount) | Analytes | DES (Molar Ratio; Amount) | Extraction Procedure | Analytical Technique | Recovery % | LODs | Comments | Reference |
|----------------|----------|---------------------------|----------------------|---------------------|------------|------|----------|-----------|
| River, lagoon, lake and well water (20 mL) | 6 PAHs | TBAB:decanoic acid (1:2; 80 µL) | UA-SFOD-LLME | HPLC–FD | 80–117 | 0.7–6.6 ng/L | - Oleic, decanoic, octanoic, propionic, acrylic, acetic and butyric acids were also tested as HBDs. - Molar ratios of 1:1, 1:1.5 and 2:1 were also studied. - Final extract was 2.5-fold diluted with mobile phase. - The method was applied to the analysis of real samples. | [22] |
| Rice husk, rice straw and wheat straw (2.25 g) | Lignin | ChCl:oxalic acid:n-butanol (2:2:1; 15 mL) | Heating and stirring | Microscopy and CPMAS/NMR studies | 50 | - | - DES combined with n-butanol was used for biomass delignification. - Other alcohols were tested, including n-propanol and ethyl acetate. - Different DES-to-alcohol ratios were studied, including 2:1, 1:1 and 1:2. | [23] |
| Well and surface water and soil (10 mL) | 11 explosives (nitrogen compounds) | Menthol:decanoic acid (1:2; 50 µL) | m-µ-dSPE | HPLC–UV | 88–104 | 0.22–0.91 µg/L | - DES was combined with montmorillonite clay@Fe₃O₄ (50 mg) to form a ferrofluid. - The extraction capacity of the nanocomposite, DES and ferrofluid was evaluated separately. - Seventeen carboxylic acids were tested as HBDs. - Molar ratios of 2:1 and 1:1 were tested in some cases. - ACN was used as back-extraction solvent (500 µL). - The method was applied to the analysis of real samples. | [24] |
### Table 1. Cont.

| Sample (Amount) | Analytes | DES (Molar Ratio; Amount) | Extraction Procedure | Analytical Technique | Recovery % | LODs | Comments | Reference |
|-----------------|----------|---------------------------|----------------------|----------------------|------------|------|----------|-----------|
| Farm, rural, lake and river water (50 mL) | 18 OPPs | ChCl:urea (1:2; 50 µL) | m-µ-dSPE | GC–µ-ECD | 80–115 | 0.04–0.27 ng/L | - DES was combined with MWCNTs@Fe₃O₄ (5 mg) to form a ferrofluid.  
- DES has a dual role: carrier and stabiliser for MWCNTs.  
- Phenol, acetic acid and glycerol were also tested as HBDs.  
- Molar ratios of 1:1, 1:1.5 and 2:1 were also studied.  
- ACN was used as back-extraction solvent (150 µL).  
- The method was applied to the analysis of real samples. | [25] |
In this sense, an interesting example of the application of DESs as extraction solvents of organic compounds in environmental samples is the work carried out by Sereshti et al. [12] for the extraction of three tetracyclines from various water samples using a disperser/extraction solvents mixture based on DESs. In this case, two hydrophilic DESs composed of ChCl as HBA and urea or ethylene glycol as HBDs at molar ratio 1:2, and three HDESs formed by thymol as HBA and different medium-chain fatty acids including octanoic, nonanoic or decanoic acids as HBDs at a molar ratio of 1:1, were prepared and evaluated. The best extraction efficiency for the target analytes was obtained with ChCl:ethylene glycol and thymol:octanoic acid as disperser and extraction solvents, respectively. In addition, the authors found that doping the extraction medium with beta-cyclodextrin (β-CD) gave rise to a higher and more selective extraction performance. These results were explained based on the structure of the β-CD, since its hydrophilic surface allowed its solvation in the hydrophilic DES, whereas its hydrophobic cavity broke the HDESs into finer droplets, facilitating their dispersion in the aqueous sample, as well as the mass transfer of target analytes to the extraction medium. Likewise, additional sorption sites for tetracyclines were provided. Under the optimised extraction conditions, the limits of detection (LODs) between 1.37 and 4.38 µg/L and good recovery values in the range of 74–113% were obtained for well, rainforest, coastal sea, gardening and mineral water samples. Finally, an evaluation of the greenness of the methodology was carried out. Both the Green Analytical Procedure Index (GAPI) pictograms and the 76-point score obtained by the analytical eco-scale showed the good greenness of the analysis method, mainly because the proposed method completely eliminated the use of volatile and toxic solvents.

Following this trend of avoiding the use of conventional organic solvents to favour phase separation after the extraction process, Ma and Row [13] developed an LLME procedure influenced by pH changes for the analysis of two antibiotics, levofloxacin and ciprofloxacin, in feed, tap and wastewater samples. The extraction protocol consisted of a homogenous solution from which the target analytes migrated to a water-immiscible phase thanks to the phase separation induced by adjusting the solution pH. For this purpose, the phase transition behaviour was studied on DESs prepared from thymol and medium-chain fatty acids including hexanoic, octanoic, decanoic and dodecanoic acids, changing the pH medium with the addition of base and acid solutions. The results showed that thymol:hexanoic acid at a molar of 2:1 (100 µL) was the most suitable extraction solvent for the target analytes, due to the stronger hydrogen bond between the hydroxyl group (OH) of the fatty acid and thymol. Among the different affecting parameters investigated, the concentration levels of base and acid solutions played an important role in promoting the formation of a homogeneous mixture and breaking it down to separate the DES phase containing the target analytes from the aqueous sample, respectively. In this way, 100 µL of a 6 M potassium hydroxide (KOH) solution and 150 µL of a 6 M hydrochloric acid (HCl) solution were necessary to achieve a good extraction performance with recovery values in the range of 95–111%. After the extraction procedure, the DES droplet was collected and 10-fold diluted with methanol prior to the high performance liquid chromatography (HPLC)-UV determination.

Another strategy to favour phase separation has been the solidification of the floating organic droplet containing the analytes. This is the case of the work carried out by El-Deen and Shimizu [16] for the extraction of five endocrine disrupting compounds (EDCs) (i.e., plastic migrants, hormones and UV-filters) from environmental waters. For selecting the best extraction solvent, binary and ternary combinations of dodecanoic acid with other fatty acids (octanoic, nonanoic and decanoic acids) were studied at different molar ratios. The authors found that the length of the fatty acid chain significantly affected the extraction efficiency of the compounds of interest, since better results were obtained using binary DESs based on nonanoic acid compared with those based on octanoic acid due to their higher affinity to the target analytes through hydrophobic interactions. Although the addition of a third component significantly improved the extraction performance, as well as allowed to control density, the melting point and viscosity of the solvent met the
requirements of the SFOD technique. Among the evaluated TDESs, the combination of nonanoic, decanoic and dodecanoic acids, at a molar ratio of 1:1:1, was selected as the most appropriate extraction solvent since it provided a better chromatographic separation and peak shapes of target analytes. The phase separation was assisted by air cycles of pulling in/pushing out, avoiding the use of additional laboratory devices. The floating organic droplet obtained was frozen, then retrieved with a spatula, and 2-fold diluted with acetonitrile (ACN) prior to HPLC–photodiode array detector (PDA) analysis. The optimised methodology achieved low LODs between 0.96 and 2.30 µg/L and recovery values in the range of 90–104% for river and tap water samples. Finally, the green profile of the method was assessed by analytical eco-scale, obtaining an 89-point score that proved its eco-friendly behaviour. As can be seen in Figure 1, Raynie and GAPI pictograms also confirmed these results.

Figure 1. Greenness assessment of the developed and other reported DLLME methods for the determination of EDCs by Raynie (A) and GAPI (B) pictograms. Reprinted from El-Deen, A. K.; Shimizu, K. A Green Air Assisted-Dispersive Liquid-Liquid Microextraction Based on Solidification of a Novel Low Viscous Ternary Deep Eutectic Solvent for the Enrichment of Endocrine Disrupting Compounds from Water. J. Chromatogr. A, 2020, 1629, 461498 with permission from Elsevier [16].

However, other studies in which the phase separation has only been favoured by mechanical assistance (i.e., VA, SA, UA and air-assisted (AA) methods) can also be found in the literature [11,15,17–19,21]. In these cases, the analytical procedures are simpler, faster and cheaper since the use of additional solvents or solutions is avoided.

In addition to HDESs, quasi-HDESs have also been used as extraction solvents of organic contaminants from environmental samples. As an example, Gissawong et al. [15] prepared a DESs from tetrabutylammonium bromide (TBAB) and various fatty acids
(i.e., heptanoic, decanoic and 4-phenylbutyric acids) for the removal of five organophosphorus pesticides (OPPs) and two dyes from wastewater and water and soil destined to agricultural activities by the VA-LLME technique. In this case, the centrifugation step for phase separation was avoided by embedding the synthesised DESs into a sponge. After the removal process, the residual OPPs and dyes were determined by HPLC and UV–visible spectrophotometry analysis, respectively. In this way, the authors found that TBAB:decanoic acid at an optimised molar ratio of 1:3 gave rise to the highest removal efficiency (70–95%) of the pollutants. However, the main drawback of this work was the lack of characterisation of the DES phase after the removal step, since as previously demonstrated by Florindo et al. [26], the hydrogen bonds responsible for the formation of tetrabutylammonium chloride (TBAC):decanoic acid are partially broken in aqueous solution and the hydrophilic compound is solubilised into the water phase according to its water solubility. Therefore, considering that the counter anion of the quaternary ammonium salt has no influence on the DESs, the removal process that occurs in this study could be mainly attributed to the hydrophobic interactions between pollutants and one of the components of quasi-HDESs, decanoic acid, since TBAB could be suspected to leak into the aqueous phase. However, it could facilitate the dispersion of the fatty acid in the aqueous phase, as well as the mass transfer of the target analytes to the extraction phase by the salting-out effect. The sponge for its part also promoted the removal by the adsorption of pollutants into its pores. The proposed method achieved a point-score of 80 and 92 by the analytical eco-scale for OPPs and dyes, respectively, which indicated its green nature.

Apart from liquid-phase extraction methods, DESs have also been explored in sorbent-based extraction techniques, although to a significantly lesser extent. In this sense, Zarei et al. [24] prepared a ferrofluid based on a nanocomposite of montmorillonite clay@Fe₃O₄ modified with a menthol-based DES for the m-µ-dSPE of eleven explosives (nitrogen compounds) from water and soil samples. In order to successfully act as a carrier, the DES should meet some requirements, such as establishing interactions with the nano-material to form a stable ferrofluid, establishing interactions with the analytes to improve the extraction performance, showing good stability in water, among others. In this regard, among the seventeen carboxylic acids evaluated as HBDs, only those formed by octanoic, decanoic, dodecanoic and oleic acids were chemically stable in water during the extraction process, with the combination of menthol:decanoic acid (1:2) being the one that provided the highest extraction efficiency for all target analytes. In addition, the authors investigated the effect of the nanocomposite, DES and ferrofluid on the extraction efficiency, separately, finding that the nanocomposite could be used for the extraction of the target analytes, but irreversible adsorptions could occur for some of them. While using the ferrofluid, this effect did not take place, and additionally, a higher extraction efficiency was obtained. Under the optimised extraction conditions, low LODs between 0.22 and 0.91 µg/L, as well as recovery values in the range of 88–104%, were achieved using only 50 µL of the ferrofluid. In this way, the limitation of DESs to be applied only in solvent-based extraction techniques is overcome, and simultaneously, green sorbent-based extraction methods are developed.

In summary, DESs have been widely exploited for the extraction of organic compounds from environmental matrices, especially, different types of waters. In this sense, DESs composed of natural components such as terpenes and fatty acids stand out, although DESs prepared from synthetic quaternary ammonium or phosphonium salts have also been explored, and both have led to the development of green analytical methods [12,15]. These solvents have mainly been applied in solvent-based extraction methods, in which the phase separation after the extraction process was promoted by different types of forces, both chemical and physical, either by the use of organic solvents or DESs as dispersing agents, as well as by pH changes in the extraction medium, and different agitation methods, among others. Likewise, quasi-HDESs have also been used in this field, the hydrophobic part being mainly responsible for the extraction of the target analytes, while the water-soluble component acts simultaneously as salting-out and disperser agent favouring the extraction process. In addition to liquid-phase extraction methods, the use of DESs in sorbent-based
extraction techniques has also been investigated thanks to their combinations with other nanomaterials to form ferrofluids. With respect to the compatibility of DESs with the separation and determination techniques, their combinations with liquid chromatography coupled to conventional detectors and to a lesser extent to mass spectrometry (MS) detectors stand out above all others. In some cases, the final extracts are diluted with organic solvents or a mobile phase prior to injection into the chromatographic systems in order to avoid possible DES residues that could cause damage to the needle, column or detector, as well as to reduce the irreproducibility problems due to the high viscosity of DESs and improve the shapes of the peaks obtained.

2.2. Analysis of Inorganic Compounds in Environmental Samples

Although most applications of DESs in environmental samples analysis have mainly been focused on the evaluation of organic contaminants, the study of inorganic species has also been carried out (see Table 2 [27–41]). In this regard, heavy metals such as copper [29,35], lead [27,29,35,40], tungsten [28], arsenic [28,31,37,38], cadmium [27,35,40], cobalt [27], nickel [27,33,35], palladium [34,35], antimony [31,37], mercury [30], and chromium [37,41] represent the main applications of DESs to the analysis of inorganic species, but also trace elements like molybdenum [37], selenium [37,39], and vanadium [37], and compounds including ammonia [36], metal oxides [32], chlorides [32], acetates [32], phosphates [32], sulphates [32], and carbonates [32] have been studied. Regarding the matrices evaluated, the analysis of environmental waters stands out and different types of waters have been analysed [27,29–31,33–36,38–41], including lake, tap, river, well, sea, dam waters and wastewater. However, other samples such as sediments [29,38] and soils [29,37,38,40], mining residues [28], incinerated sewage sludge ash [32], or dust [34] and catalytic converter [34] have also been evaluated.

Table 2. Some examples of recent applications of DESs to the analysis of inorganic species in environmental samples.

| Sample (Amount)       | Analytes       | DES (Molar Ratio; Amount) | Extraction Procedure | Analytical Technique | Recovery % | LODs         | Comments                                                                 | Reference |
|-----------------------|----------------|---------------------------|----------------------|---------------------|------------|--------------|---------------------------------------------------------------------------|-----------|
| River, lake, and well water (15 mL) | Pb(II), Cd(II), Co(II), Ni(II) | THTDPC:thiosalicylic acid (1:2; 30 µL) | UA-SAP–LLME | HPLC–UV | 91–102 | 0.05–0.13 µg/L | - DES has a dual role: extractant and complexing agent. | [27] |
| Mining residues (39 g) | W, As | ChCl:malonic acid (1:2; 5 mL) | Electrolytic removal | ICP–OES | 22–35 | - | - ChCl:lactic acid (1:2) and propionic acid:urea (2:1) were also tested. | [28] |
| Sample (Amount)                      | Analytes                      | DES (Molar Ratio; Amount) | Extraction Procedure | Analytical Technique | Recovery % | LODs       | Comments                                                                 | Reference |
|-------------------------------------|-------------------------------|---------------------------|----------------------|---------------------|------------|------------|---------------------------------------------------------------------------|-----------|
| Lake and tap water (50 mL)          | Cu(II), Pb(II)                | ChCl:urea (1:2; -)        | m-µ-dSPE             | ICP–OES             | 94–102     | 0.29–0.51 µg/L       | - DES@Fe₃O₄ m-NPs (30 mg) was used as adsorbent.   | [29]      |
| Sediments and soil (0.05 g)         |                              |                           |                      |                     |            |            | - Ethylene glycol, oxalic acid, and glycerol were also tested as HBDs at different molar ratios. |           |
|                                     |                              |                           |                      |                     |            |            | - Molar ratios of 1:1.5 and 1:3 were also studied.                        |           |
|                                     |                              |                           |                      |                     |            |            | - 1 M HNO₃ was used as back-extraction solvent (500 µL).                  |           |
|                                     |                              |                           |                      |                     |            |            | - A selectivity study was carried out using potential interfering ions.   |           |
|                                     |                              |                           |                      |                     |            |            | - Accuracy was evaluated using CRMs.                                      |           |
|                                     |                              |                           |                      |                     |            |            | - The method was applied to the analysis of real samples.                |           |
| Well, tap, river, and wastewater (125 mL) | As(III/V), Sb(III/V)               | ChCl:oxalic acid (1:3; 700 µL) | VA-ELLME            | HG–AAS             | 94–96      | 7.5-15.6 ng/L            | - TBAC and TOAC as HBAs and phenol, glycerol, and decanoic acid as HBDs were also tested at different molar ratios. | [31]      |
|                                     |                              |                           |                      |                     |            |            | - Molar ratios of 1:1, 1:2, 1:4, and 2:1 were also studied.              |           |
|                                     |                              |                           |                      |                     |            |            | - Dithizone (600 µL) was used as complexing agent.                       |           |
|                                     |                              |                           |                      |                     |            |            | - THF was used as emulsifier (300 µL).                                    |           |
|                                     |                              |                           |                      |                     |            |            | - Final extract was diluted with acidic ethanol up to 2.5 mL.            |           |
|                                     |                              |                           |                      |                     |            |            | - A selectivity study was carried out using potential interfering ions. |           |
|                                     |                              |                           |                      |                     |            |            | - Bottled water, honey, and rice were also evaluated.                    |           |
|                                     |                              |                           |                      |                     |            |            | - The method was applied to the analysis of real samples.                |           |
| Well, tap, river, and wastewater (125 mL) | As(III/V), Sb(III/V)               | ChCl:oxalic acid (1:3; 700 µL) | VA-ELLME            | HG–AAS             | 94–96      | 7.5-15.6 ng/L            | - TBAC and TOAC as HBAs and phenol, glycerol, and decanoic acid as HBDs were also tested at different molar ratios. | [31]      |
Table 2. Cont.

| Sample (Amount)                      | Analytes                          | DES (Molar Ratio; Amount) | Extraction Procedure | Analytical Technique | Recovery % | LODs       | Comments                                                                 | Reference |
|-------------------------------------|-----------------------------------|---------------------------|----------------------|----------------------|------------|------------|---------------------------------------------------------------------------|-----------|
| Incinerated sewage sludge ash (0.1 g) | AlPO$_4$ and Ca$_3$(PO$_4$)$_2$ | ChCl and DMU-based DESs (< 5 g) | SLE                  | ICP-OES ICP-MS       | 1-47       | -          | - D-sorbitol, tartaric and citric acid, urea, D-fructose, and mannose were tested as HBDs. - Solubility experiments of 12 metal oxides, 7 chlorides, 3 acetates, 2 phosphates, CaSO$_4$, and CaCO$_3$ in 7 different DESs were carried out. - Heavy metals were also measured by ICP-MS, AAS, or cold-vapor atomic spectrometry. | [32]      |
| Sea, well, and wastewater (30 mL)   | Ni(II)                            | TBAC:decanoic acid (1:5; 100 µL) | UA-DLLME            | FAAS                 | 91-99      | 0.13 µg/L   | - Molar ratios of 1:2 and 1:4 were also studied. - Sodium diethylthiocarbamate was used as complexing agent (200 µL, 0.15% w/v). - THF was used as disperser (250 µL). - Final extract was 2-fold diluted with HNO$_3$ conc. - A selectivity study was carried out using potential interfering ions. - Accuracy was evaluated using CRMs. - Mineral water samples were also evaluated. - The method was applied to the analysis of real samples. | [33]      |
| Tap, river, and sea water (20 mL)   | Cd, Ni, Pb, Cu                    | ChCl:5,6,7,8-tetrahydro-5,5,8,8-tetramethylnapthalen-2-ol (1:2; 70 µL) | AA-ELLME            | FAAS                 | 99-106     | 0.31-0.99 µg/L | - Molar ratios of 1:1 and 1:3 were also studied. - A mixture of DESS triethylamine (1:1, v/v) was used as extraction solvent (100 µL). - THF was used as emulsifier (100 µL). - Five pulling in/pushing out cycles were performed. - A selectivity study was carried out using potential interfering ions. - Accuracy was evaluated using a CRM. - Bottled water, black tea, and urine samples were also evaluated. | [34]      |
Table 2. Cont.

| Sample (Amount) | Analytes                  | DES (Molar Ratio; Amount) | Extraction Procedure | Analytical Technique | Recovery % | LODs          | Comments                                                                 | Reference |
|-----------------|---------------------------|---------------------------|----------------------|----------------------|------------|----------------|--------------------------------------------------------------------------|-----------|
| NH₃ gas (-)     | NH₃                       | ChCl:resorcinol:glycerol (1:5:5; 10 g) | GLE                   | Gravimetry           | -          | -             | - Different HBIs were tested to form binary DESs and TDESs.               | [36]      |
|                 |                           |                           |                      |                      |            |                | - A maximum mass solubility of 0.13 g/g at 40 °C was achieved.           |           |
|                 |                           |                           |                      |                      |            |                | - A selectivity study of NH₃ to CO₂ was carried out.                     |           |
| Soil (100 mg)   | As, Cr, Mo, Sb, Se, V    | ChCl:oxalic acid (1:2; 10 mL) | UAE                   | ICP-OES              | 99–102     | 0.009–0.1 mg/kg | - Molar ratios of 1:1, 1:1.5, and 2:1 were also studied.                | [37]      |
|                 |                           |                           |                      |                      |            |                | - 2 M HNO₃ was used as co-extractant (5 mL).                              |           |
|                 |                           |                           |                      |                      |            |                | - Final extract was diluted with water up to 25 mL.                       |           |
|                 |                           |                           |                      |                      |            |                | - Optimisation of the method was carried out using a CRM.                |           |
|                 |                           |                           |                      |                      |            |                | - Accuracy was evaluated using a CRM.                                    |           |
|                 |                           |                           |                      |                      |            |                | - The method was compared with a conventional acid digestion method.     |           |
|                 |                           |                           |                      |                      |            |                | - The method was applied to the analysis of real clay-loamy soil, silt loam, and loamy sand samples. |           |
| Lake, mineral, tap and river water (25 mL) | As(III/V) | ChCl:phenol (1:3; 1000 µL) | UA-ELLME             | ETAAS                | 96–99      | 10 ng/L        | - Solid samples were previously acid digested.                           | [38]      |
| Sediments and soil (500 mg) |             |                           |                      |                      |            |                | - Molar ratios of 1:1 and 1:2 were also studied.                         |           |
|                 |                           |                           |                      |                      |            |                | - Sodium diethylthiocarbamate was used as complexing agent (500 µL, 0.1% w/v). |           |
|                 |                           |                           |                      |                      |            |                | - THF was used as emulsifier (500 µL).                                    |           |
|                 |                           |                           |                      |                      |            |                | - Final extract was diluted with acidic ethanol up to 1 mL.               |           |
|                 |                           |                           |                      |                      |            |                | - A selectivity study was carried out using potential interfering ions.  |           |
|                 |                           |                           |                      |                      |            |                | - Accuracy was evaluated using CRMs.                                     |           |
|                 |                           |                           |                      |                      |            |                | - Edible mushrooms, green and black tea, rice, and cigarette samples were also evaluated. |           |
|                 |                           |                           |                      |                      |            |                | - The method was applied to the analysis of real samples.                |           |
| Tap water (25 mL) | Se, Se(IV/VI) | ChCl:phenol (1:3; 500 µL) | UA-ELLME             | ETAAS                | 96–99      | 4.61 ng/L      | - TOAC and TBAC as HBAs and decanoic acid as HBIs were also tested at molar ratio 1:2. | [39]      |
|                 |                           |                           |                      |                      |            |                | - Molar ratios of 1:1 and 1:2 were also studied.                         |           |
|                 |                           |                           |                      |                      |            |                | - 3,3′-diaminobenzidine was used as complexing agent (400 µL, 4 mM).        |           |
|                 |                           |                           |                      |                      |            |                | - THF was used as emulsifier (500 µL).                                    |           |
|                 |                           |                           |                      |                      |            |                | - Final extract was diluted with acidic ethanol up to 500 µL.             |           |
|                 |                           |                           |                      |                      |            |                | - A selectivity study was carried out using potential interfering ions.  |           |
|                 |                           |                           |                      |                      |            |                | - Accuracy was evaluated using a CRM.                                    |           |
|                 |                           |                           |                      |                      |            |                | - Mineral water and iced tea, as well as different food samples were also evaluated. |           |
Table 2. Cont.

| Sample (Amount) | Analytes | DES (Molar Ratio; Amount) | Extraction Procedure | Analytical Technique | Recovery % | LODs | Comments | Reference |
|-----------------|----------|--------------------------|----------------------|---------------------|------------|------|----------|-----------|
| *Soil (0.2 g)*  | Pb(II),  | ChCl:urea (1:2; 200 µL)  | m-µ-dSPE FAAS         | 95–105              | 0.1–0.4 µg/L|      |          | [40]      |
| River, tap,     | Cd(II)   |                         |                      |                     |            |      |          |           |
| *well, and sea* | water (60 mL) |                 |                      |                     |            |      |          |           |
| *Tap, lake, and  | *Cr(III/VI)| ChCl:phenol (1:3; 450 µL) | UA-ELLME FAAS        | 93–108              | 5.5 µg/L   |      |          | [41]      |
| *factory        |          |                         |                      |                     |            |      |          |           |
| *wastewater*    |          |                         |                      |                     |            |      |          |           |
| (10 mL)         |          |                         |                      |                     |            |      |          |           |

- Soil samples were previously acid digested.
- Fe₂O₃ m-NPs (20 mg) were separately added to the sample.
- Ethylene glycol and oxalic acid were also tested as HBDs at molar ratio 1:2.
- Other molar ratios of ChCl:urea were tested.
- Al₂O₃ and TiO₂ were also evaluated in combination with DES.
- 1 M HNO₃ was used as back-extraction solvent (600 µL).
- A selectivity study was carried out using potential interfering ions.
- Hair samples were also evaluated.
- The method was applied to the analysis of real samples.

With this aim, both NaDESs [29–32,37,40] or non-NaDESs [27,28,32–36,38,39,41] have been used for the analysis of inorganic species in environmental samples. Regarding their aqueous compatibility, most cases imply the use of hydrophilic DESs [28–32,34–41] even though some examples of quasi-HDESs [33] and HDESs [27] can be found in the literature. As it is shown in Table 2, ChCl constitutes the most used HBA [28,29,31,32,34–41], although other quaternary salts such as trihexyl(tetradecyl)phosphonium chloride (THT-DPC) [27] or TBAC [33], as well as N,N'-dimethyl urea (DMU) [32], or betaine [30] have also been employed. With respect to the HBDs, different alcohols [30,32,34–36,38,39,41] and organic acids [27,28,31,32,37] as well as urea [29,40], sugars [32], and fatty acids [33] have been used.

DESs were mainly used as extraction solvents and without any doubt, LLME approaches [27,30,31,33–35,38,39,41] stand out, but other extraction techniques were applied based on solid–liquid extraction (SLE) [32,37], m-µ-dSPE [29,40], and gas–liquid extraction (GLE) [36]. In the case of LLME techniques, the emulsification LLME (ELLME) based on the use of an aprotic solvent as emulsifier to achieve phase separation was the mainly used extraction method [30,31,34,35,38,39,41], although some works in which a disperser has been applied can be also found in the literature [33]. In these cases, one of the main challenges is the collection of the drop after the extraction and as previously mentioned,
among the proposed solutions was the solidification of the organic droplets to promote the obtention of the analytes-enriched extract. However, this alternative cannot be useful when a DES with a very low freezing point is used. Thus, the solidification of the aqueous phase could be a tedious task, but at the same time, it could be a great solution to this issue [27]. Besides, regardless of the procedure used, most cases involve the use of external assistance including UA [27,30,33,37–39,41], VA [31], AA [34,35], magnetic assistance [29,40], or current intensity [28], among others, as it was mentioned for the extraction of organic compounds.

An interesting application of additional assistance on the extraction of inorganic compounds was the work of Almeida et al. [28]. In this case, the authors performed an electrodialytic system based on DESs for the removal and separation of tungsten and arsenic from mining residues. With this aim, three extraction systems were compared: (i) a conventional SLE, in which 2.2 g of sample was extracted with 20 mL of DES for 10 days; (ii) an SLE of 11.1 g of mining residues in 98.5 mL of water mixed with 1.5 mL of DES and applying current intensities of 50 and 100 mA for 4 days; and (iii) an electrodialytic system with two compartments: the cathode in which 39 g of samples were mixed with 345 mL of water and 5 mL of DES and the anode, in which 250 mL of 0.01 M NaNO₃ were placed. Both parts were divided by an anion exchange membrane, and current intensities of 50 and 100 mA were applied for 4 days. In the initial study, four DESs were tested composed of ChCl and malonic, oxalic, and lactic acids at molar ratios of 1:2, 1:1, and 1:2, respectively, and urea:propionic acid at a molar ratio of 1:2, showing that the best extraction yields were obtained with the first two DESs for As (16.2%) and W (8.8%), respectively. ChCl:malonic acid presents lower viscosity which improved the mass transfer of As. For its part, W extraction is enhanced by high concentrations of chloride ions provided by ChCl and oxalate ions through the availability of tungsten complexes in solution. Thus, these DESs were selected for further experiments. When this experiment was carried out applying a current intensity of 100 mA, better results were obtained using ChCl:oxalic acid DESs (recovery of 27.6% for As and 15.6% for W). The use of an electrical field may contribute to accelerate the dissolution of tungsten, which could explain this improvement. In the case of the electrodialytic removal, the absence of DESs during the extraction performance caused the W recovery to fall lower than 1%. In DES-assisted extraction, the removal of 35% for As and 22% for W was obtained using ChCl:oxalic acid and a current intensity of 100 mA. However, the best electromigration conditions for As and W were obtained using ChCl:malonic acid (100 and 50 mA, respectively) with migration percentages of 82.3 and 76.5%. This work constitutes a promising strategy for the remediation of As and W from mining residues and the subsequent exploitation of treated residues in the construction sector, although the material is not free of contaminants and further studies should be carried out in this way.

A commonly used strategy for the extraction of metal ions from aqueous samples or solutions is to use a complexing agent that allows the efficient extraction of analytes [30,31,33,34,38,39,41]. In this case, the formation of a hydrophobic complex between metal ions and the complexing ligand takes place, favouring the extraction of the metal–ligand complex into the extraction phase and improving the selectivity of the procedure. An interesting approach is the one developed by Werner [27], in which taking advantage of the versatile properties of DESs, an HDES constituted of the IL THTDPC (HBA) and thiosalicylic acid (HBD) was synthesised at a molar ratio of 1:2 and used as both extraction and complexing agent. Thanks to the presence of thiol groups, the HDES was capable of executing this dual role, obtaining good recovery values (99–102%) as well as low LODs (0.05–0.13 µg/L) for divalent cations of lead, cadmium, cobalt, and nickel. Additionally, considering that the freezing point of the HDES was much lower than that of water, the UA-solidified aqueous phase (SAP)–LLME of 15 mL of water samples with 30 µL of extraction solvent was carried out and the DES extract was 3-fold diluted prior to its injection into the HPLC–UV system for the determination of DES-based metal complexes. However, despite the good results obtained, freezing 15 mL of water is not a quick task to
carry out. In addition, since it is an HDES, although it is lighter than water, its collection can be easier than the proposed SAP procedure.

Although most applications of DESs for the analysis of environmental samples have been based on LLME procedures, a few works on extractions with sorbents based on DESs can be found in the literature. This is the case of the work of Karimi et al. [40] who synthesised a DES-based magnetic sorbent for the preconcentration of Pb(II) and Cd(II) from soil, river, tap, well and sea water and their determination by flame atomic absorption spectrometry (FAAS). Bare nanoparticles of Fe$_3$O$_4$, Al$_2$O$_3$ and TiO$_2$, and DESs of ChCl with oxalic acid, urea and ethylene glycol were evaluated. The best results were obtained with the DES of ChCl:urea 1:2.5 and Fe$_3$O$_4$ magnetic nanoparticles (m-NPs), as the most suitable sorbent due to the ease of separating the phases thanks to its magnetic properties. Interestingly, according to the authors, 200 µL of DES and 20 mg of m-NPs were added to 60 mL of sample solutions at pH 6.5 and stirred for 10 min. At this step, both processes took place: the interaction of DES with the metal ions and the adsorption of DESs in the m-NPs surface. After the separation of the sorbent with an external magnet, the analytes were re-extracted with 600 µL of 1M HNO$_3$. The recovery of 95–105% and LODs between 0.1 and 0.4 µg/L were obtained. Despite the good results obtained in this work and other similar applications, the combination of hydrophilic DESs with m-NPs for its use in aqueous samples is a controversial topic. According to Karimi et al. [40], the DES acts as a hydroxy functionalised IL and it is adsorbed on the surface of m-NPs, probably through strong hydrogen bonds and electrostatic interactions, losing its liquid state, and it allowed its separation from the aqueous solution. However, two major issues must be considered at this point. Firstly, the supposition that a hydrophilic DES-based sorbent can be formed in situ in an aqueous solution, more so when the instability DES based on ChCl has been amply demonstrated due to its decomposition in the sample. Secondly, and related to the first point, the authors stand up for the possibility that the binding forces of the sorbent are hydrogen bonds and electrostatic interactions that can easily be broken in the sample solution. In a similar work, Tan et al. [42] used m-NPs combined with ChCl:acetic acid 1:3 for the extraction of plant growth regulators from edible oils. In this case, in which a fatty sample was evaluated, and hydrogen bonds can be formed between DESs and the m-NPs, the authors indicated that when an external magnet was used, the m-NPs moved with the magnet while DES dropped to the bottom of the tube. This suggests that interactions of this kind of DESs with the m-NPs surface are very weak and contradict the idea proposed by Karimi et al. [40]. Apart from that, in none of these works were two important aspects evaluated. Firstly, the extraction capacity of the unmodified sorbent versus the one modified with DESs, which would respond to the need of combining both materials. Secondly, a thorough characterisation of the sorbent before and after the extraction procedure. Although Karimi et al. [40] performed Fourier transform infrared spectroscopy analysis of bare and modified m-NPs after the extraction procedure, these tests are not conclusive to determine if both materials remain in the final phase.

One of the current concerns of government agencies, the scientific community, and popular society is the lack of resources prognosticated for the next century. For this reason, great efforts are being made aimed at the recovery of valuable resources and the reuse of wastes and secondary resources. With this aim, Söldner et al. [32] presented a broad study of the potential of some biodegradable DESs for the extraction of metal salts and oxides, as well as phosphates from incinerated sewage sludge ash, as the main secondary resource of sewage sludge. In this regard, seven DESs based on ChCl and D-sorbitol, tartaric or citric acid, and urea, or DMU with D-fructose, mannose, and citric acid, as HBA and HBDs, respectively, were evaluated. As can be seen in Figure 2, the solubility in terms of mass fraction (wt%) of twelve metal oxides [Al(III), Ca(II), Fe(III), Cu(II), Zn(II), Mo(III), Ru(IV), Sn(IV), Ce(IV), Pt(IV), Pb(II/IV)], seven metal chlorides [Fe(III), Cu(II), Zn(II), La(III), Ce(III), Eu(III), Pb(II)], three metal acetates [Cu(II), Zn(II), Pb(II)], two metal phosphates [Al(III), Ca(II)], CaSO$_4$, and CaCO$_3$ in the tested DESs showed that metal oxides were better dissolved in eutectic mixtures containing carboxylic acids while those
formed by urea or derivatives are preferable by metal chlorides or phosphates. These facts can be partially explained because of the pH values of the eutectic mixtures. DESs containing organic acids present pH values in the range of 0–2, very favourable for metal oxides dissolution, and metal chlorides dissolve in neutral or slightly basic media such as the main values of urea or DMU (pH of 6.9–7.7). However, although phosphates also dissolve in neutral or slightly basic DESs media, this does not appear to conform to this pH trend. For their part, acetates tend to dissolve in DESs composed of ChCl. Thus, based on these data, the selective extraction of the studied compounds is possible, however, as indicated by the authors, it should be determined experimentally. As incinerated sewage sludge ash contained both phosphate-based compounds and trace components such as metal oxides, which possessed very similar solubility properties in conventional solvents, the authors proposed the evaluation of neutral to slightly basic DESs containing urea or derivatives in order to selectively separate both kinds of compounds. Thus, ChCl:urea (1:2), DMU:D-fructose (3:1), and DMU:mannose (5:1) were tested, while ChCl:D-sorbitol (5:1) was selected as the reference medium because of its slightly acidic pH and does not possess a urea derivative. As expected, the best extraction yields of around 45 and 47% were found for DMU with fructose and mannose, respectively, after 24 h of extraction. However, when the accumulation of phosphates was studied, it showed that the main accumulation took place in the first few hours (31% in 2 h for DMU:mannose), while the accumulation was very little in the following hours (7% in 24 h). Additionally, the authors studied the content of toxic heavy metals in both the original matrix and in the extract following the requirements of the German Ordinance for the Recovery of Sewage Sludge. Results showed that the amounts of toxic metals, which are relatively low in the raw material, not only do not decrease, but some of them also accumulate, such as cadmium and nickel. In conclusion, the work developed by Sölder et al. served as a preliminary study for phosphorus resources obtention, however, further studies should be carried out in order to improve the extraction performance and removal of undesirable components such as toxic metals.

In general terms, for the evaluation of inorganic species in environmental samples, there is not much variability in the use of DESs and they are mainly formed by ChCl as HBA and/or alcohols, organic acids, or urea as HBDs. Several metal ions were evaluated, although other inorganic compounds such as ammonia and metal oxides and salts were also determined. In addition, different kinds of waters, as the sample most evaluated, as well as soils and sediments, were analysed. To a lesser extent, mining residues and incinerated sewage sludge ash as a possible source of valuable secondary resources were studied. Regarding the extraction techniques, LLME approaches in combination with different external assistance stand out, but other extraction techniques were performed, such as m-µ-dSPE, SLE, or even GLE. The detection systems were mainly FAAS, and inductively coupled plasma (ICP)–optical emission spectrometry (OES), and only in one case, the extraction procedure was coupled to a chromatographic system. Additionally, it is worth remarking that, although many of the authors commented in the papers about the greenness of the method, in all cases they do so, it is based on the nature of the components that make up the DESs and their easy synthesis, as well as the volume of solvents used. However, in none of them an exhaustive study was carried out in which penalty points were assigned based on all the stages that come into play during the procedure, from sample pre-treatment to analysis. In this regard, it seems that authors that are focused on the evaluation of inorganic species prioritise the accuracy and selectivity of the method over the concern to follow the principles of green chemistry by conducting accuracy studies of the method using certified reference materials (CRMs), as well as evaluating possible interfering species, both organic and inorganic, despite the fact that the application of DESs shows the current trend, also in this field, of developing greener procedures.
organic acids present pH values in the range of 0–2, very favourable for metal oxides dissolution, and metal chlorides dissolve in neutral or slightly basic media such as the main values of urea or DMU (pH of 6.9–7.7). However, although phosphates also dissolve in neutral or slightly basic DESs media, this does not appear to conform to this pH trend. For their part, acetates tend to dissolve in DESs composed of ChCl. Thus, based on these data, the selective extraction of the studied compounds is possible, however, as indicated by the authors, it should be determined experimentally. As incinerated sewage sludge ash contained both phosphate-based compounds and trace components such as metal oxides, which possessed very similar solubility properties in conventional solvents, the authors proposed the evaluation of neutral to slightly basic DESs containing urea or derivatives in order to selectively separate both kinds of compounds. Thus, ChCl:urea (1:2), DMU:D-fructose (3:1), and DMU:mannose (5:1) were tested, while ChCl: D-sorbitol (5:1) was selected as the reference medium because of its slightly acidic pH and does not possess a urea derivative. As expected, the best extraction yields of around 45 and 47% were found for DMU with fructose and mannose, respectively, after 24 h of extraction. However, when the accumulation of phosphates was studied, it showed that the main accumulation took place in the first few hours (31% in 2 h for DMU:mannose), while the accumulation was very little in the following hours (7% in 24 h). Additionally, the authors studied the content of toxic heavy metals in both the original matrix and in the extract following the requirements of the German Ordinance for the Recovery of Sewage Sludge. Results showed that the amounts of toxic metals, which are relatively low in the raw material, not only do not decrease, but some of them also accumulate, such as cadmium and nickel. In conclusion, the work developed by Sölder et al. served as a preliminary study for phosphorus resources obtention, however, further studies should be carried out in order to improve the extraction performance and removal of undesirable components such as toxic metals.

Figure 2. Maximum solubility as the mass fraction $\omega_{\text{max}}$ (wt%) of metal compounds in seven different DESs: (a) oxides; (b) chlorides; (c) acetates; and (d) phosphates. The mass fractions represent an average of three independent measurements. Reprinted from Söldner, A.; Zach, J.; König, B. Deep Eutectic Solvents as Extraction Media for Metal Salts and Oxides Exemplarily Shown for Phosphates from Incinerated Sewage Sludge Ash. Green Chem., 2019, 21 (2), 321–328 with permission from Royal Society of Chemistry [32].

3. Conclusions

The introduction of DESs in analytical chemistry to replace traditional toxic and volatile organic solvents is, without any doubt, a practice that is growing and consolidating due to their remarkable benefits, such as their easy and inexpensive preparation, low volatility and toxicity, biodegradability and biocompatibility. These solvents exhibit a high tunability of their physicochemical properties (melting point, viscosity, conductivity, vapour pressure, density, miscibility and polarity) mainly by changing the starting components and their respective molar ratios, as well as a high solvation capacity, which together make them suitable as extraction solvents of both organic compounds (pharmaceuticals, pesticides, dyes, UV-filters, etc.) and inorganic species (metal ions, metal oxides, metal salts, ammonia, etc.) from different environmental matrices. In this sense, DESs and NaDESs have been applied in several liquid-phase extraction methods, especially in miniaturised approaches, which require low volumes of solvents to obtain satisfactory extraction efficiencies. Due to the viscosity of DESs, it has sometimes been necessary to apply different assistance methods (ultrasound, vortex, air cycles, etc.) in order to disperse them through the sample solution, and consequently, enhance the mass transfer of the target analytes into the extraction phase. Apart from that, sorbent-based extraction techniques using DESs combined with other nanomaterials as extractant agents can also be found in the field.
of environmental analysis. Likewise, other applications of DESs such as gas absorption, extraction of bioactive compounds, revalorisation of industrial wastes, as well as the recovery of value-added substances, have also been reported in the literature. In order to overcome the limitations of extracting a group of compounds of interest from aqueous solutions, HDESs have been widely employed for the analysis of environmental water samples, although quasi-HDESs have also been developed for this purpose, fundamentally for the extraction of organic compounds. Likewise, hydrophilic DESs have also been used for the extraction of organic compounds and metal species from non-aqueous media or aqueous samples with the use of additional steps. Regarding the combination of DESs with analytical instruments, chromatographic techniques and spectrophotometric methods have been the most frequently used. However, to the best of our knowledge, these solvents have not been applied to modify chromatographic techniques in the analysis of environmental matrices. Although the use of DESs has not only given rise to highly selective and sensitive sample preparation steps but also easier analytical performance, further studies should be addressed in terms of the characterisation, greenness and reuse of these solvents.

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**Abbreviations**

| Analytes     | Definition                                  |
|--------------|---------------------------------------------|
| EDC          | endocrine disrupting compound               |
| iHg          | inorganic mercury                           |
| OPP          | organophosphorus pesticide                  |
| PAE          | phthalic acid ester                         |
| PAH          | polycyclic aromatic hydrocarbon             |
| DES          | components                                  |
| ChCl         | choline chloride                            |
| DMU          | N,N′-dimethyl urea                           |
| DTMAC        | dodecyltrimethylammonium chloride           |
| HBA          | hydrogen bond acceptor                      |
| TBD          | hydrogen bond donor                         |
| TBAB         | tetrabutylammonium bromide                  |
| TBAC         | tetrabutylammonium chloride                 |
| THTDPC       | trihexyl(tetradecyl)phosphonium chloride    |
| TOAC         | trioctylammonium chloride                   |
| TOMAC        | trioctylmethylammonium chloride             |
Extraction procedure

- **AA**: air-assisted
- **DLLME**: dispersive liquid–liquid microextraction
- **ELLME**: emulsification liquid–liquid microextraction
- **GAPI**: Green Analytical Procedure Index
- **GLE**: gas–liquid extraction
- **LLME**: liquid–liquid microextraction
- **m-µ-dSPE**: magnetic-micro-dispersive solid-phase extraction
- **SA**: shaker-assisted
- **SAP**: solidified aqueous phase
- **SFOD**: solidified floating organic droplet
- **SLE**: solid–liquid extraction
- **UA**: ultrasound-assisted
- **UAE**: ultrasound-assisted extraction
- **VA**: vortex-assisted

Analytical technique

- **µ-ECD**: micro-electron capture detector
- **AAS**: atomic absorption spectrometry
- **CPMAS/NMR**: cross-polarisation magic-angle spinning/nuclear magnetic resonance
- **DAD**: diode array detector
- **ETAAS**: electrothermal atomic absorption spectrometry
- **FAAS**: flame atomic absorption spectrometry
- **FD**: fluorescence detector
- **GC**: gas chromatography
- **HG**: hydride generation
- **HPLC**: high performance liquid chromatography
- **ICP**: inductively coupled plasma
- **LOD**: limit of detection
- **MS/MS**: tandem mass spectrometry
- **MS**: mass spectrometry
- **OES**: optical emission spectrometry
- **PDA**: photodiode array detector
- **QqQ**: triple quadrupole
- **UHPLC**: ultra-high performance liquid chromatography
- **UV**: ultraviolet
- **VWD**: variable wavelength detector

Reagents, sorbents and solvents

- **ACN**: acetonitrile
- **CRM**: certified reference material
- **DES**: deep eutectic solvent
- **GRAS**: generally recognised as safe
- **HDES**: hydrophobic deep eutectic solvent
- **IL**: ionic liquid
- **m-NP**: magnetic nanoparticle
- **MWCNT**: multi-walled carbon nanotube
- **NaDES**: natural deep eutectic solvent
- **SUPRAS**: supramolecular solvent
- **TDES**: ternary deep eutectic solvent
- **THF**: tetrahydrofuran
- **β-CD**: beta-cyclodextrin

References

1. Huang, T.; Tang, X.; Luo, K.; Wu, Y.; Hou, X.; Tang, S. An overview of graphene-based nanoadsorbent materials for environmental contaminants detection. *TrAC Trends Anal. Chem.* 2021, 139, 116255. [CrossRef]
2. Chen, T.-L.; Kim, H.; Pan, S.-Y.; Tseng, P.-C.; Lin, Y.-P.; Chiang, P.-C. Implementation of green chemistry principles in circular economy system towards sustainable development goals: Challenges and perspectives. *Sci. Total Environ.* 2020, 716, 136998. [CrossRef] [PubMed]
3. Schaeffer, N.; Passos, H.; Billard, I.; Papaiconomou, N.; Coutinho, J.A. Recovery of metals from waste electrical and electronic equipment (WEEE) using unconventional solvents based on ionic liquids. *Crit. Rev. Environ. Sci. Technol.* 2018, 48, 859–922. [CrossRef]

4. Hashemi, B.; Zoohrabi, P.; Dehdashtian, S. Application of green solvents as sorbent modifiers in sorptive-based extraction techniques for extraction of environmental pollutants. *TrAC Trends Anal. Chem.* 2018, 109, 50–61. [CrossRef]

5. Musarurwa, H.; Tavengwa, N.T. Emerging green solvents and their applications during pesticide analysis in food and environmental samples. *Talanta* 2021, 223, 121507. [CrossRef]

6. Huang, J.; Guo, X.; Xu, T.; Fan, L.; Zhou, X.; Wu, S. Ionic deep eutectic solvents for the extraction and separation of natural products. *J. Chromatogr. A* 2019, 1598, 1–19. [CrossRef] [PubMed]

7. Santana-Mayor, A.; Rodríguez-Ramos, R.; Herrera-Herrera, A.V.; Socas-Rodriguez, B.; Rodríguez-Delgado, M.A. Deep eutectic solvents. The new generation of green solvents in analytical chemistry. *TrAC Trends Anal. Chem.* 2021, 134, 116108. [CrossRef]

8. Martins, M.A.R.; Pinho, S.P.; Coutinho, J.A.P. Insights into the Nature of Eutectic and Deep Eutectic Mixtures. *J. Solut. Chem.* 2019, 48, 962–982. [CrossRef]

9. Hansen, B.B.; Spittle, S.; Chen, B.; Poe, D.; Zhang, Y.; Klein, J.M.; Horton, A.; Adhikari, L.; Zelovich, T.; Doherty, B.W.; et al. Deep Eutectic Solvents: A Review of Fundamentals and Applications. *Chem. Rev.* 2021, 121, 1232–1285. [CrossRef]

10. Lee, J.; Kim, H.; Kang, S.; Baik, N.; Hwang, I.; Chung, D.S. Applications of deep eutectic solvents to quantitative analyses of pharmaceuticals and pesticides in various matrices: A brief review. *Arch. Pharmacal. Res.* 2020, 43, 900–919. [CrossRef] [PubMed]

11. Santana-Mayor, A.; Socas-Rodriguez, B.; Rodríguez-Ramos, R.; Herrera-Herrera, A.V.; Rodríguez-Delgado, M.A. Quality assessment of environmental water by a simple and fast non-ionic hydrophobic natural deep eutectic solvent-based extraction procedure combined with liquid chromatography tandem mass spectrometry for the determination of plastic migrants. *Anal. Bioanal. Chem.* 2021, 413, 1967–1981. [CrossRef] [PubMed]

12. Sereshti, H.; Karami, F.; Nouri, N. A green dispersive liquid-liquid microextraction based on deep eutectic solvents doped with β-cyclodextrin: Application for determination of tetracyclines in water samples. *Microchem. J.* 2021, 163, 105914. [CrossRef]

13. Ma, W.; Row, K.H. pH-induced deep eutectic solvents based homogeneous liquid-liquid microextraction for the extraction of two antibiotics from environmental water. *Microchem. J.* 2021, 160, 105642. [CrossRef]

14. Hu, X.; Zhang, L.; Xia, H.; Peng, M.; Zhou, Y.; Xu, Z.; Peng, X. Dispersive liquid-liquid microextraction based on a new hydrophobic deep eutectic solvent for the determination of phenolic compounds in environmental water samples. *J. Sep. Sci.* 2021, 1510–1520. [CrossRef]

15. Gissavong, N.; Mukdasai, S.; Boonchianma, S.; Sansuk, S.; Srijaranai, S. A rapid and simple method for the removal of dyes and organophosphorus pesticides from water and soil samples using deep eutectic solvent embedded sponge. *Chemosphere* 2020, 260, 127590. [CrossRef]

16. El-Deen, A.K.; Shimizu, K. A green air assisted-dispersive liquid-liquid microextraction based on solidification of a novel low viscous ternary deep eutectic solvent for the enrichment of endocrine disrupting compounds from water. *J. Chromatogr. A* 2020, 1629, 461498. [CrossRef]

17. Li, K.; Jin, Y.; Jung, D.; Park, K.; Kim, H.; Lee, J. In situ formation of thymol-based hydrophobic deep eutectic solvents: Application to antibiotics analysis in surface water based on liquid-liquid microextraction followed by liquid chromatography. *J. Chromatogr. A* 2020, 1614, 460730. [CrossRef]

18. Liu, X.; Liu, C.; Qian, H.; Qu, Y.; Zhang, S.; Lu, R.; Gao, H.; Zhou, W. Ultrasound-assisted dispersive liquid-liquid microextraction based on a hydrophobic deep eutectic solvent for the preconcentration of pyrethroid insecticides prior to determination by high-performance liquid chromatography. *Microchem. J.* 2019, 146, 614–621. [CrossRef]

19. Liu, Y.; Xu, W.; Zhang, H.; Xu, W. Hydrophobic deep eutectic solvent-based dispersive liquid–liquid microextraction for the simultaneous enantiomeric analysis of five β-agonists in the environmental samples. *Electrophoresis* 2019, 40, 2828–2836. [CrossRef]

20. Haghbakhash, R.; Raeissi, S. Deep eutectic solvents for CO₂ capture from natural gas by energy and exergy analyses. *J. Environ. Chem. Eng.* 2019, 7, 103411. [CrossRef]

21. Ge, D.; Zhang, Y.; Dai, Y.; Yang, S. Air-assisted dispersive liquid-liquid microextraction based on a new hydrophobic deep eutectic solvent for the preconcentration of benzo phenone-type UV filters from aqueous samples. *J. Sep. Sci.* 2018, 41, 1635–1643. [CrossRef] [PubMed]

22. Yousefi, S.M.; Shemiranf, F.; Ghorbanian, S.A. Hydrophobic Deep Eutectic Solvents in Developing Microextraction Methods Based on Solidification of Floating Drop: Application to the Trace HPLC/FLD Determination of PAHs. *Chromatographia* 2018, 81, 1201–1211. [CrossRef]

23. Kandanelli, R.; Thulluri, C.; Mangala, R.; Rao, P.V.; Gandham, S.; Velankar, H.R. A novel ternary combination of deep eutectic solvent-alcohol (DES-OL) system for synergistic and efficient delignification of biomass. *Bioreour. Technol.* 2018, 265, 573–576. [CrossRef]

24. Zarei, A.R.; Nedaei, M.; Ghorbanian, S.A. Ferrofluid of magnetic clay and menthol based deep eutectic solvent: Application in directly suspended droplet microextraction for enrichment of some emerging contaminant explosives in water and soil samples. *J. Chromatogr. A* 2018, 1553, 32–42. [CrossRef] [PubMed]

25. Yousefi, S.M.; Shemiran, F.; Ghorbanian, S.A. Deep eutectic solvent magnetic bouncy gels in developing dispersive solid phase extraction: Application for ultra trace analysis of organochlorine pesticides by GC-micro ECD using a large-volume injection technique. *Talanta* 2017, 168, 73–81. [CrossRef]
26. Florindo, C.; Branco, L.; Marruco, I. Development of hydrophobic deep eutectic solvents for extraction of pesticides from aqueous environments. *Fluid Phase Equilib.* **2017**, *448*, 135–142. [CrossRef]

27. Werner, J. Ligandless, deep eutectic solvent-based ultrasound-assisted dispersive liquid-liquid microextraction with solidification of the aqueous phase for preconcentration of lead, cadmium, cobalt and nickel in water samples. *J. Sep. Sci.* **2019**, *43*, 1297–1305. [CrossRef] [PubMed]

28. Almeida, J.; Craveiro, R.; Faria, P.; Silva, A.; Mateus, E.; Barreiros, S.; Paiva, A.; Ribeiro, A. Electrolytic removal of tungsten and arsenic from secondary mine resources–Deep eutectic solvents enhancement. *Sci. Total Environ.* **2020**, *710*, 136364. [CrossRef] [PubMed]

29. Liu, Q.; Huang, X.; Liang, P. Preconcentration of Copper and Lead Using Deep Eutectic Solvent Modified Magnetic Nanoparticles and Determination by Inductively Coupled Plasma Optical Emission Spectrometry. *At. Spectrosc.* **2020**, *41*, 36–42. [CrossRef]

30. Altunay, N.; Elik, A.; Gürkan, R. Natural deep eutectic solvent-based ultrasound-assisted microextraction for extraction, preconcentration and analysis of methylmercury and total mercury in fish and environmental waters by spectrophotometry. *Food Addit. Contam. Part A* **2019**, *36*, 1079–1097. [CrossRef]

31. Altunay, N.; Elik, A.; Gürkan, R. Innovative and practical deep eutectic solvent based vortex assisted microextraction procedure for separation and preconcentration of low levels of arsenic and antimony from sample matrix prior to analysis by hydride generation–atomic absorption spectrometry. *Food Chem.* **2019**, *293*, 378–386. [CrossRef]

32. Söldner, A.; Zach, J.; König, B. Deep eutectic solvents as extraction media for metal salts and oxides exemplarily shown for phosphates from incinerated sewage sludge ash. *Green Chem.* **2018**, *21*, 321–328. [CrossRef]

33. Ërbas, Z.; Soyak, M.; Yilmaz, E.; Dogan, M. Deep eutectic solvent based liquid phase microextraction of nickel at trace level as its diethylthiocarbamate chelate from environmental samples. *Microchem. J.* **2019**, *145*, 745–750. [CrossRef]

34. Panhwar, A.; Tuzen, M.; Kazi, T.G. Use of Deep Eutectic Solvent-based Air-assisted Emulsification Liquid-liquid Microextraction of Palladium and Determination by Flame Atomic Absorption Spectrometry in Water and Environmental Samples. *At. Spectrosc.* **2019**, *40*, 227–232. [CrossRef]

35. Ezoddin, M.; Lamei, N.; Siami, F.; Abdi, K.; Karimi, M.A. Deep Eutectic Solvent Based Air Assisted Ligandless Emulsification Liquid–Liquid Microextraction for Preconcentration of Some Heavy Metals in Biological and Environmental Samples. *Bull. Environ. Contam. Toxicol.* **2018**, *101*, 814–819. [CrossRef] [PubMed]

36. Li, Y.; Ali, M.C.; Yang, Q.; Zhang, Z.; Bao, Z.; Su, B.; Xing, H.; Ren, Q. Hybrid Deep Eutectic Solvents with Flexible Hydrogen-Bonded Supramolecular Networks for Highly Efficient Uptake of NH3. *ChemSusChem* **2017**, *10*, 3368–3377. [CrossRef]

37. Matong, J.M.; Nyaba, L.; Nonnmgongo, P.N. Determination of As, Cr, Mo, Sb, Se and V in agricultural soil samples by inductively coupled plasma optical emission spectrometry after simple and rapid solvent extraction using choline chloride-oxalic acid deep eutectic solvent. *Ecotoxicol. Environ. Saf.* **2017**, *135*, 152–157. [CrossRef] [PubMed]

38. Zounr, R.A.; Tuzen, M.; Khuwawar, M.Y. Ultrasound assisted deep eutectic solvent based on dispersive liquid microextraction of arsenic speciation in water and environmental samples by electrothermal atomic absorption spectrometry. *J. Mol. Liq.* **2017**, *242*, 441–446. [CrossRef]

39. Panhwar, A.H.; Tuzen, M.; Kazi, T.G. Ultrasonic assisted dispersive liquid-liquid microextraction method based on deep eutectic solvent for speciation, preconcentration and determination of selenium species (IV) and (VI) in water and food samples. *Talanta* **2017**, *175*, 352–358. [CrossRef]

40. Karimi, M.; Shabani, A.M.H.; Dadfarinia, S. Deep eutectic solvent-mediated extraction for ligand-less preconcentration of lead and cadmium from environmental samples using magnetic nanoparticles. *Microchim. Acta* **2016**, *183*, 563–571. [CrossRef]

41. Yilmaz, E.; Soyak, M. Ultrasound assisted-deep eutectic solvent based on emulsification liquid phase microextraction combined with microsample injection flame atomic absorption spectrometry for valence speciation of chromium(III/VI) in environmental samples. *Talanta* **2016**, *160*, 680–685. [CrossRef] [PubMed]

42. Tan, T.; Xu, X.; Wan, Y. DES-Fe$_3$O$_4$ composite for rapid extraction of residual plant growth regulators in edible vegetable oil. *Chin. Chem. Lett.* **2019**, *30*, 1182–1185. [CrossRef]