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Application of deep eutectic solvents in atomic absorption spectrometry

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Abstract

Atomic absorption spectroscopy (AAS) is a widely applied technique for metal quantification due to its practicality, easy use and low cost. However, to improve the metrological characteristics of AAS, in particular the sensitivity and the detection limit, sample pretreatment is commonly used before the detection step itself. In consideration of the principles of Green Analytical Chemistry, new solvents are being introduced into analytical practice. Deep eutectic solvents (DES) are often employed in the sample preparation prior to AAS due to their unique properties. This article deals with the potential of DES for the separation of metals and metalloids followed by AAS quantification. The primary focus is on DES employed in various liquid–liquid microextraction procedures, such UA-LPME, VA-LPME and DLLME; however, examples of less frequently occurring combinations are also presented. We believe that this review can be useful for readers as a starting point for future research in the field of DESs and their application in AAS.

Keywords: deep eutectic solvents; atomic absorption spectrometry; inorganic analysis; speciation

Content

1 Introduction

Metals have been a part of people's lives to a greater or lesser extent since ancient times. The development and progress of civilizations have been linked to the ability to process metals and make useful tools from them. Metals and their compounds are present in almost all aspects of modern life. In general, metals are toxic, but some metals, in trace amounts, are essential for all higher forms of life. Therefore, determining the concentration of metals in environmental components, such as different types of water and soils, and in a variety of food and biological samples, is an important task. Many techniques can be used for such elemental analysis, but atomic absorption spectrometry (AAS), whether with flame or electrothermal atomization or hydride or vapor generation, is perhaps the most-recognized and well-established among them [1].

Despite the excellent indicators of current analytical equipment and ongoing progress in the development of new instruments, before quantification itself can be performed, the pre-treatment of samples is necessary to reduce the influence of the matrix as well as to pre-concentrate the studied analytes due to their low content in the sample [2]. What needs to be noted is that classical pre-concentration techniques, such as liquid–liquid extraction (LLE) and solid-phase extraction (SPE), are gradually being replaced by new microextraction techniques which are more in line with today's requirements for sustainable development and, in addition, often provide better performance and metrological characteristics. The choice of a sample pre-treatment technique depends on the method to be used for the final determination. A great amount of effort has been expended to improve methods of sample preparation for elemental determination (**Figure 1**) [3-6].

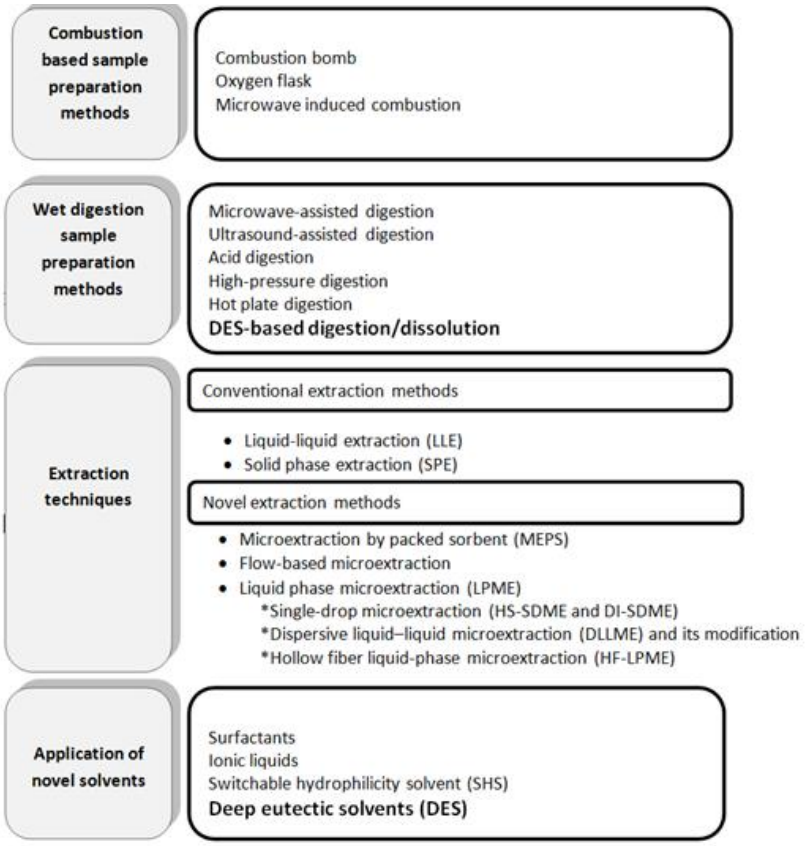

Figure 1. The evolution of sample preparation procedures

In the last two decades, various liquid-phase microextraction (LPME) techniques have been gradually introduced. These include single-drop microextraction (SDME) [7], dispersive liquid–liquid microextraction (DLLME) [8], solidification of floating organic drop microextraction (SFODME) [9], hollow-fiber liquid-phase microextraction (HF-LPME) [10] as well as many modifications of them. Such techniques satisfy the current requirements of Green Analytical Chemistry (GAC), as they use only microliter volumes of organic solvents. Another current trend is the effort to replace hazardous organic solvents with new, environmentally friendly ones, for example surfactants or ionic liquids (IL). In this context, the introduction of switchable solvents [11] as well as so-called deep eutectic solvents (DES) [12] into analytical practice in the last decade must be mentioned. In this review article, we will deal with the latter mentioned solvents, mostly in regard to their potential use in the separation of metals and metalloids, with subsequent AAS quantification.

The number of research papers on the topic of DES is growing rapidly, including articles devoted to the application of DES in analytical chemistry. Of course, this has also resulted in an increase in the number of review articles. Here we list just a few of them. Lee et al. [13] discussed the potential of a new sub-class of DES termed hydrophobic deep eutectic solvents (HDES) for the extraction of nonpolar analytes. The authors focus on the preparation and physicochemical properties of HDES and their applications in the extraction of organic and inorganic analytes from aqueous environments [13]. Li and Row [14] discussed the properties (melting point, density, viscosity, conductivity, surface tension, polarity) as well as the application of DES in various modalities of DLLME [14]. Recently, Sekharan et al. discussed DES as an alternative to other harmful solvents [15], and Tang et al. [16] summarized the use of hydrophilic/hydrophobic DES in analytical microextraction procedures. **Figure 2** shows the evolution in the number of publications devoted to the topic of this review. Although the total number of papers is not particularly large, we must emphasize the trend in the annual growth of such publications, which clearly indicates that the topic has found a response in the community of analytical chemists and is an interesting area worth addressing in the near future. However, to the best of our knowledge, there is currently no review article focused on the use of DES for metal and metalloids extraction followed by AAS quantification, and this has motivated us to collect data in this area and write this review, which may be useful for readers as a starting point for future research in this area.

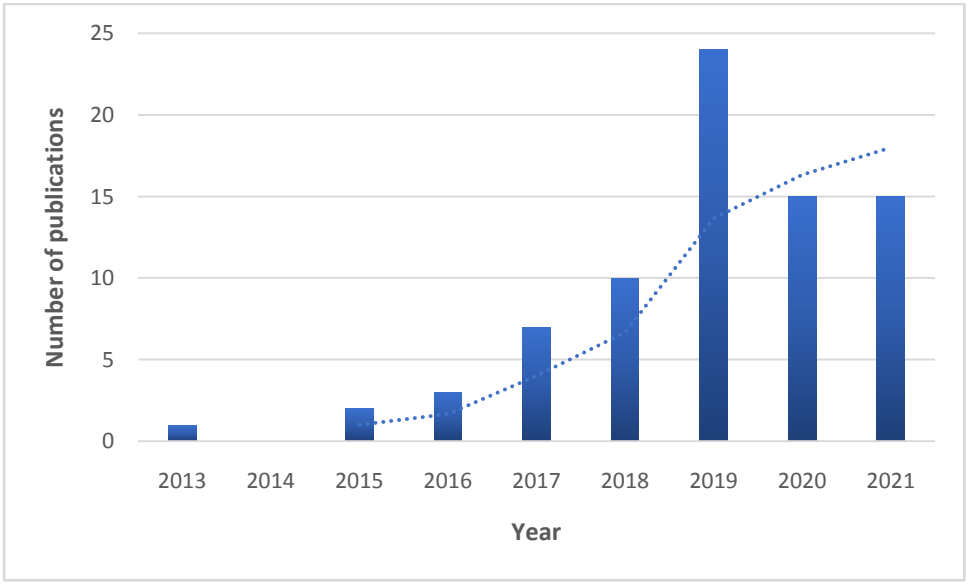

Figure 2. Evolution in the number of publications devoted to the topic published during 2013–2021 based on Scopus and the moving average (searched keywords: deep eutectic solvents and atomic absorption spectrometry; accessed on 18 July 2021)

2 Procedure for DES-based extraction

DES-based extraction is suitable for the analysis of both aqueous and solid samples. Aqueous samples can be analyzed without or with only minimal pretreatment [17]. Procedures for analyzing oil samples have been described, though they are rare, while solid samples typically must be decomposed by a suitable means before analysis, and the residue formed should be dissolved to obtain an aqueous sample solution. Biological samples comprise a separate group and may require special treatment prior to DES extraction [17].

The DES extraction procedures proposed by various authors differ significantly in their individual steps, in the order of those steps, in the reagents used, as well as in the composition and type of DES used (hydrophilic, hydrophobic). Until recently, most synthesized DES were hydrophilic, which prevented their use in the extraction of aqueous samples. However, in the last few years studies on the synthesis and application of hydrophobic deep eutectic solvents has rapidly expanded [17]. Therefore, to describe a general procedure suitable for every procedure is incredibly difficult or almost impossible.

All the reagents needed to adjust the pH, ionic strength and ligand solution are added to the pretreated sample solution. If necessary, the solution is mixed and allowed to stand for the reaction to occur between the analyte and the reagents. The DES is then added to this solution, followed by tetrahydrofuran (THF) (if necessary), and the mixture is shaken, stirred, vortexed or sonicated depending on the selected procedure. If temperature control of one or more steps is required, these steps are performed in a water bath. The analytes pass into the DES phase, which is then separated by centrifugation. The enriched DES phase can then be diluted with a suitable solvent to reduce the viscosity and complete the volume required for introduction into the analytical equipment. An overview of applications involving the combination of DES and AAS is provided below, and the relevant information obtained from the papers discussed is summarized in Tables 1-3.

3 Elements determined by AAS following DES-based extraction

To date, DES-based procedures coupled with atomic absorption spectrometry have been suggested for a variety of elements (**Figure 3**); examples of their application are given in Tables 1-3. The developed procedures mainly allow the determination of one specific element, such as aluminum [18], cadmium [19-23], chromium [24, 25], cobalt [26-29], copper [30-33], gold [34], iron [35], manganese [36], mercury [37, 38], nickel [39, 40], lead [41-48], palladium [49-51] and silver [52], in the sample, but procedures that allow the determination of two elements (Table 2), such as arsenic and antimony [53], arsenic and selenium [54], cadmium and arsenic [55], cadmium and zinc [56, 57], cobalt and nickel [58], copper and nickel [59], nickel and cobalt [60], lead and cadmium [61-65], and selenium and arsenic [66, 67], or three or more elements simultaneously (Table 2), such as cadmium, copper and lead [68], cadmium, lead and arsenic [69], copper, cadmium and lead [70], copper, iron, and zinc [71], mercury, lead and cadmium [72], cadmium, lead, copper and arsenic [73], lead, cobalt,

nickel and manganese [74], have also been reported. Particular emphasis needs to be placed on articles examining speciation analysis (Table 3).

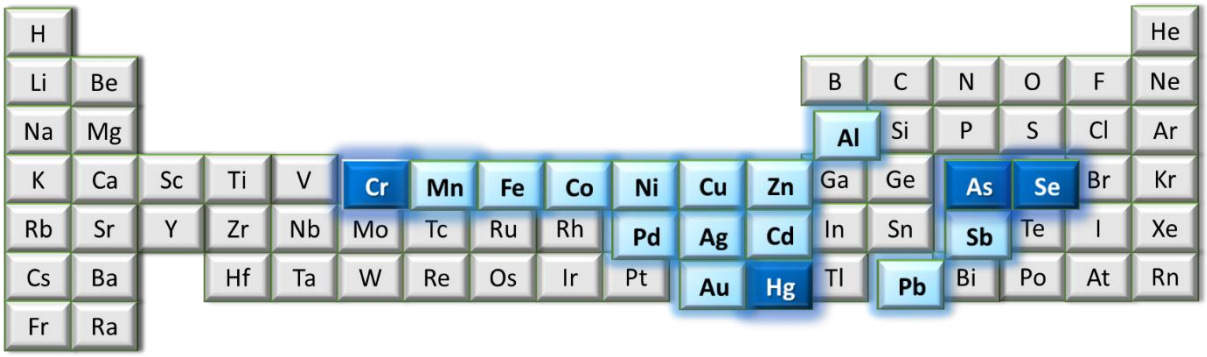

Figure 3 Applications of DES-based (micro)extraction coupled with atomic spectroscopy, based on the data in Tables 1-3. The dark blue color highlights the elements about which articles on speciation analysis have been published

3.1 Speciation analysis

AAS is a non-speciating spectroscopic method; therefore, it can be used for speciation analysis only by introducing an additional step to separate the various analyte species. In addition, measures must be taken to prevent alteration of the form of the species during sampling as well as during the sample pretreatments steps [75]. It is common practice to determine the total concentration of the target analyte as well as the concentration of one particular form. The concentration of the second form is calculated by subtracting the concentration of the experimentally determined form from the total concentration of the analyte. Speciation analysis using DES extraction and subsequent AAS detection have been published for the following elements: arsenic [76-78], selenium [78-80], chromium [81-85] and organic and inorganic mercury [78, 86, 87] (Table 3).

Figure 4 shows the distribution of metals by total concentration and speciation analysis using DES-AAS methods. In all cases of speciation analysis of arsenic or selenium, the reduction of arsenic(V) to arsenic(III) or selenium(VI) to selenium(IV) was used, and the total arsenic or selenium concentration was measured by electrothermal atomic absorption spectrometry (ETAAS). However, both reduction and oxidation procedures were used for the speciation analysis of chromium. Fasihi et al. [83, 84] applied ascorbic acid to convert chromium(VI) to chromium(III), and the total chromium concentration in food and water samples was detected by flame atomic absorption spectrometry (FAAS). In contrast, the oxidation of chromium(III) to chromium(VI) with $KMnO_4$ and H_2SO_4 was used for the speciation analysis of chromium in aqueous samples by ETAAS [81], or in tea and water samples by FAAS [82, 85]. In the case of mercury speciation analysis, Akramipour et al. [78, 87] published a method based on the conversion of organic mercury species into mercury(II) using ultraviolet light and microwave and the determination of total mercury in blood samples by ETAAS. Thongsaw et al. [86] took a different approach, extracting the individual species of mercury separately: (1) mercury(II) in the form of a hydrophobic dithizone complex by DES and (2) methylmercury extracted directly into the DES phase. Finally, the determination of mercury in water and freshwater fish samples was carried out by ETAAS.

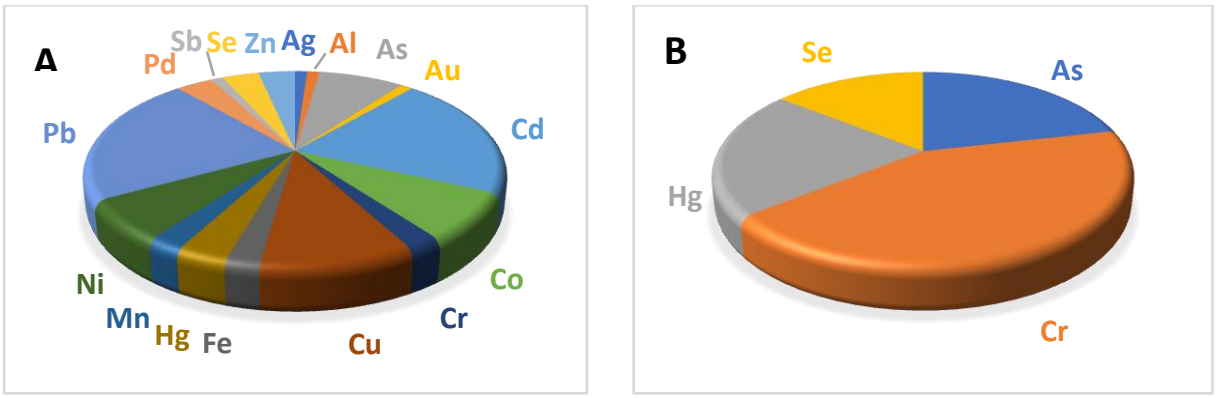

Figure 4 The distribution of metals in total concentration (A) and speciation analysis (B) by the DES-AAS method

4 Samples of different matrix composition: sampling and sample pre-treatment

Procedures for analyzing both liquid and solid samples using DES extraction have been published. However, we must emphasize that methods devoted to the analysis of liquid samples prevail, although it is true that procedures suitable for the analysis of solid samples are generally not exceptional. On the other hand, it should be noted that before DES extraction, solid samples most often need to be decomposed using a suitable pretreatment procedure. DES-based extraction procedures have been widely applied for various types of samples, including water, vegetable, food, environmental and biological samples (**Figure 5**).

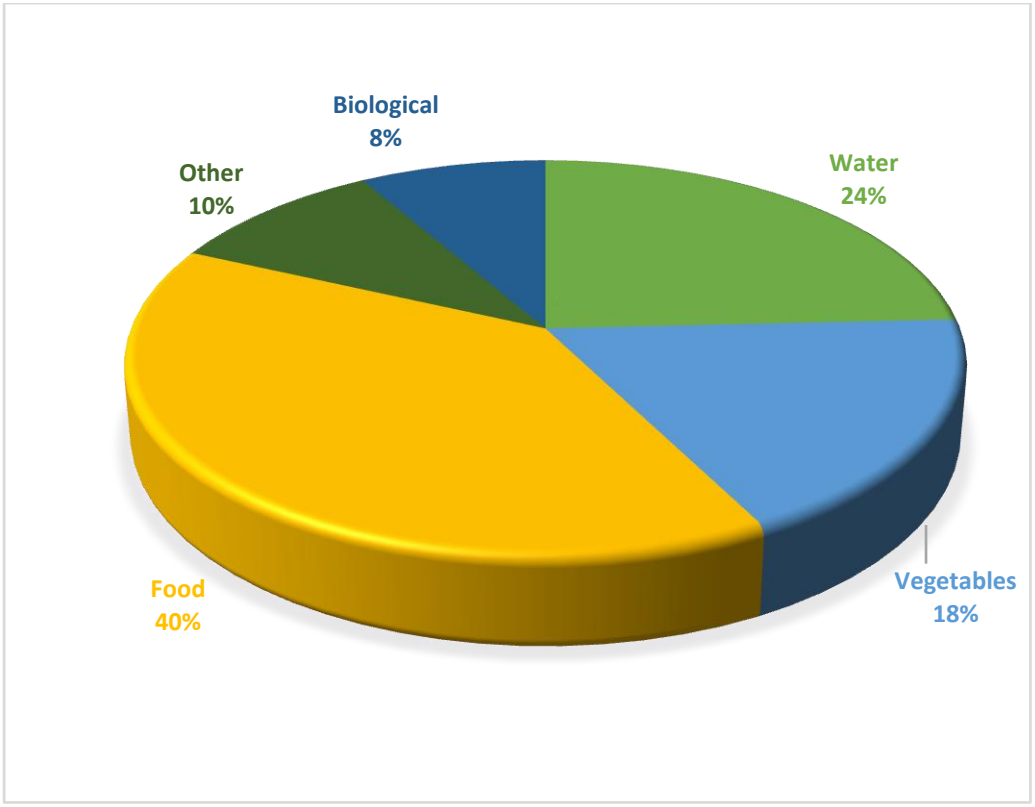

Figure 5 Types of samples analyzed by DES-AAS. Data extracted from Tables 1-3

4.1 Water samples

Many different types of water samples have been analyzed. However, **Figure 6** clearly shows that different types of drinking water, surface water and wastewater predominate. The analyzed water samples can be divided into the following more detailed subgroups: tap water [19, 22, 24, 26, 33, 37, 41, 42, 44, 46, 49, 51-53, 57, 59, 60, 64, 77, 79, 81, 83-86], groundwater [21, 24], spring water [18, 52, 59], well water [26, 40, 53, 58, 64, 81], mineral water [18, 24, 40, 41, 51, 60, 77, 79, 84, 86], bottled water [53], surface water [57], river water [18, 26, 42, 44, 46, 47, 51-53, 58, 60, 64, 73, 77, 81, 83, 84, 86], canal water [24, 44], lake water [33, 42, 47, 77, 85], seawater [18, 24, 40, 46, 47, 49, 51, 59, 60, 64], rainwater [19], snowmelt water [19] and wastewater [19, 24, 26, 36, 40, 44, 47, 49, 52, 53, 81, 85].

Water samples are usually taken in clean polyethylene bottles using standard sampling methods. After collection, they are filtered to remove suspended particles, acidified, if necessary, and stored in a refrigerator at 4 °C until analysis. The aim of the treatment is to prevent the loss of analyte and contamination of the sample. However, some authors analyzed tap water samples without any pre-treatment (dilution or purification) [37]. Altunay et al. reported a deep eutectic solvent-based vortex-assisted microextraction (DES-VAME) procedure for arsenic and antimony in which 50 mL samples of environmental water (wastewater, tap water, well water, river water) were concentrated down to 5 mL by evaporation [53].

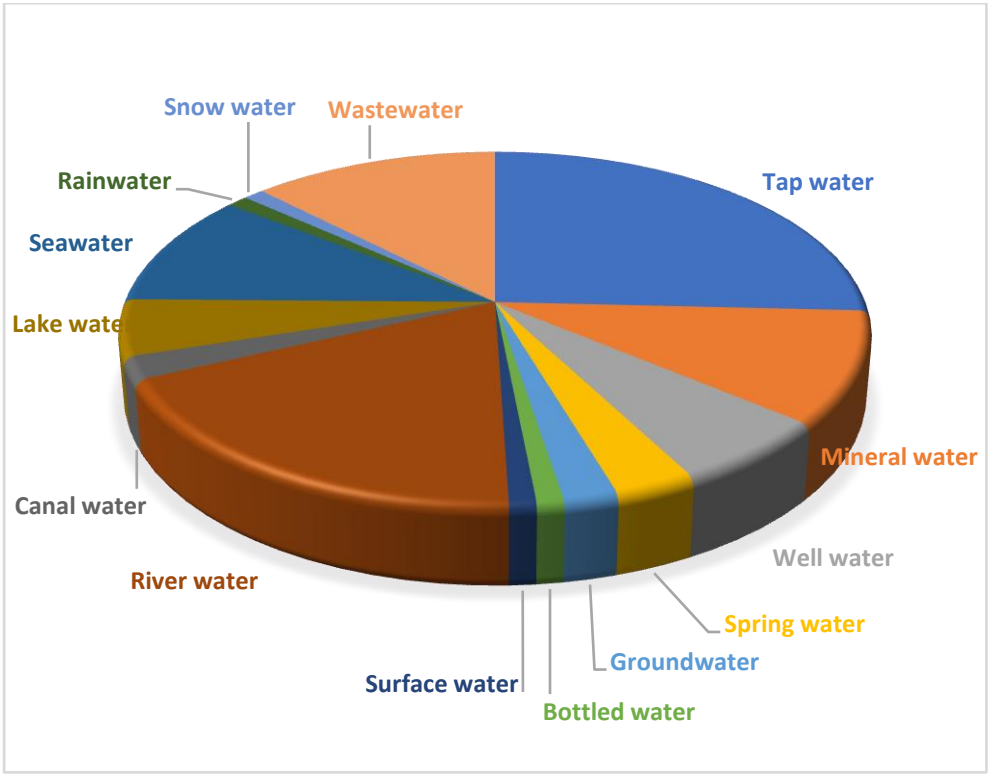

Figure 6 Types of water samples analyzed by DES-AAS. Data extracted from Tables 1-3

4.2 Food samples

Food products represent the largest group of samples analyzed, with 40% of the total number of analyzed samples. Articles devoted to the analysis of food samples include (a) meat samples, such as liver [32, 35], fish [22, 37, 38, 67, 71, 77, 86], canned fish [22, 44, 47, 79], chicken meat [18, 44, 47], chicken shawarma [22] and beef [44, 47]; (b) milk and dairy products [68], such as cow milk [26, 79], cow and goat milk [19], sheep milk [79], cheese [22], cow and goat cheese [19] and yogurt [79]; (c) juices, including cherry and peach [57], grapefruit [79], grape and peach [58], orange [73, 79] and mixed fruit juice [79]; (d) tea samples, including black tea [22, 44, 47, 73, 77], green tea [44, 47, 77], herbal tea [26] and linden tea [28]; as well as other foods, such as bean stew [22], biscuits [26], bitter chocolate wafers [26], butter [56], margarine [56], chocolate [26], chocolate milk [26], cigarettes [40, 45, 77], coffee [36], corn [22, 26], roasted yellow corn [42], canned corn [22], egg [79], honey [53, 70, 79], mushrooms [18, 22, 66, 77, 79, 83], canned mushrooms [22, 44], salted peanuts [42], brown rice [53], white rice [53], tomato paste [73], sausage [84], wine [26, 55], wheat [26] and boiled wheat [44]. The distribution of food samples among the different subgroups is shown in **Figure 7** and described below.

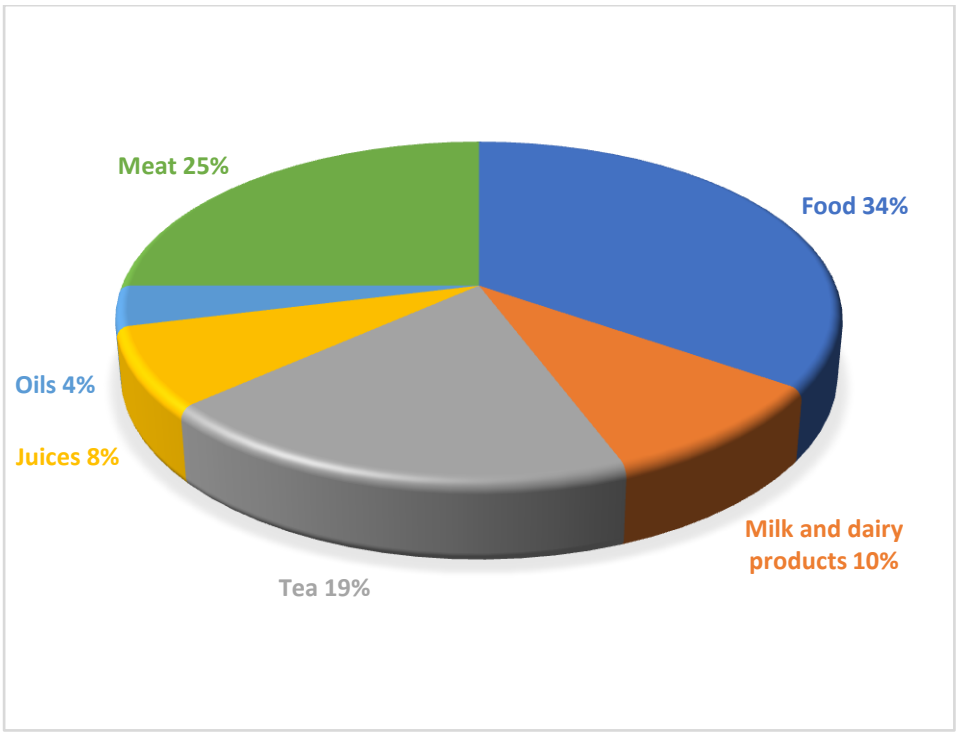

Figure 7 The distribution of food samples between different subgroups. Data extracted from Tables 1-3

Solid food samples are digested by wet acid digestion, in a microwave digestion system or even an ultrasonic-assisted digestion system [53] using previously described procedures or modifications thereof. Fish samples were washed thoroughly with deionized water, dried, cut into small pieces, homogenized and then digested [37, 77, 86]. The digested samples are adjusted to the required pH, and the solution filled to the mark in volumetric flasks with distilled water. Finally, the obtained solution or aliquot is subjected to the developed (micro)extraction procedure.

4.2.1 Vegetable and fruit samples

Another large group of samples analyzed using the DES-AAS method are vegetables and fruits, specifically: almonds [42], apple [20], arugula [63], basil [69], broccoli [31, 60], carrot [31, 41, 72, 76], celery [20, 41], chickpeas [42], coriander [69, 72, 76], cumin [47], dill [63], eggplant [63], leek [63], lettuce [31], linseed [47], mint [26, 43, 63], onion [40, 41, 45], parsley [31, 40, 45, 63], pistachios [42], potato [31, 47], quince [30], radish [69, 72, 76], rice [18, 22, 54, 73, 77, 84], soybean [83], spinach [22, 26, 31, 39, 44, 60, 63, 69, 72, 73, 76], tomato [22, 41] and walnut [73]. Vegetable samples are often carefully washed with distilled water to remove impurities, then drained and dried to remove all moisture. They are then homogenized and digested.

4.2.2 Drink samples

Juice samples may be subjected directly to the extraction procedure without any pretreatment or dilution [57], or diluted with water to suppress the matrix effect [58], or possibly even digested [79]. Coffee samples in the form of whole beans were powdered using a grinder, extracted with 50 mL of boiling deionized water for 15 min, passed through a syringe filter and diluted ten-fold [36]. Tea samples can be analyzed in a similar way. A sample of tea (0.25 g) was boiled in a beaker for 10 min

with 25 mL of a 0.1 M Na_2CO_3 solution. After cooling, the mixture was transferred to a tube and the volume was adjusted to 25 mL with deionized water [82]. Linden samples (20 g) were boiled in water for 45 min. The brewed samples were allowed to cool and then filtered while warm to remove solid particles, and the volume made up to 100 mL [28]. However, procedures using wet acid digestion or microwave digestion are more often described [29, 63, 73, 77].

4.2.3 Oil samples

The direct determination of metals in oils is difficult, due particularly to their high viscosity and their high content of organic compounds. To eliminate these difficulties, decomposition of the sample by a suitable digestion method or dilution of the sample with an appropriate organic solvent is usually used. However, a few published works have used DES instead of sample decomposition to separate and preconcentrate heavy metals from edible oil samples prior to their determination via AAS [56, 65, 74].

4.3 Biological samples

Biological samples were typically pretreated as follows: Urine samples were centrifuged, passed through a filter and diluted with distilled water [59] or a 10.0 mM sodium phosphate monobasic solution to adjust the pH and ionic strength and decrease the matrix effect [25]. Microwave-assisted digestion has also been described [27]. Blood samples were usually deproteinated by the addition of acetonitrile and a zinc sulfate solution, vortexed and centrifuged, and then the supernatant was diluted using ultrapure water to decrease the matrix effects [48, 78, 80, 87]. Hair [37, 52, 64] and nail [37] samples were washed with acetone to remove contaminants, then dried and digested.

4.4 Other type of samples

The smallest group comprises environmental/technical samples, such as soil [64, 69, 72, 76, 77], sediment [77], ore [52], road dust [49, 51], tunnel dust [51], catalytic converter samples [49-51], as well as cosmetic products (lipsticks and eye shadows) [61], pharmaceutical supplement [29] and cigarette samples [45, 77]. These kinds of samples should also be digested before DES-based extraction.

The variety of analyzed samples and analytes determined clearly testifies to the great potential of DES in sample pretreatment prior to AAS quantification, especially in the analysis of water, vegetable and food samples. On the other hand, analysts have thus far paid significantly less attention to the analysis of more complex samples, especially biological and technical ones.

5 Type of atomization in DES-AAS procedures

In the case of a combination of DES-based extraction and AAS detection for the extraction, preconcentration and detection of elements from various samples, all types of atomization in AAS, such as flame, electrothermal and vapor generation, are represented. In the presented works, good compatibility of the DES solvents with AAS was observed for all mentioned types of atomization. As we can see in Figure 8, the most common type is flame atomization, which accounts for up to 62% of all applications. A significant part of more than two -thirds of these applications are conventional FAAS systems, mainly due to their simplicity and economy [19, 21, 26, 31, 35, 36, 41, 42, 45, 46, 50-

52, 55-61, 63, 64, 68, 70, 71, 74, 82-84]. But conventional FAAS has low sensitivity of detection, and the DES-rich phase needs to be sufficiently diluted before being injected into the FAAS system. In order to improve nebulization efficiency and/or atomization of analytes in conventional FAAS, several authors have used a basic slotted quartz tube (SQT) [20, 23, 27, 28, 30, 34, 39, 43]. Due to the small volumes of the DES-rich phase after the extraction process, in some cases it was more advantageous to use a micro-sample injection system coupled to a flame atomic absorption spectrometer (MS-FAAS), where the injection volumes after diluting of the DES-rich phase were hundreds of microliters [29, 32, 40, 44, 62, 85]. The problem with the small volume of DES and sensitivity of detection was eliminated when using electrothermal atomization: ETAAS or graphite furnace atomic absorption spectrometry (GFAAS) was used, where the DES-rich phase was injected directly or only after a minimal dilution into the AAS spectrometer after the extraction procedure [18, 22, 24, 25, 33, 37, 47-49, 65-67, 69, 72, 73, 76-81, 86, 87]. Only three applications were found to use vapor generation atomization after DES-based extraction. Altunay et al. [53] and Elik et al. [54] used hydride generation-atomic absorption spectrometry (HGAAS) to determine arsenic, selenium and antimony in rice samples and Rastegarifard et al. [38] published the determination of mercury in marine fish samples by cold vapor atomic absorption spectrometry (CVAAS).

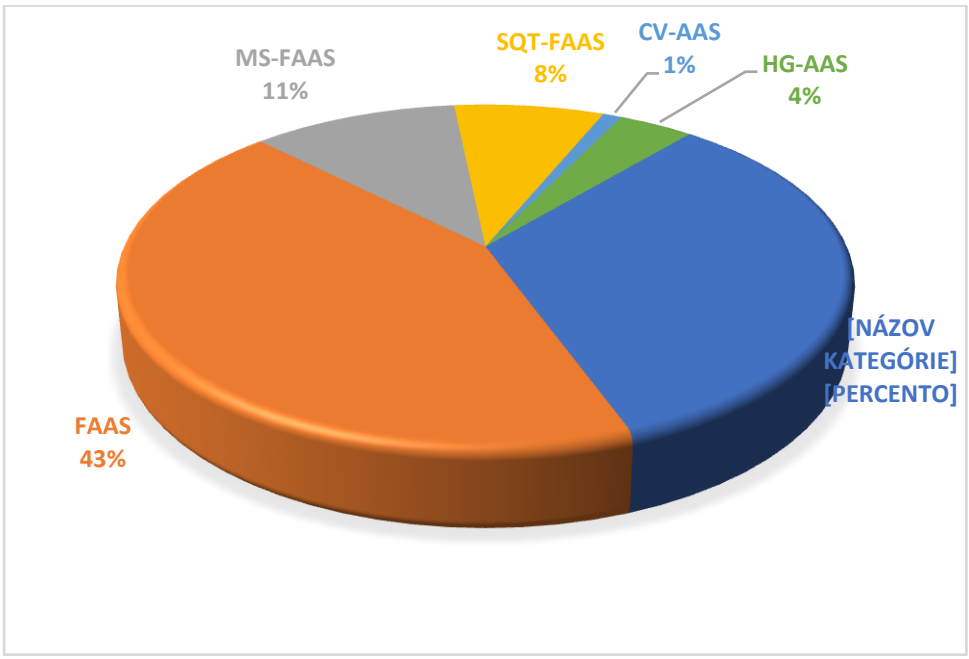

Figure 8 The distribution of the methods by type of atomization in AAS. Data extracted from Tables 1-3

6 Addition of ligands (complexing agents)

The choice of ligand (chelating agent or ion-pairing agent [54, 70]) is very important to ensure efficient separation of the analytes (metal ions) and their transport to the organic phase. It should be kept in mind that other cations may also form complexes with the chosen agent, which may lead to a decrease in the separation efficiency. Well-known commercially available complexing agents are commonly used, such as APDC [21, 61, 82], DAB [79], DDTC [19, 34, 40, 77, 85], DMDTC [32], DDTP [69, 72, 76, 78, 80, 87], DPC [20, 31, 33, 39, 81], PAN [49, 83, 84], TAR [47, 63], dithizone [26, 43, 53,

62, 86], 8-hydroxyquinoline [18], 1-nitroso-2-naphthol [29, 45] and 5-Br-PADAP [60]. However, a few papers have reported the application of synthesized reagents [22, 28, 30, 36].

We can also find articles in which the complexing agent is part of the DES itself or is dissolved in a DES. Sorouraddin et al. developed an air-assisted liquid–liquid microextraction method (AALLME) based on a ternary solidified deep eutectic solvent in the extraction and preconcentration of heavy metals in water and fruit juice samples followed by FAAS quantification. The synthesized menthol–sorbitol–mandelic acid (1:2:1) DES has a double role: it is a chelating agent to form complexes with cadmium and zinc and is also the extraction solvent in the subsequent AALLME procedure [57]. The same group later applied this approach to the development of an extraction and preconcentration procedure for heavy metals (cadmium, copper and lead) from milk samples [68]. They also reported a DLLME procedure for the extraction and preconcentration of cobalt(II) and nickel(II) from water and juice samples using a DES formed by mixing choline chloride and 4-aminophenol (1:1) [58]. Very recently, Ragheb et al. described an MSPE followed by DES-UA-DLLME using L-menthol–salicylic acid (4:1) DES as both the extractant and complexing agent for the preconcentration of mercury (II), followed by determination by graphite furnace atomic absorption spectroscopy (GFAAS) [37].

7 Less frequently occurring connections

As has already been mentioned, DES are unique solvents and we can unequivocally and without any doubt boldly claim that DES are now commonly used in various liquid–liquid microextraction procedures, such as common LPME, UA-LPME, VA-LPME, AA-LPME and DLLME. However, some connections can still be considered exceptional. When speaking about sample preparation prior to AAS analysis, we must be aware of other methods that can utilize DES for different purposes.

7.1 DES-based digestion (dissolution)

Solid food samples must be decomposed using conventional wet acid digestion, microwave-assisted digestion or ultrasonic digestion before the inorganic constituents are determined by AAS. However, researchers have also reported the disadvantages of these methods, especially the fact that concentrated acids or oxidizing agents can cause interference and the formation of nitrous vapors. Habibi et al. [71] reported the applicability of a choline chloride–oxalic acid (1:2) based DES for the dissolution of fish samples as well as solubilization of selected heavy metals (iron, copper and zinc) prior to FAAS determination. To increase the yield of Fe and Cu, 1 mol L^{-1} HNO_3 was added to the sample after dissolution in the DES. The method was used to digest various tissues from a sample of marine fish (muscle, liver and gills) [71].

A bit later, Yilmaz and Soylak [35] introduced an ultrasound-assisted deep eutectic solvent (UA-DES) procedure for separation and preconcentration of iron in bovine liver, sheep liver and chicken liver samples prior to its FAAS determination. Iron was extracted to the DES phase (choline chloride–lactic acid, 1:1) in an ultrasonic bath. The relatively uniform solution obtained was then centrifuged, filtered and diluted with water [35]. In this context, some other publications devoted to the use of DES for dissolution/decomposition of various solid samples need to be mentioned: a method for the determination of total Hg in fish samples [38], a method for the determination of copper in liver samples [32], and a method for the determination of selenium and arsenic in fish [67] and in edible mushroom [66] samples.

7.2 Solidified DES-based procedures

In the last few years, DES-based methods have been proposed whose common feature is that separation occurs by changing the temperature of the sample. For this purpose, DES with a density lower than that of water and a melting point close to room temperature are required. First, the DES forms a homogeneous phase with the aqueous sample due to the effect of temperature in a water bath, vortex mixing, dispersion solvent, ultrasound, or air-assisted stirring. The tubes are then most often immersed in an ice bath or, in some cases, transferred to a freezer [69, 76], where the DES phase solidifies; it is then separated and transferred to a clean tube, where it is quickly melted at room temperature and adjusted for analysis according to the instrument requirements. The great advantage of this approach is that it allows easy separation of the DES phase enriched with the analyte. Here are some examples:

Habibollahi et al. [72] reported a new mode of DLLME based on a solidified deep eutectic solvent (SDES) for the extraction of heavy metals (lead, cadmium and mercury) from soil and vegetable samples, followed by GFAAS determination with a LOD of 0.01–0.03 μg kg^{-1} [72]. Rapid injection of [DMIM]Cl and 1-undecanol (1:2) DES into the sample solution results in the formation of a cloudy state. After being maintained in a water bath at 55 °C, followed by vortexing and centrifugation, the fine droplets of DES floated to the top of the test tube are solidified in an ice bath within a few minutes. Unlike conventional DLLME, this procedure does not require a disperser solvent [72]. Akramipour et al. described an SDES-based microextraction procedure using choline chloride–decanoic acid (1:2) DES followed by GFAAS for the speciation of selenium(IV), selenium(VI) and total inorganic selenium [80] and for the speciation of arsenic(III), arsenic(V), selenium(IV), selenium(VI), mercury(II) and organic mercury (R–Hg) [78] in blood samples.

Seidi et al. [25] published an ultrasound-assisted microextraction method based on the solidification of dispersed fine droplets (SDFD) of a low melting point DES for preconcentration and determination of chromium(VI) in urine samples [25]. Chromium(VI) was first complexed with 1,5-diphenylcarbazone and then extracted by a water-immiscible DES consisting of benzyltriphenylphosphonium bromide (BTPPB) and phenol. The low freezing point of the DES enables the rapid collection of the extraction phase by solidification and subsequent centrifugation. The limits of detection and quantification were calculated as 2.0 and 7.0 ng L^{-1}, respectively [25].

Sorouraddin et al. developed a ternary SDES-based air-assisted LLME [57] and DLLME [68] method for the extraction and preconcentration of heavy metals from water and fruit juice [57] and from milk [68] samples prior to their determination by FAAS. Very recently, a UA-DES-DLLME-SFO method for the simultaneous preconcentration and determination of nickel and cobalt in food and water samples [60] and an IH-DES-AA-LPME method for cobalt FAAS determination in liquid and solid samples were published [26]. In this context, the work devoted to temperature-controlled HLLE is also appropriately mentioned [31, 49].

7.3 Effervescence-assisted procedures

An effervescence-assisted dispersive liquid–liquid microextraction based on the deep eutectic solvent method (EA-DLLME) for preconcentration and FAAS determination of copper ions in aqueous samples was developed [33]. The authors used 1,5-diphenylcarbazide (DPC) to form a stable hydrophobic complex, a DES prepared by mixing choline chloride and phenol in a molar ratio of 1:3 as the extraction phase, THF as the emulsifier, and a mixture of sodium dihydrogen phosphate and sodium carbonate as the effervescent powder. The application of the effervescent material allowed the extraction solvent to be dispersed without the need for additional energy (vortex, ultrasound,

shaking, etc.) [33]. The efficiency of the effervescence-assisted (EA) method was compared with other methods of sample agitation and it was concluded that the efficiency of the EA dispersion is comparable to sonication and better than manual shaking and vortexing. The method has a detection limit of 2.9 μg L^{-1} and was applied for copper determination in water samples [33].

7.4 Hollow fiber-based procedures

Alavi et al. [48] developed a three-phase carrier-mediated hollow fiber liquid-phase microextraction (CM-HFLPME) of lead from whole blood samples. First, the lead was extracted from 17 mL of an acidic sample solution into 1-octanol containing CTAB and subsequently back-extracted into 25 μL of deep eutectic solvent containing $KClO_4$ as the receiving phase. Choline chloride–urea in a 1:2 molar ratio was utilized as the deep eutectic solvent. The final analyses of extracts were carried out by ETAAS. The developed method is characterized by a wide linear range of 1 to 200 ng mL^{-1} and a detection limit of 0.1 ng mL^{-1} [48].

Karimi et al. [52] described a hollow fiber-supported graphene oxide (GO) nanosheet modified with a deep eutectic solvent (DES-GO/HF) for the extraction of silver ions [52]. First, a DES consisting of choline chloride and thiourea in a molar ratio of 1:2 was immobilized on the surface of the GO and then put into the pores and lumen of the hollow fiber. The sorbent thus prepared was used to separate and preconcentrate trace amounts of silver ions. A modified GO/HF segment was added to the sample solution, and the solution was stirred (15 min at 800 rpm). After completion of the extraction, the GO/HF containing the analyte was removed, and the retained analyte was desorbed with 250 μL of nitric acid solution (1.0 mol L^{-1}) under sonication. Finally, the desorbed analyte was determined by FAAS [52].

Karimi et al. [59] published an application of DES-modified cotton as the sorbent for SPE and for trace amounts of copper and nickel in water and biological samples [59]. The resulting sorbent was packed on a microcolumn, and 50 mL of the sample solution with the adjusted pH were passed through it. The adsorbed analytes were then eluted by an acidic solution and transported to the FAAS for quantification. The detection limits of the method were 0.05 and 0.60 μgL^{-1} for copper and nickel, respectively [59].

7.5 Magnetic nanoparticles-based procedures

Karimi et al. [64] developed a deep eutectic solvent-mediated extraction for ligand-less preconcentration of lead and cadmium from environmental samples using magnetic nanoparticles (DES-MNP) [64]. The 200 μL of DES (choline chloride–urea 1:2.5) and 20 mg of MNPs (Fe_3O_4) were added to 60 mL of sample solution and stirred thoroughly for 10 min. The metal ions interact with the DES adhering to the magnetic nanoparticles, and the sorbent was separated by means of a strong magnet. The analytes were then desorbed with 600 μL of 1.0 M nitric acid and determined by flame atomic absorption spectrometry [64]. The method had wide linear range of 2 to 250 μg L^{-1} and 0.5 to 30 μg L^{-1} and good limit of detection of 0.4 and 0.1 μg L^{-1} for lead and cadmium, respectively [64].

Shirani et al. [73] used a magnetic nanofluid (MNF) prepared by mixing magnetic carbon nanotubes (MCNTs) and a deep eutectic solvent (choline chloride–thiacetamide, 1:2) as the extraction phase prior to the ETAAS determination of cadmium, lead, copper and arsenic in food samples and non-alcoholic beverages (CL-DES-MNF-AALLME) [73]. An amount of 40 μL of DES-MNF was added to a 48 mL sample solution, and the mixture was agitated by the rapidly sucking/dispensing the solution six times with a syringe, resulting in the dispersion of fine droplets of

DES-MNF in the sample solution and the transfer of the analyte into them. Then, the DES-MNF was separated using an external magnet without centrifugation [73]. Very similar approaches were later applied for cadmium [23] and cobalt [27] determination.

8 Terminology

To date, DES has been used in a variety of LPME techniques, including their modifications, such as ultrasound-assisted, vortex-assisted, air-assisted and effervescence-assisted procedures. The ambiguity in the terminology of microextraction techniques [88] is also manifested in the case of DES-based procedures [89], which greatly complicates the literature search. Ideally, the name of the method and its abbreviation should provide the reader with sufficient information; however, it should be as simple as possible and free of unnecessary details [89].

Regarding DES-based extraction, we would recommend the simplest notation, DES-ME, regardless of the type of microextraction used, but if authors want to highlight the microextraction procedure itself, then styles such as DES-LPME, DES-DLLME, DES-AALLME, etc. seem more appropriate [89]. In this article, however, we have left the original abbreviations used by the authors (with a few exceptions), although this is not in line with our previous recommendations.

On the other hand, the acronym HDES for hydrophobic deep eutectic solvents can now be considered as established and should be used whenever a hydrophobic DES is utilized in a procedure. Further, in our opinion, with procedures based on the solidification of the DES phase after extraction, this should be emphasized in the name and abbreviation. The simplest way seems to be to use the SDES notation.

9 Conclusion and future trends

For decades, several analytical techniques, including AAS, have been used for the determination of metals. AAS is a widely applied technique which has important advantages, such as precision, accuracy and robustness. Moreover, it is a relatively inexpensive instrument that offers low cost for its use. On the other hand, this method has some drawbacks, the most important of which is its low sensitivity, which hinders the determination of metals at trace concentrations. This is why a sample preparation step, mainly based on an extraction process, is required prior to the final determination. Nowadays, traditional pretreatment techniques, such as LLE and SPE, are gradually being replaced by new microextraction techniques. The reduction or elimination of conventional hazardous organic solvents is one of the most important factors in GAC, and thus, in separation science, including sample preparation methods, leading to the innovation of these techniques but also to the introduction of new materials and solvents that can be characterized as green in nature. Due to their unique properties, DES are widely considered to be an extraction phase in sample pretreatment methodologies, even in the case of AAS application. DES are characterized by high solubility not only for organic compounds, but also for inorganic species, and this is why they are of interest for the application of AAS in metal determination. When AAS is applied as the final determination technique, DES-based extraction is suitable for the isolation of analytes in both aqueous and solid samples, although it needs to be noted that for solid samples some additional processes are also recommended to decompose the sample by means of a suitable procedure. Indeed, the analysis of

oil samples is also possible, though it is problematic, with some requirements for the sample preparation procedures. The same issue arises with most biological samples, which may need special pretreatment before DES-based extraction. In sum, DES-based extraction procedures prior to AAS determination can be applied to a wide range of samples characterized by different matrix composition, but they differ significantly in the individual steps, the reagents utilized and generally in the composition of the DES used. In general, procedures based on DES-AAS are characterized by a linear range with a good correlation coefficient and a low LOD.

In summary, it can be concluded that the combination of a DES-based sample preparation process and the detection power of AAS creates a sensitive analytical procedure with high accuracy and precision. However, there are still some future directions that can be followed to improve existing solutions. For example, the use of innovative magnetic nanoparticles (MNPs) as sorbents modified by DES will be the focus of research in the future. Nowadays, most studies on MNPs containing a DES are limited to the laboratory. Thus, further complementary assessment of their practicability as well as their economic benefits is required for industrial application. Another point that must be considered in the future is the possibility of regenerating DES as well as sorbents/nanoparticles and their future characterization and possible re-use. In addition, a broader comparison as well as evaluation for the performance of DES in AAS can still be expected.

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Conflicts of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Table 1 Selected examples of DES-based microextraction for the determination of inorganics by AAS

Analyte	Sample	Microextraction[1]	Detection	Comments[2]	LOD	Ref.
Aluminum	Water (*drinking, river, sea, mineral and spring water*) and food (*rice, cultivated mushrooms, chicken meat*) samples	DES-UALPME	ETAAS	**DES**: choline chloride–phenol, 1:4; 25 mL sample solution; 8-hydroxyquinoline solution; 0.5 mL DES; 0.5 mL THF; sonicated, 2 min; centrifuged, 5 min, 4000 rpm; DES phase filled up to 500 µL with acidic ethanol; 20 µL directed to nebulizer	0.032 µg L^{-1}	[18]
Cadmium	Food (*cow and goat cheese, cow and goat milk*) and water (*wastewater, snow water, rainwater and tap water*) samples	HDES-LPME	FAAS	**HDES**: $[P_{666(14)}][Cl]$–pivalic acid, 1:4; 12 mL sample solution; 0.8 mg DDTC; 200 µL HDES; shaken manually for one minute; centrifuged, 5 min, 116.41 G	1.6 µg L^{-1}	[19]
Cadmium	Celery and apple samples	UA-DES-ME	SQT-FAAS	**DES**: choline chloride–phenol, 1:2; 8 mL sample solution, 1 mL 0.05% (w/v) DPC solution; 0.5 mL DES; sonicated, 15 s; 1 mL THF; centrifuged, 120 s, 3461g	0.35 µg L^{-1}	[20]
Cadmium	Groundwater samples from aquifers at different depth in a coal mining area	UDDLLµE	FAAS	**DES**: $ZnCl_2$ and acetamide, 1:2; 20 mL sample solution; 1 mL APDC solution 0.1–0.5% (m/v); 100 µL DES; sonicated, 80 s, 50°C; centrifuged, 15 min, 3500 rpm; back extracted into 0.2 mL to 0.5 mL of 2 mol L^{-1} of HNO_3	0.046 µg L^{-1}	[21]
Cadmium	Food (*bean stew, black tea, chicken shawarma, canned corn, corn, canned mushrooms, cheese, mushrooms, fish tissue, tomatoe, meat, canned fish, rice and spinach*) and water (*tap, waste*) samples	UA-DES-LPME	ETAAS	**DES**: choline chloride–phenol, 1:4; 50 mL sample solution; (Z)-N-(3,5-diphenyl-1H-pyrrol-2-yl)-3,5-diphenyl-2H-pyrrol-2-imine solution; 0.5 mL DES; 600 µL THF; sonicated, 3 min; centrifuged, 5 min, 4000; DES phase, 0.5 mL acidic ethanol added	0.023 ng L^{-1}	[22]
Cadmium	Eucalyptus and rosemary tea	DES-MNF-LPME	SQT-FAAS	**DES**: choline chloride–phenol, 1:3;	0.25 ng mL^{-1}	[23]

				8 mL sample solution; 1 mL DPC (0.05% w/v in ethanol); shaken, 15 s; aspiration/dispersion cycles, 4 times; vortexed, 15 s; centrifuged, 2 min, 3000 rpm; DES–MNF separated using an external magnet; analytes eluted with 150 µL 5 M nitric acid solution under ultrasonication for one minute		
Chromium(III)	Water samples (*wastewater, groundwater, seawater, canal water, mineral water and tap water*)	DES-UA-DLLME	GFAAS	**DES**: $ZnCl_2$ and acetamide, 1:3; 25 mL sample solution; calmagite solution; 800 µL DES and 900 µL THF; sonicated, 5 min	6.0 ng L^{-1}	[24]
Chromium(VI)	Urine samples	SDFD-DES	ETAAS	**DES**: BTPPB–phenol, 1:7; (water-immiscible DES); 10 mL pretreated and diluted human urine sample; 128 µL DES; sonicated, 1 min; ice bath, 3 min; centrifuged, 4 min, 5000 rpm; solidified droplets melted at room temperature; extract diluted with methanol (1:1)	2.0 ng L^{-1}	[25]
Cobalt	Solid (*biscuit, bitter chocolate wafers, white, chocolate, corn, wheat, herbal tea, spinach and mint*) and liquid (*tap water, wastewater, river water, well water, chocolate milk, cow milk and red wine*) samples	AA-IHDES-LPME	FAAS	**HDES**: Tetraheptylammonium chloride–oleic acid, 1:1; 5 mL sample solution; dithizone solution; 200 µL DES; aspiration/dispersion cycles, 7 times; ice bath, 5 min	0.04 µg L^{-1}	[26]
Cobalt	Urine samples	DES-MCG-DSPE	SQT-FAAS	**DES**: choline chloride–phenol, 1:3; 8 mL sample solution; 150 µL DES-MCG; sonicated, 60 s; centrifuged, 2 min, 6000 rpm; MNPs separated using a strong magnet; 0.10 mL 2 M nitric acid added as	4.6 ng mL^{-1}	[27]

				eluent for desorption process; sonicated, 60 s		
Cobalt	Linden tea samples	DES-LPME	SQT-FAAS	**DES**: choline chloride–phenol, 1:2 10 mL sample solution; (Z)-3-bromo-5-((p-tolylimino)methyl) phenol solution as ligand; 0.60 mL DES; 1 mL THF; centrifuged, 120 s, 6000 rpm	2.0 μg L^{-1}	[28]
Cobalt	Pharmaceutical supplement and tea samples	DES-UA-LPME	MS-FAAS	**DES**: choline chloride–phenol, 1:4; 10 mL sample solution; 1-nitroso-2-naphthol solution; 0.5 mL DES; 0.5 mL THF; sonicated, 2 min; centrifuged, 5 min, 4000 rpm	1.10 μg L^{-1}	[29]
Copper	Quince samples	VA-DES-ELPME	SQT-FAAS	**DES**: choline chloride–phenol, 1:2; 8 mL sample solution, (Z)-4-bromo-2[(naphthalene-2-ylimino)methyl]phenol solution; 0.40 mL DES; 1.5 mL THF; vortexed, 45 s; centrifuged, 2 min, 6000 rpm	0.5 μg L^{-1}	[30]
Copper	Vegetable samples (*spinach, lettuce, broccoli, potato, carrot and parsley*)	DES-HLLME	FAAS	**DES**: benzyl triphenyl phosphonium bromide–ethylene glycol, 1:8; 20 mL sample solution; DPC solution; 80 mg DES; water bath, 40 °C, 4 min, vortexed; ice bath; centrifuged, 5 min, 4000 rpm	0.13 μg L^{-1}	[31]
Copper	Liver samples	DES-digestion and UA-LPME	MS-FAAS	**DES**: choline chloride–lactic acid, 1:2 (for digestion step) and tetrabuthylamonium chloride–decanoic acid, 1:2 (for UA-LPME)	4.00 μg L^{-1}	[32]
Copper	Water samples (*tap water and lake water*)	EA-DLLME-DES	FAAS	**DES**: choline chloride–phenol, 1:3; 0.4 g effervescence powder in 50 mL conical bottom centrifuge tube; 25 mL sample solution; 500 μL 1% (w/v) DPC; 1000 μL DES and 1000 μL THF; centrifuged, 3 min, 4020×g; DES phase completed to 500 μL with 1% acidic ethanol	2.9 μg L^{-1}	[33]

Gold	Plating bath solution	DES-LPME	SQT-FAAS	**DES**: choline chloride–phenol, 1:2; 8 mL sample solution; 1 mL 0.05% (w/v) DDTC; 0.50 mL DES; 0.50 mL THF; mechanical shaker, 45 s; centrifuged, 2 min, 6000 rpm	5.1 µg/L	[34]
Iron	Sheep, bovine and chicken liver samples	UA-DES-E (*extraction from solid samples*)	FAAS	**DES**: choline chloride–lactic acid, 1:1; 50 mg bovine liver CRM; 8 mL DES; ultrasonic extraction in ultrasonic bath, 45 min; centrifuged, 3 min, 4000 rpm	0.026 µg mL^{-1}	[35]
Manganese	Coffee and wastewater samples	DES-LPME	FAAS	**DES**: choline chloride–phenol, 1:2; 8 mL sample solution, 3-[[(2-hydroxyphenyl)imino]methyl]-2-naphthalenol solution; 500 µL DES, vortexed, 30 s; 1 mL THF; vortexed, 30 s; centrifuged, 2 min, 3451 g	0.52 µg L^{-1}	[36]
Mercury	Fish, hair, nail, and tap water samples	MSPE followed by DES-USA-DLLME	ETAAS	**HDES**: L-menthol–salicylic acid, 4:1; MSPE step; elution; 50 µL DES; sonicated, 120 sec; centrifuged, 10 min, 4000 rpm	0.34 ng mL^{-1}	[37]
Total mercury	Marine fish samples	DES-assisted digestion	CVAAS	**DES**: choline chloride–oxalic acid, 1:2; 0.20 g fish sample; 3 mL DES; stirred, 120 rpm, 10 min. During this stage, the majority of the powdered fish sample was dissolved. However, some small particles could still be observed; 5 mL 7 M HNO_3 was added, stirred, 5 min; diluted to 25 mL with water	0.03 µg g^{-1}	[38]
Nickel	Spinach samples	DES-LPME	SQT-FAAS	**DES**: choline chloride–phenol, 1:2; 8 mL sample solution; 1 mL 0.50% DPC ligand; 0.50 mL DES; 1 mL THF; centrifuged, 2 min, 6000 rpm	3.8 µg L^{-1}	[39]
Nickel	Water (*wastewater, seawater, mineral water, well water*), cigarette and food (*onion, parsley*)	DES-LPME	MS-FAAS	**DES**: tetrabutyl ammonium chloride–decanoic acid, 1:3; sample solution; 0.2 mL 0.15% (w/v) DDTC; 0.1 mL DES; 0.25 mL THF; sonicated, 3 min;	0.13 µg L^{-1}	[40]

	samples			centrifuged, 10 min, 4000 rpm; DES phase completed to 500 µL with HNO_3 (65%); 100 µL injected		
Lead	Water (*tap water, mineral water*) and vegetable (*onion, celery, carrot, and tomato*) samples	dSPE-poly (TBAB-2AA DES)	FAAS	**PolyDES**: tetrabutylammonium bromide–acrylic acid, 1:2, poly (TBAB-2AA DES) 10 mg poly TBAB-2AA DES dispersed in 50 mL sample solution; shaken vigorously, 15 min; centrifuged, 5 min, 6000 rpm; 1 mL HNO_3 (5 mol L^{-1}) as elution solvent; sonicated, 5 min; centrifuged, 5 min, 6000 rpm	2.0 µg L^{-1}	[41]
Lead	Water (*tap, lake, and river water*) and food samples extracts (*salted peanuts, chickpeas, roasted yellow corn, pistachios, and almonds*)	DES-ME	FAAS	**DES**: α-benzoin oxime, iron(III) chloride–phenol, 1:5; sample solution; 150 µL DES; vortexed, 5 min; centrifuged, 12 min, 4000 rpm; dissolved in nitric acid to 500 µL	0.008 µg L^{-1}	[42]
Lead	Milk samples	DES-LPME	SQT-FAAS	**DES**: choline chloride–phenol, 1:1; 8 mL sample solution; dithizone solution; 0.50 mL DES; 1 mL THF; centrifuged, 2 min, 6000 rpm	8.7 µg L^{-1}	[43]
Lead	Water (*fresh canal water and wastewater*) and food (*black tea, canned fish, green tea, spinach, canned mushrooms, chicken, beef, boiled wheat*) samples	DES-µSS	MS-FAAS	**HDES**: choline chloride–decanoic acid, 1:1; 10 mL sample solution; 500 µL (1 mol L^{-1}) (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline); 100 µL DES; aspiration/dispersion cycles, 10 times; ice bath	0.086 µg L^{-1}	[44]
Lead	Cigarette tobacco and food samples (*onion, parsley*)	UA-LPME-DES	FAAS	**DES**: decanoic acid–tetrabutyl ammonium chloride; sample solution; 100 µL 0.01% 1-nitroso-2-naphthol; 100 µL DES; 100 µL THF; sonicated, 5 min; centrifuged, 4 min, 4000 rpm; DES phase completed to 500 µL with	4.4 µg L^{-1}	[45]

				0.2 M HNO_3		
Lead	Water samples (*tap water, river water and seawater*)	ELLME-DES	FAAS	**DES**: choline chloride and 2-chlorophenol, 1:2; 10 mL sample solution; 0.5 mL 0.03% (w/v) purpurin solution; 150 µL DES; 0.75 mL THF; manually shaken, 2 min; centrifuged, 4000 rpm, 5 min; DES phase diluted to 1 mL with 0.5 mol L^{-1} HNO_3 in ethanol	5.93 µg L^{-1}	[46]
Lead	Water (*lake, wastewater, river and seawater*) and food (*black tea, green tea, cumin, cow meat, linseed, canned fish, chicken meat, potato*) samples	AA-DES-LPME	GFAAS	**DES**: choline chloride–phenol, 1:4; 30 mL sample solution; 500 µL TAR solution; left for 5 min; 600 µL DES; 800 µL THF; aspiration/dispersion cycles, 9 times; centrifuged, 3500 rpm, 4 min	0.60 ng L^{-1}	[47]
Lead	Whole blood samples	CM-HFLPME	ETAAS	**DES**: choline chloride–urea 1:2; lead extracted from 17 mL acidic sample solution into 1-octanol containing CTAB and back-extracted into 25 µL DES containing $KClO_4$ as the receiving phase	0.1 ng mL^{-1}	[48]
Palladium	Environmental water (*tap water, wastewater and seawater*), road dust and catalytic converter samples	TC-DES-LLME	ETAAS	**DES**: phenyl salicylate–DL-menthol, 1:1; 10 mL sample solution; PAN solution; 60 µL DES; incubated in water bath, 65 °C, 1 min; ice bath, 3 min	0.03 µg L^{-1}	[49]
Palladium	Marble mine and catalytic converter samples	DES-ME	FAAS	**DES**: disodium 4,5-dihydroxy-1,3-benzenedisulfonate, hydroxyl ammonium chloride, $FeCl_3$ and phenol, 1:1:2:1; sample solution; 100 µL DES; vortexed, 1 min, centrifuged, 5 min, 4000 rpm; DES layer dissolved in 300 µL concentrated nitric acid	1.18 µg·L^{-1}	[50]
Palladium	Water (*tap, mineral, river, and seawater*) and environmental (*road dust,*	DES-AA-ELLME	FAAS	**DES**: choline chloride–phenol, 1:4; sample solution; 500 µL DES; 400 µL 0.1% HMBATSC; 0.8 mL THF;	1.2 µg L^{-1}	[51]

	tunnel dust, and a catalytic converter) samples			aspiration/dispersion cycles, 10 times; centrifuged, 5 min, 4000 rpm		
Silver	Water, wastewater, ore and hair samples	DES-GO/HF	FAAS	**DES**: choline chloride–thiourea; 1:2; 50 mL sample solution; segment of modified GO/HF added; stirred, 15 min, 800 rpm; modified GO/HF containing the analyte taken out, transferred to a test tube, retained analyte desorbed into 250 µL of nitric acid (1 mol L^{-1}) solution under sonically agitation, 5 min	0.2 µg L^{-1}	[52]

[1] We left the abbreviations used by the authors (apart from some exceptions), even if this is not in accordance with our previous recommendations [89].
[2] For a detailed description of the procedure, please see the original articles.

Table 2 Selected examples of DES-based microextraction for multi-elemental analysis by AAS

Analyte	Sample	Microextraction[1]	Detection	Comments[2]	LOD	Ref.
Arsenic and antimony	Water (*wastewater, tap water, well water, river water, and bottled water*), honey and rice samples	DES-VAME	HG-AAS	**DES**: choline chloride–oxalic acid, 1:1; 2 mL sample solution; 600 µL dithizone (3×10^{-3} mol L^{-1}); 700 µL DES; vortexed, 1 min; 300 µL THF; vortexed, 3 min; centrifuged, 5 min, 4000 rpm; DES phase diluted to 2.5 mL with acidic ethanol	7.5 (As) and 15.6 (Sb) ng L^{-1}	[53]
Arsenic and selenium	Rice samples	NADES-UAME	HG-AAS	**DES**: proline–malic acid, 1:1; 1.5 mL sample solution; 800 mL 1×10^{-4} mol L^{-1} celestine blue solution; 500 µL NADES; 600 µL THF; filled to 15 mL with water; sonicated, 7 min, 35 °C; centrifuged, 3 min, 3500 rpm; DES phase made up to 3 mL with acidic ethanol	Se(IV): 3.0 ng L^{-1} As(III): 1.7 ng L^{-1}	[54]
Cadmium and arsenic	Wine samples	UA-DLLME	FAAS	**HDES**: trioctylmethylammonium chloride–DL-lactic acid, 1:3;	0.080 (Cd) and 0.30	[55]

				5 mL sample solution; mixture of 400 µL DES and 300 µL methanol; vortexed, 1 min; sonicated, 4 min; centrifuged, 5 min, 4000 rpm	(As) µg·L^{-1}	
Cadmium and zinc	Oil samples (*fish oil capsules, butter and margarine*)	RP-DLLME	FAAS	**DES**: glycolic acid–mandelic acid, 2:1; 7 mL oil sample solution (2 g diluted with ethyl acetate till 7 mL); mixture of 750 µL DES (as disperser solvent) and 400 µL 3%, v/v nitric acid solution (as extraction solvent) injected into the tube at 45 °C with a 2-mL glass syringe; centrifuged, 5 min, 6000 rpm; aqueous phase containing the extracted cations were settled at the bottom of the tube	0.12 and 0.18 µg L^{-1} for Cd(II) and Zn(II), respectively	[56]
Cadmium and zinc	Water (*surface water and tap water*) and fruit juice (*cherry and peach juice*) samples	AALLME-SFO	FAAS	**DES**: menthol, sorbitol, and mandelic acid, (1:2:1) as chelating agent and extraction solvent; 5 mL sample solution; 125 µL DES; aspiration/dispersion cycles, 9 times; ice bath, 2 min	0.15 and 0.12 µg L^{-1} for Cd(II) and Zn(II), respectively	[57]
Cobalt and nickel	Water (*well water, urban water, river water*), and juices (*grape and peach*) samples	DLLME-DES	FAAS	**DES**: choline chloride and 4-aminophenol, 1:1 as complexing agent and extraction solvent; 5 mL sample; 125 mg DES and 1 mL methanol; centrifuged, 8 min, 8000 rpm	0.30 and 0.22 µg L^{-1} for Ni(II) and Co(II), respectively	[58]
Copper and nickel	Water (*spring water, tap water, and seawater*) and biological (*human serum and urine*) samples	SPE (*DES modified cotton*)	FAAS	**DES**: choline chloride–urea, 1:2; 50 mL sample solution; passed through the microcolumn (7 mL min^{-1}); adsorbed analytes were eluted by 250 µL nitric acid (2 mol L^{-1}) at a flow rate 3.5 mL min^{-1}	0.05 and 0.60 µg L^{-1} for Cu and Ni, respectively.	[59]
Nickel and cobalt	Food (*broccoli and spinach*) and water (*tap, mineral, sea, and river*) samples	UA-DES-DLLME-SFO	FAAS	**DES**: DL-menthol–decanoic acid, 1:1; 50 mL sample solution, 5-Br-PADAP solution; 150 µL DES; sonicated, 2 min; ice	0.3 µg L^{-1}	[60]

				bath; DES phase increased to 1 mL with ethanol		
Lead and cadmium	Cosmetic samples (*lipsticks and eye shadows*)	UAμE-DES	FAAS	**DES**: $ZnCl_2$ and acetamide, 1:3; 10 mL sample solution; APDC solution; DES; THF; sonicated; centrifuged, 5 min, 3500 rpm	Cd and Pb 0.86 and 0.66 μg L^{-1}, respectively	[61]
Lead and cadmium	Hair dyes and henna samples	UA-DES-LPME	MS-FAAS	**DES**: choline chloride–phenol; dithizone as complexing agent; and THF (an aprotic solvent)	2.5 μg L^{-1} (Pb) and 0.75 μg L^{-1} (Cd)	[62]
Lead and cadmium	Vegetable samples (*leek, spinach, dill, parsley, mint, arugula, eggplant, dry tea*)	HI-DES-ME	FAAS	**DES**: citric acid–sucrose, 1:3; 2 mL vegetable solution; 600 μL 100 μmol L^{-1} TAR; 100/150 μL DES and 200 μL acetonitrile (aprotic solvent); volume completed to 15 mL with water; sonicated, 5 min, 55 °C/38 °C; centrifuged, 2 min, 4000 rpm	0.17–0.35 ng mL^{-1}	[63]
Lead and cadmium	Water (*tap water, well water, river water and Caspian Sea*), human hair and soil samples	DES-MNP	FAAS	**DES**: choline chloride–urea, 1:2.5; 60 mL sample solution; 200 μL DES and 20 mg MNP; stirred, 10 min; bulk aqueous phase decanted; analytes desorbed upon addition 600 μL nitric acid (1 mol L^{-1})	0.4 (Pb) and 0.1 (Cd) μg L^{-1}	[64]
Lead and cadmium	Edible oils (*sesame oil, soybean oil, olive oil, sunflower oil, and corn oil*)	DES-LPME	ETAAS	**DES**: choline chloride–urea, 1:2; 4:1 mixture of DES and 2% nitric acid (200 μL) added to oil sample; vortexed; water bath, 50 °C and stirred, 5 min	8 (Pb) and 0.2 (Cd) ng kg^{-1}	[65]
Selenium and arsenic	Edible mushroom samples	DES-based digestion	GFAAS	**DES**: choline chloride–oxalic acid, 1:2; DES maintained at 100°C; 100 mg mushroom sample; stirred, 150 rpm, 40 min; sample completely dissolved and homogenous solution formed; 5 mL HNO_3 1.5 M and stirred, 5 min; centrifuged, 5 min, 3000 rpm; supernatant separated,	Se: 0.32 μg L^{-1}, As: 0.50 μg L^{-1}	[66]

				filtered; diluted with water to 10 mL		
Selenium and arsenic	Fish samples	DES-based digestion	ETAAS	**DES**: choline chloride–oxalic acid, 1:2; 80 mg sample dissolved in DES at 105°C, 40 min; subsequent addition of 4 mL HNO_3 (1 M) and heating, 5 min; centrifuged; supernatant solution filtered, diluted	0.75 µg kg^{-1} for Se and 0.46 µg kg^{-1} for As	[67]
Cadmium, copper, lead	Milk samples	DLLME-DES	FAAS	**DES**: menthol, sorbitol, mandelic acid, 1:2:1 as chelating agent and extraction solvent; 5 mL sample solution; mixture of 1.5 mL methanol (as dispersive solvent) and 100 µL DES (as extraction solvent and a complexing agent); ice bath, 2 min	0.38–0.42 µg L^{-1}	[68]
Cadmium, lead and arsenic	Vegetables (*spinach, coriander, basil and radish*) and soil samples irrigated with treated sewage	VALPME-DES	GFAAS	**DES**: choline chloride–citric acid, 1:1; 10 mL sample solution; 50 µL DES containing 10 µL DDTP; vortexed, 5 min; centrifuged, 5 min, 5000 rpm; freezer for a few minutes	0.03–0.1 µg kg^{-1}	[69]
Copper, cadmium and lead	Honey samples	UA-DLLME-NADES	FAAS	**DES**: citric acid–sucrose, 3:2; 15 mL sample solution; 80 µmol L^{-1} Methyl green; 400 µL NADES and 350 µL THF; sonicated, 10 min, 35 °C; centrifuged, 5 min, 1431×g; DES phase diluted to 2 mL with 1 mol L^{-1} HNO_3 in methanol	0.077, 0.16, 0.29 µg L^{-1} for Cu(II),Cd(II), Pb(II)	[70]
Copper, iron, and zinc	Fish samples (*muscle, liver, and gills*)	DES-based digestion	FAAS	**DES**: choline chloride–oxalic acid, 1:2; 100 mg sample; dissolved in DES at 100°C for 45 min; 5 mL HNO_3 (1 M) added; centrifuged; supernatant solution filtered, diluted	Fe, Zn, and Cu: 0.053, 0.012, and 0.006 µg mL^{-1}, respectively	[71]
Mercury, lead and cadmium	Soil and vegetables (*radish, spinach, coriander and carrot*) irrigated with treated municipal wastewater	DLLME-SDES	GFAAS	**DES**: 1-decyl-3-methylimidazolium chloride and 1-undecanol, 1:2; 10 mL sample solution; 50 µL DES containing DDTP; water bath, 55 °C;	0.01–0.03 µg kg^{-1}	[72]

				vortexed, 4 min; ice bath, 5 min		
Cadmium, lead, copper, and arsenic	Food samples (*walnut, rice, tomato paste, spinach*) and non-alcoholic beverages (*orange juice, black tea, and river water*)	CL-DES-MNF-AALLME	ETAAS	**DES**: choline chloride–thiacetamide, 1:2; sample solution; 40 µL DES-MNF; aspiration/dispersion cycles, 9 times; DES-MNF separated using an external magnet; back extraction step, 75 µL nitric acid (1 mol L^{-1}); sonicated, 10 s; 10 µL supernatant solution injected	4.2, 3, 3.5 and 3.6 ng L^{-1} for cadmium, lead, copper, and arsenic respectively	[73]
Lead, cobalt, nickel and manganese	Edible oil samples (*sunflower oil, baby oil, trout, waste frying oil and syrup-soaked pastry oil*)	DES-ME	MS-FAAS	**DES**: choline chloride–urea, 1:2; 20 mL oil sample, 200 µL DES; vortexed, 1 min; 75 µL HNO_3; water bath, 30 min, 100 °C; vortexed 2 min; centrifuged, 5 min, 4000 rpm (*oil and DES rich phase obtained*); DES decanted and methanol added	Pb: 2.4, Co: 4.6, Ni: 7.5, Mn: 1.0 µg L^{-1}	[74]

[1] We left the abbreviations used by the authors (apart from some exceptions), even if this is not in accordance with our previous recommendations [89].
[2] For a detailed description of the procedure, please see the original articles.

Table 3 Selected examples of DES-based microextraction for speciation analysis by AAS

Analyte	Sample	Microextraction[1]	Detection	Comments[2]	LOD	Ref.
Speciation of arsenic	Soil and vegetables (*radish, spinach, coriander and carrot*) irrigated with treated municipal wastewater	VAME-DES	GFAAS	**DES**: choline chloride–citric acid monohydrate, 1:1; 10 mL sample solution; 50 µL DES containing 10 µL DDTP; vortexed, 5 min; centrifuged, 4 min, 5000 rpm; freezer, 5 min; melted; 30 µL injected	0.10 µg kg^{-1}	[76]
Speciation of arsenic	Water (*lake water, mineral water, tap water and river water*), food (*edible mushrooms, fish, green tea,*	DES-UALPME	ETAAS	**DES**: choline chloride–phenol, 1:3; 25 mL sample solution; 500 µL DDTC (0.1% w/v); 1000 µL DES; 500 µL THF; sonicated, 5 min; centrifuged5 min, 3500 rpm; DES	10 ng L^{-1}	[77]

	black tea, rice), cigarette and soil samples			phase, acidic ethanol added up to 1 mL; injected 20 µL		
Speciation of chromium	Water (*river, tap, well, industrial wastewater*) and urine samples	DES based-CSDF-ME	ETAAS	**DES**: choline chloride–phenol, 2:3; 10 mL sample solution; 0.15 mL DCP solution; 59 µL DES; 0.5 mL THF; centrifuged, 10 min, 5000 rpm	0.096 µg L^{-1}	[81]
Speciation of chromium	Tea and water samples	UA-DES-LLME	FAAS	**DES**: choline chloride–phenol, 1:2; sample solution; APDC solution; 0.4 mL DES; vortexed, 3 min; 0.4 mL THF; sonicated, 4 min; centrifuged, 6 min, 4000 rpm	0.8 µg L^{-1}	[82]
Speciation of chromium	food (*mushrooms and soybean*) and water (*tap and river*) samples	UA-LPME	FAAS	**DES**: choline chloride–phenol; 1:2; 10 mL sample solution; PAN solution; 350 µL DES; sonicated, 90 s; centrifuged, 4 min, 5000 rpm; 400 µL THF	0.4 ng mL^{-1}	[83]
Speciation of chromium	Food (*rice and sausage*) and water (*tap water, river water, and mineral water*) samples	AA-EME-DES	FAAS	**DES**: choline chloride–phenylethanol, 1:2; 10 mL sample solution; PAN solution; 250 µL DES; aspiration/dispersion cycles; 9 times; centrifuged, 4 min, 4000 rpm	0.4 ng mL^{-1}	[84]
Speciation of chromium	Water samples (*tap water, chromium plating factory wastewater and lake water*)	UA-DES-ELPME	MS-FAAS	**DES**: choline chloride–phenol, 1:3; 10 mL sample; DDTC solution; 450 µL DES; 450 µL THF; sonicated 2 min; centrifuged, 10 min, 4000 rpm; DES phase completed to 750 µL with ethanol	5.5 µg L^{-1}	[85]
Speciation of mercury	Water (*bottled mineral water, river water, tap water*) and biological (*freshwater fish*) samples	UA-DES-LPME	ETAAS	**DES**: choline chloride–phenol, 1:3; 10 mL sample solution; dithizone solution; 500 µL DES; 500 µL THF; sonicated, 2 min; centrifuged, 10 min, 4032g	Hg^{2+} and CH_3Hg^+ 0.073 and 0.091 ng mL^{-1}, respectively	[86]
Speciation of mercury	Blood samples	VADLLME-FDES	GFAAS	**DES**: [DMIM]Cl and 1-undecanol, 1:2; 10 mL sample solution; 55 µL DES containing 15 µL DDTP; maintained at 50°C	0.10 µg L^{-1}	[87]

				in a water bath; 350 mg NaCl to break the emulsion; vortexed, 3 min; centrifuged, 4 min, 5000 rpm; ice bath, 5 min		
Speciation of selenium	Blood samples	SDES-ME	GFAAS	**DES**: choline chloride–decanoic acid, 1:2; 5 mL pretreated/diluted blood sample; 60 µl DES containing DDTP; DDTP; vortexed, 4 min; ice bath	0.015 µg L^{-1}	[80]
Speciation of selenium	Water (*tap water and mineral water*) and food (*sheep milk, cow milk, yogurt, mixed fruit juice, egg, orange juice, grapefruit, honey, canned fish and edible mushrooms*) samples	UALPME-DES	ETAAS	**DES**: choline chloride–phenol, 1:3; 25 mL sample solution; 0.4 mL 2×10^{-3} to 5×10^{-5} mol L^{-1} DAB; 0.5 mL DES, 0.5 mL THF; sonicated, 3 min, 45°C; centrifuged, 5 min, 4000 rpm; DES phase, acidic ethanol up to 0.5 mL	4.61 ng L^{-1}	[79]
Speciation of arsenic, selenium and mercury	Blood samples	LPME-SDES	ETAAS	**HDES**: choline chloride–decanoic acid, 1:2; 10 mL pretreated/diluted blood sample; 60 µL DES containing DDTP; vortexed, 5 min; centrifuged, 4 min, 5000 rpm; ice bath; DES phase, 20 µL acidic ethanol added	As, Se and Hg 0.05, 0.015 and 0.10 µg L^{-1}	[78]

[1] We left the abbreviations used by the authors (apart from some exceptions), even if this is not in accordance with our previous recommendations [89].
[2] For a detailed description of the procedure, please see the original articles.

Abbreviations

[DMIM]Cl, 1-Octyl-3-methylimidazolium chloride and 1-undecanol;
[$P_{666(14)}$][Cl], Trihexyltetradecylphosphonium chloride;
5-Br-PADAP, 2-(5-Bromo-2-pyridylazo)-5-(diethylamino) phenol;
AA-, Air-assisted;
APDC, Ammonium pyrrolidine dithiocarbamate;
BTPPB, Benzyltriphenylphosphonium bromide;
CL-, Centrifuge-less;
CM-HFLPME, Carrier-mediated hollow fiber liquid-phase microextraction;
CSDF-ME, Continuous sample drop flow-microextraction;
CTAB, N,N,N-cetyltrimethylammonium bromide;
CVAAS, Cold vapor atomic absorption spectrometry;
DAB, 3,3'-Diaminobenzidine;
DDTC, Diethyl dithiocarbamate;
DDTP, Diethyl dithiophosphoric acid;
DES, Deep eutectic solvent;
DMDTC, Dimethyl dithiocarbamate;
DPC, Diphenylcarbazone;
EA, effervescence-assisted;
ETAAS, Electrothermal atomic absorption spectrometry;
FAAS, Flame atomic absorption spectrometry;
GAC, Green Analytical Chemistry;
GF-AAS, Graphite furnace atomic absorption spectrometry;
GO, Graphene oxide;
HF-, Hollow fiber;
HI-, Heat-induced;
HLLME, Homogeneous liquid–liquid microextraction;
HMBATSC, 2-Hydroxy-3-methoxybenzaldehyde thiosemicarbazone;
ICP-MS, Inductively coupled plasma-mass spectrometry;
ICP-OES, Inductively coupled plasma-optical emission spectrometry;
LPME, Liquid-phase microextraction;
MNF, Magnetic nanofluid-linked;
MS-, Microsampling;
MSPE, Magnetic solid-phase extraction;
PAN, 1-(2-pyridylazo)-2-naphthol;
SDES, Solidification of deep eutectic solvent;
SDES-ME, Solidified deep eutectic solvent microextraction;
SDFD, Solidification of dispersed fine droplets;
SPE, Solid-phase extraction;
SQT, Slotted quartz tube;
TAR, 4-(2-Thiazolylazo) resorcinol;
TC-DES-LLME, Temperature-controlled liquid–liquid microextraction;
THF, Tetrahydrofuran;
UDDLLME, Modified ultrasonic-assisted dual dispersive liquid–liquid microextraction;

VADLLME−FDES, Vortex assisted dispersive liquid−liquid microextraction based on the freezing of deep eutectic solvent;

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