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Application of deep eutectic solvents in atomic absorption spectrometry

Vasil Andruch ^a, Radoslav Halko ^b, Jozef Tuček ^b, Justyna Płotka-Wasyłka ^{c,d,*}

^a Department of Analytical Chemistry, Institute of Chemistry, Faculty of Science, P. J. Šafárik University, Košice, Slovakia

^b Department of Analytical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, SK-842 15 Bratislava, Slovakia

^c Department of Analytical Chemistry, Faculty of Chemistry, Gdańsk University of Technology, 80-233 Gdańsk, Poland

^d BioTechMed Center, Gdańsk University of Technology, 80-233 Gdańsk, Poland

*Corresponding author: juswasyl@pg.edu.pl; plotkajustyna@gmail.com (J. Płotka-Wasyłka)

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 as 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

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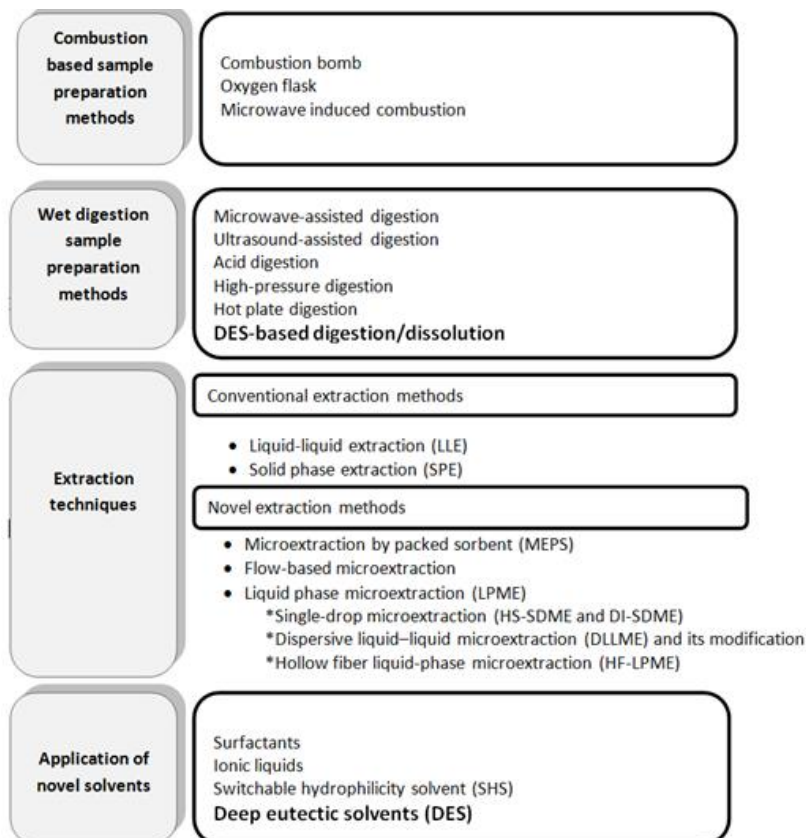
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66 1 Introduction

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

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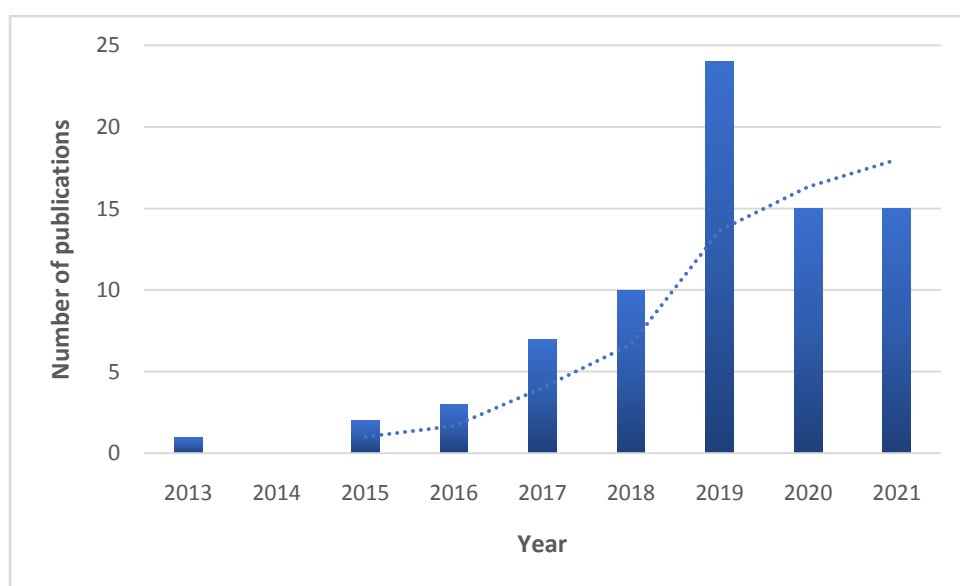
89 **Figure 1.** The evolution of sample preparation procedures

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

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

120



121

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

125
126

127 2 Procedure for DES-based extraction

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

134 The DES extraction procedures proposed by various authors differ significantly in their
135 individual steps, in the order of those steps, in the reagents used, as well as in the composition and
136 type of DES used (hydrophilic, hydrophobic). Until recently, most synthesized DES were hydrophilic,
137 which prevented their use in the extraction of aqueous samples. However, in the last few years
138 studies on the synthesis and application of hydrophobic deep eutectic solvents has rapidly expanded
139 [17]. Therefore, to describe a general procedure suitable for every procedure is incredibly difficult or
140 almost impossible.

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

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153 3 Elements determined by AAS following DES-based extraction

154 To date, DES-based procedures coupled with atomic absorption spectrometry have been suggested
155 for a variety of elements (**Figure 3**); examples of their application are given in Tables 1-3. The
156 developed procedures mainly allow the determination of one specific element, such as aluminum
157 [18], cadmium [19-23], chromium [24, 25], cobalt [26-29], copper [30-33], gold [34], iron [35],
158 manganese [36], mercury [37, 38], nickel [39, 40], lead [41-48], palladium [49-51] and silver [52], in
159 the sample, but procedures that allow the determination of two elements (Table 2), such as arsenic
160 and antimony [53], arsenic and selenium [54], cadmium and arsenic [55], cadmium and zinc [56, 57],
161 cobalt and nickel [58], copper and nickel [59], nickel and cobalt [60], lead and cadmium [61-65], and
162 selenium and arsenic [66, 67], or three or more elements simultaneously (Table 2), such as cadmium,
163 copper and lead [68], cadmium, lead and arsenic [69], copper, cadmium and lead [70], copper, iron,
164 and zinc [71], mercury, lead and cadmium [72], cadmium, lead, copper and arsenic [73], lead, cobalt,

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

167

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra																

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

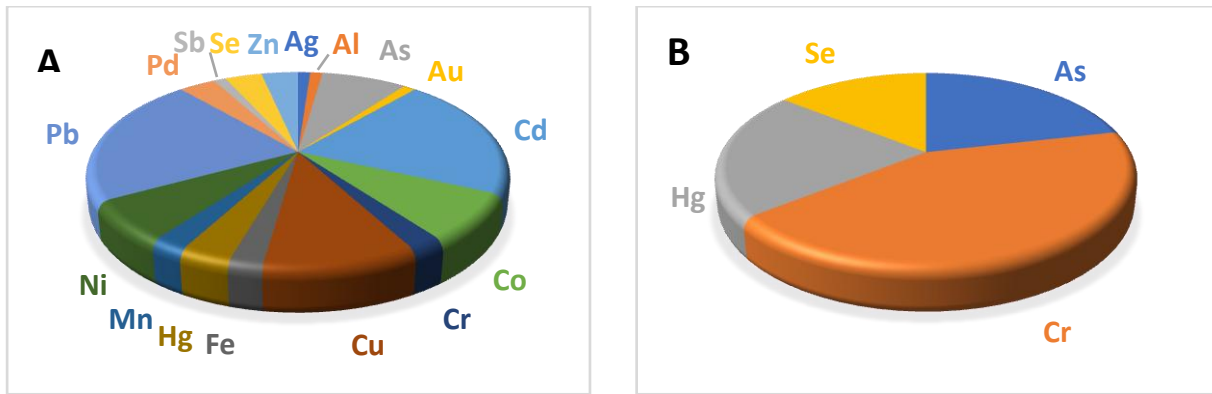
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174 3.1 Speciation analysis

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

184 **Figure 4** shows the distribution of metals by total concentration and speciation analysis using
 185 DES-AAS methods. In all cases of speciation analysis of arsenic or selenium, the reduction of
 186 arsenic(V) to arsenic(III) or selenium(VI) to selenium(IV) was used, and the total arsenic or selenium
 187 concentration was measured by electrothermal atomic absorption spectrometry (ETAAS). However,
 188 both reduction and oxidation procedures were used for the speciation analysis of chromium. Fasihi
 189 et al. [83, 84] applied ascorbic acid to convert chromium(VI) to chromium(III), and the total
 190 chromium concentration in food and water samples was detected by flame atomic absorption
 191 spectrometry (FAAS). In contrast, the oxidation of chromium(III) to chromium(VI) with KMnO_4 and
 192 H_2SO_4 was used for the speciation analysis of chromium in aqueous samples by ETAAS [81], or in tea
 193 and water samples by FAAS [82, 85]. In the case of mercury speciation analysis, Akramipour et al. [78,
 194 87] published a method based on the conversion of organic mercury species into mercury(II) using
 195 ultraviolet light and microwave and the determination of total mercury in blood samples by ETAAS.
 196 Thongsaw et al. [86] took a different approach, extracting the individual species of mercury
 197 separately: (1) mercury(II) in the form of a hydrophobic dithizone complex by DES and (2)
 198 methylmercury extracted directly into the DES phase. Finally, the determination of mercury in water
 199 and freshwater fish samples was carried out by ETAAS.

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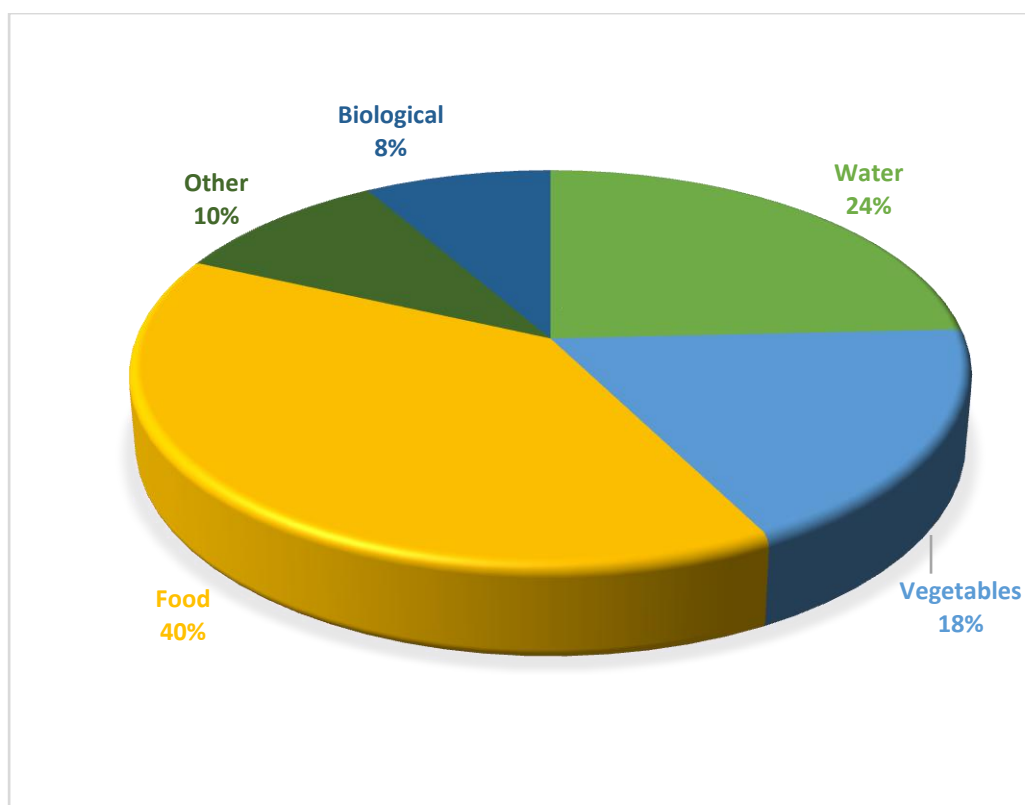
201
 202 **Figure 4** The distribution of metals in total concentration (A) and speciation analysis (B) by the DES-
 203 AAS method

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206 4 Samples of different matrix composition: sampling and sample pre- 207 treatment

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

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

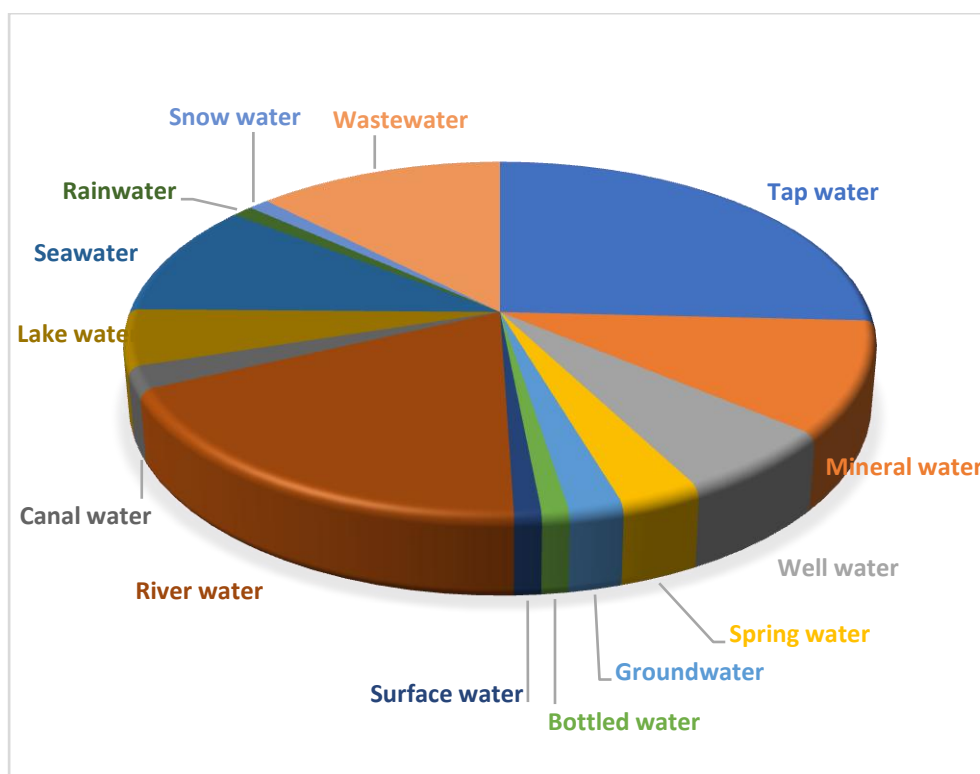
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220 4.1 Water samples

221 Many different types of water samples have been analyzed. However, **Figure 6** clearly shows that
222 different types of drinking water, surface water and wastewater predominate. The analyzed water
223 samples can be divided into the following more detailed subgroups: tap water [19, 22, 24, 26, 33, 37,
224 41, 42, 44, 46, 49, 51-53, 57, 59, 60, 64, 77, 79, 81, 83-86], groundwater [21, 24], spring water [18,
225 52, 59], well water [26, 40, 53, 58, 64, 81], mineral water [18, 24, 40, 41, 51, 60, 77, 79, 84, 86],
226 bottled water [53], surface water [57], river water [18, 26, 42, 44, 46, 47, 51-53, 58, 60, 64, 73, 77,
227 81, 83, 84, 86], canal water [24, 44], lake water [33, 42, 47, 77, 85], seawater [18, 24, 40, 46, 47, 49,
228 51, 59, 60, 64], rainwater [19], snowmelt water [19] and wastewater [19, 24, 26, 36, 40, 44, 47, 49,
229 52, 53, 81, 85].

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

238



239

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

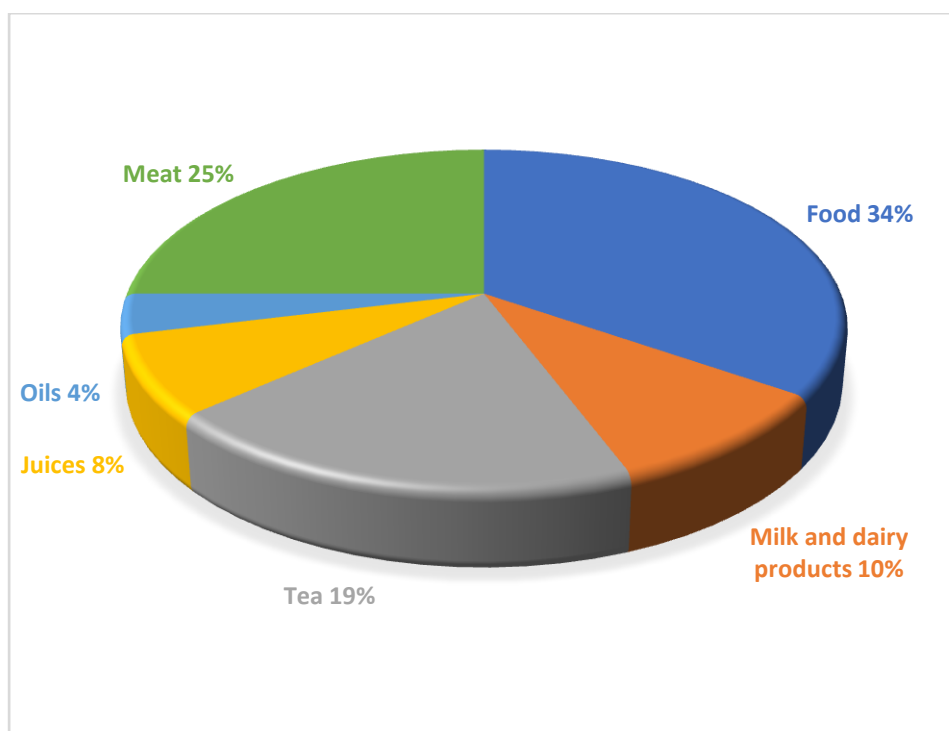
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243 4.2 Food samples

244 Food products represent the largest group of samples analyzed, with 40% of the total number of
 245 analyzed samples. Articles devoted to the analysis of food samples include (a) meat samples, such as
 246 liver [32, 35], fish [22, 37, 38, 67, 71, 77, 86], canned fish [22, 44, 47, 79], chicken meat [18, 44, 47],
 247 chicken shawarma [22] and beef [44, 47]; (b) milk and dairy products [68], such as cow milk [26, 79],
 248 cow and goat milk [19], sheep milk [79], cheese [22], cow and goat cheese [19] and yogurt [79]; (c)
 249 juices, including cherry and peach [57], grapefruit [79], grape and peach [58], orange [73, 79] and
 250 mixed fruit juice [79]; (d) tea samples, including black tea [22, 44, 47, 73, 77], green tea [44, 47, 77],
 251 herbal tea [26] and linden tea [28]; as well as other foods, such as bean stew [22], biscuits [26], bitter
 252 chocolate wafers [26], butter [56], margarine [56], chocolate [26], chocolate milk [26], cigarettes [40,
 253 45, 77], coffee [36], corn [22, 26], roasted yellow corn [42], canned corn [22], egg [79], honey [53, 70,
 254 79], mushrooms [18, 22, 66, 77, 79, 83], canned mushrooms [22, 44], salted peanuts [42], brown rice
 255 [53], white rice [53], tomato paste [73], sausage [84], wine [26, 55], wheat [26] and boiled wheat
 256 [44]. The distribution of food samples among the different subgroups is shown in **Figure 7** and
 257 described below.

258



259

260 **Figure 7** The distribution of food samples between different subgroups. Data extracted from Tables
 261 1-3

262

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

269

270 4.2.1 Vegetable and fruit samples

271 Another large group of samples analyzed using the DES-AAS method are vegetables and fruits,
 272 specifically: almonds [42], apple [20], arugula [63], basil [69], broccoli [31, 60], carrot [31, 41, 72, 76],
 273 celery [20, 41], chickpeas [42], coriander [69, 72, 76], cumin [47], dill [63], eggplant [63], leek [63],
 274 lettuce [31], linseed [47], mint [26, 43, 63], onion [40, 41, 45], parsley [31, 40, 45, 63], pistachios [42],
 275 potato [31, 47], quince [30], radish [69, 72, 76], rice [18, 22, 54, 73, 77, 84], soybean [83], spinach
 276 [22, 26, 31, 39, 44, 60, 63, 69, 72, 73, 76], tomato [22, 41] and walnut [73]. Vegetable samples are
 277 often carefully washed with distilled water to remove impurities, then drained and dried to remove
 278 all moisture. They are then homogenized and digested.

279

280 4.2.2 Drink samples

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

286 with 25 mL of a 0.1 M Na₂CO₃ solution. After cooling, the mixture was transferred to a tube and the
287 volume was adjusted to 25 mL with deionized water [82]. Linden samples (20 g) were boiled in water
288 for 45 min. The brewed samples were allowed to cool and then filtered while warm to remove solid
289 particles, and the volume made up to 100 mL [28]. However, procedures using wet acid digestion or
290 microwave digestion are more often described [29, 63, 73, 77].
291

292 4.2.3 Oil samples

293 The direct determination of metals in oils is difficult, due particularly to their high viscosity and their
294 high content of organic compounds. To eliminate these difficulties, decomposition of the sample by a
295 suitable digestion method or dilution of the sample with an appropriate organic solvent is usually
296 used. However, a few published works have used DES instead of sample decomposition to separate
297 and preconcentrate heavy metals from edible oil samples prior to their determination via AAS [56,
298 65, 74].
299

300 4.3 Biological samples

301 Biological samples were typically pretreated as follows: Urine samples were centrifuged, passed
302 through a filter and diluted with distilled water [59] or a 10.0 mM sodium phosphate monobasic
303 solution to adjust the pH and ionic strength and decrease the matrix effect [25]. Microwave-assisted
304 digestion has also been described [27]. Blood samples were usually deproteinated by the addition of
305 acetonitrile and a zinc sulfate solution, vortexed and centrifuged, and then the supernatant was
306 diluted using ultrapure water to decrease the matrix effects [48, 78, 80, 87]. Hair [37, 52, 64] and nail
307 [37] samples were washed with acetone to remove contaminants, then dried and digested.
308

309 4.4 Other type of samples

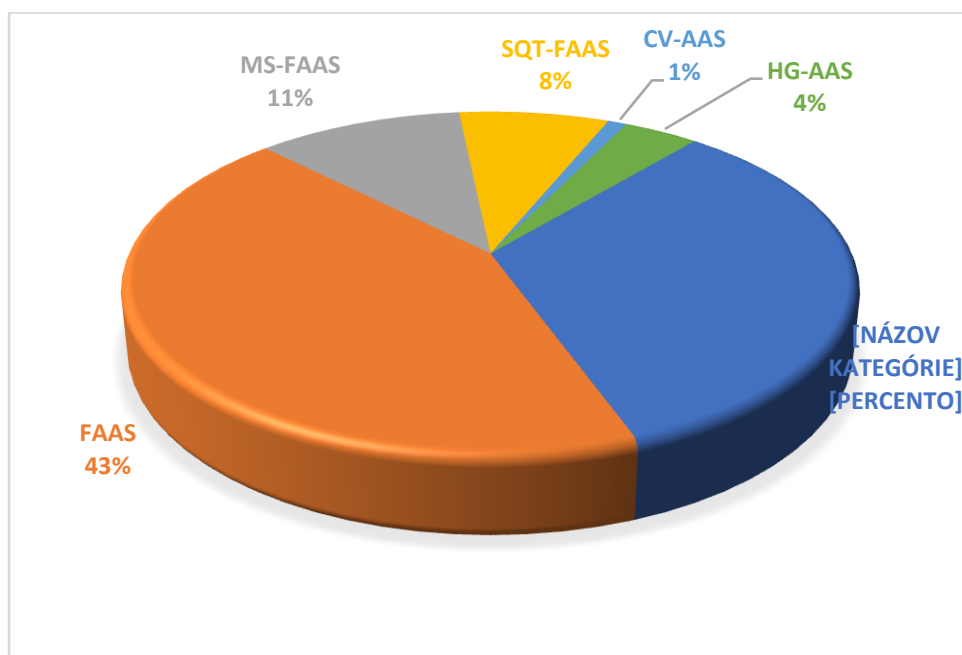
310 The smallest group comprises environmental/technical samples, such as soil [64, 69, 72, 76, 77],
311 sediment [77], ore [52], road dust [49, 51], tunnel dust [51], catalytic converter samples [49-51], as
312 well as cosmetic products (lipsticks and eye shadows) [61], pharmaceutical supplement [29] and
313 cigarette samples [45, 77]. These kinds of samples should also be digested before DES-based
314 extraction.
315

316 The variety of analyzed samples and analytes determined clearly testifies to the great
317 potential of DES in sample pretreatment prior to AAS quantification, especially in the analysis of
318 water, vegetable and food samples. On the other hand, analysts have thus far paid significantly less
319 attention to the analysis of more complex samples, especially biological and technical ones.
320
321

322 5 Type of atomization in DES-AAS procedures

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

330 52, 55-61, 63, 64, 68, 70, 71, 74, 82-84]. But conventional FAAS has low sensitivity of detection, and
 331 the DES-rich phase needs to be sufficiently diluted before being injected into the FAAS system. In
 332 order to improve nebulization efficiency and/or atomization of analytes in conventional FAAS,
 333 several authors have used a basic slotted quartz tube (SQT) [20, 23, 27, 28, 30, 34, 39, 43]. Due to the
 334 small volumes of the DES-rich phase after the extraction process, in some cases it was more
 335 advantageous to use a micro-sample injection system coupled to a flame atomic absorption
 336 spectrometer (MS-FAAS), where the injection volumes after diluting of the DES-rich phase were
 337 hundreds of microliters [29, 32, 40, 44, 62, 85]. The problem with the small volume of DES and
 338 sensitivity of detection was eliminated when using electrothermal atomization: ETAAS or graphite
 339 furnace atomic absorption spectrometry (GFAAS) was used, where the DES-rich phase was injected
 340 directly or only after a minimal dilution into the AAS spectrometer after the extraction procedure
 341 [18, 22, 24, 25, 33, 37, 47-49, 65-67, 69, 72, 73, 76-81, 86, 87]. Only three applications were found to
 342 use vapor generation atomization after DES-based extraction. Altunay et al. [53] and Elik et al. [54]
 343 used hydride generation-atomic absorption spectrometry (HGAAS) to determine arsenic, selenium
 344 and antimony in rice samples and Rastegarifard et al. [38] published the determination of mercury in
 345 marine fish samples by cold vapor atomic absorption spectrometry (CVAAS).
 346



347
 348
 349 **Figure 8** The distribution of the methods by type of atomization in AAS. Data extracted from Tables
 350 1-3
 351

352 6 Addition of ligands (complexing agents)

353 The choice of ligand (chelating agent or ion-pairing agent [54, 70]) is very important to ensure
 354 efficient separation of the analytes (metal ions) and their transport to the organic phase. It should be
 355 kept in mind that other cations may also form complexes with the chosen agent, which may lead to a
 356 decrease in the separation efficiency. Well-known commercially available complexing agents are
 357 commonly used, such as APDC [21, 61, 82], DAB [79], DDTC [19, 34, 40, 77, 85], DMDTC [32], DDTP
 358 [69, 72, 76, 78, 80, 87], DPC [20, 31, 33, 39, 81], PAN [49, 83, 84], TAR [47, 63], dithizone [26, 43, 53,

359 62, 86], 8-hydroxyquinoline [18], 1-nitroso-2-naphthol [29, 45] and 5-Br-PADAP [60]. However, a few
360 papers have reported the application of synthesized reagents [22, 28, 30, 36].

361 We can also find articles in which the complexing agent is part of the DES itself or is dissolved
362 in a DES. Sorouraddin et al. developed an air-assisted liquid–liquid microextraction method (AALLME)
363 based on a ternary solidified deep eutectic solvent in the extraction and preconcentration of heavy
364 metals in water and fruit juice samples followed by FAAS quantification. The synthesized menthol–
365 sorbitol–mandelic acid (1:2:1) DES has a double role: it is a chelating agent to form complexes with
366 cadmium and zinc and is also the extraction solvent in the subsequent AALLME procedure [57]. The
367 same group later applied this approach to the development of an extraction and preconcentration
368 procedure for heavy metals (cadmium, copper and lead) from milk samples [68]. They also reported
369 a DLLME procedure for the extraction and preconcentration of cobalt(II) and nickel(II) from water
370 and juice samples using a DES formed by mixing choline chloride and 4-aminophenol (1:1) [58]. Very
371 recently, Ragheb et al. described an MSPE followed by DES-UA-DLLME using L-menthol–salicylic acid
372 (4:1) DES as both the extractant and complexing agent for the preconcentration of mercury (II),
373 followed by determination by graphite furnace atomic absorption spectroscopy (GFAAS) [37].

374

375

376 7 Less frequently occurring connections

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

382

383 7.1 DES-based digestion (dissolution)

384 Solid food samples must be decomposed using conventional wet acid digestion, microwave-assisted
385 digestion or ultrasonic digestion before the inorganic constituents are determined by AAS. However,
386 researchers have also reported the disadvantages of these methods, especially the fact that
387 concentrated acids or oxidizing agents can cause interference and the formation of nitrous vapors.
388 Habibi et al. [71] reported the applicability of a choline chloride–oxalic acid (1:2) based DES for the
389 dissolution of fish samples as well as solubilization of selected heavy metals (iron, copper and zinc)
390 prior to FAAS determination. To increase the yield of Fe and Cu, 1 mol L⁻¹ HNO₃ was added to the
391 sample after dissolution in the DES. The method was used to digest various tissues from a sample of
392 marine fish (muscle, liver and gills) [71].

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

402

403 7.2 Solidified DES-based procedures

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

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

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

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

439

440 7.3 Effervescence-assisted procedures

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

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

452

453 7.4 Hollow fiber-based procedures

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

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

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

476

477 7.5 Magnetic nanoparticles-based procedures

478 Karimi et al. [64] developed a deep eutectic solvent-mediated extraction for ligand-less
479 preconcentration of lead and cadmium from environmental samples using magnetic nanoparticles
480 (DES-MNP) [64]. The 200 μL of DES (choline chloride–urea 1:2.5) and 20 mg of MNPs (Fe_3O_4) were
481 added to 60 mL of sample solution and stirred thoroughly for 10 min. The metal ions interact with
482 the DES adhering to the magnetic nanoparticles, and the sorbent was separated by means of a strong
483 magnet. The analytes were then desorbed with 600 μL of 1.0 M nitric acid and determined by flame
484 atomic absorption spectrometry [64]. The method had wide linear range of 2 to 250 $\mu\text{g L}^{-1}$ and 0.5 to
485 30 $\mu\text{g L}^{-1}$ and good limit of detection of 0.4 and $0.1 \mu\text{g L}^{-1}$ for lead and cadmium, respectively [64].

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

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

495
496

497 8 Terminology

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

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

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

514
515

516 9 Conclusion and future trends

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

Radoslav Halko: Conceptualization, Writing – Original Draft, Writing – Review & Editing, Visualization

Jozef Tuček: Visualization

Justyna Płotka-Wasyłka: Conceptualization, Writing – Original Draft, Writing – Review & Editing, Visualization, Supervision

Vasil Andruch: Conceptualization, Writing – Original Draft, Writing – Review & Editing, Supervision

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 (<i>drinking, river, sea, mineral and spring water</i>) and food (<i>rice, cultivated mushrooms, chicken meat</i>) 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 μ L with acidic ethanol; 20 μ L directed to nebulizer	0.032 μ g L ⁻¹	[18]
Cadmium	Food (<i>cow and goat cheese, cow and goat milk</i>) and water (<i>wastewater, snow water, rainwater and tap water</i>) samples	HDES-LPME	FAAS	HDES: [P ₆₆₆₍₁₄₎][Cl]–pivalic acid, 1:4; 12 mL sample solution; 0.8 mg DDTC; 200 μ L HDES; shaken manually for one minute; centrifuged, 5 min, 116.41 G	1.6 μ g 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 μ g L ⁻¹	[20]
Cadmium	Groundwater samples from aquifers at different depth in a coal mining area	UDDL μ E	FAAS	DES: ZnCl ₂ and acetamide, 1:2; 20 mL sample solution; 1 mL APDC solution 0.1–0.5% (m/v); 100 μ L 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 μ g L ⁻¹	[21]
Cadmium	Food (<i>bean stew, black tea, chicken shawarma, canned corn, corn, canned mushrooms, cheese, mushrooms, fish tissue, tomatoe, meat, canned fish, rice and spinach</i>) and water (<i>tap, waste</i>) 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 μ L 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 μ L 5 M nitric acid solution under ultrasonication for one minute		
Chromium(III)	Water samples (<i>wastewater, groundwater, seawater, canal water, mineral water and tap water</i>)	DES-UA-DLLME	GFAAS	DES: ZnCl ₂ and acetamide, 1:3; 25 mL sample solution; calmagite solution; 800 μ L DES and 900 μ L 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 μ L 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 (<i>biscuit, bitter chocolate wafers, white, chocolate, corn, wheat, herbal tea, spinach and mint</i>) and liquid (<i>tap water, wastewater, river water, well water, chocolate milk, cow milk and red wine</i>) samples	AA-IHDES-LPME	FAAS	HDES: Tetraheptylammonium chloride–oleic acid, 1:1; 5 mL sample solution; dithizone solution; 200 μ L DES; aspiration/dispersion cycles, 7 times; ice bath, 5 min	0.04 μ g L ⁻¹	[26]
Cobalt	Urine samples	DES-MCG-DSPE	SQT-FAAS	DES: choline chloride–phenol, 1:3; 8 mL sample solution; 150 μ L 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 $\mu\text{g L}^{-1}$	[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 $\mu\text{g L}^{-1}$	[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 $\mu\text{g L}^{-1}$	[30]
Copper	Vegetable samples (<i>spinach, lettuce, broccoli, potato, carrot and parsley</i>)	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 $\mu\text{g L}^{-1}$	[31]
Copper	Liver samples	DES-digestion and UA-LPME	MS-FAAS	DES: choline chloride–lactic acid, 1:2 (for digestion step) and tetrabutylammonium chloride–decanoic acid, 1:2 (for UA-LPME)	4.00 $\mu\text{g L}^{-1}$	[32]
Copper	Water samples (<i>tap water and lake water</i>)	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 \times g; DES phase completed to 500 μL with 1% acidic ethanol	2.9 $\mu\text{g L}^{-1}$	[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 $\mu\text{g/L}$	[34]
Iron	Sheep, bovine and chicken liver samples	UA-DES-E (<i>extraction from solid samples</i>)	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 $\mu\text{g mL}^{-1}$	[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 $\mu\text{g L}^{-1}$	[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 $\mu\text{g g}^{-1}$	[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 $\mu\text{g L}^{-1}$	[39]
Nickel	Water (<i>wastewater, seawater, mineral water, well water</i>), cigarette and food (<i>onion, parsley</i>)	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 $\mu\text{g L}^{-1}$	[40]

	samples			centrifuged, 10 min, 4000 rpm; DES phase completed to 500 μL with HNO_3 (65%); 100 μL injected		
Lead	Water (<i>tap water, mineral water</i>) and vegetable (<i>onion, celery, carrot, and tomato</i>) 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 $\mu\text{g L}^{-1}$	[41]
Lead	Water (<i>tap, lake, and river water</i>) and food samples extracts (<i>salted peanuts, chickpeas, roasted yellow corn, pistachios, and almonds</i>)	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 $\mu\text{g L}^{-1}$	[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 $\mu\text{g L}^{-1}$	[43]
Lead	Water (<i>fresh canal water and wastewater</i>) and food (<i>black tea, canned fish, green tea, spinach, canned mushrooms, chicken, beef, boiled wheat</i>) 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 $\mu\text{g L}^{-1}$	[44]
Lead	Cigarette tobacco and food samples (<i>onion, parsley</i>)	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 $\mu\text{g L}^{-1}$	[45]

				0.2 M HNO ₃		
Lead	Water samples (<i>tap water, river water and seawater</i>)	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 (<i>lake, wastewater, river and seawater</i>) and food (<i>black tea, green tea, cumin, cow meat, linseed, canned fish, chicken meat, potato</i>) 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 (<i>tap water, wastewater and seawater</i>), 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 (<i>tap, mineral, river, and seawater</i>) and environmental (<i>road dust,</i>	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]

	<i>tunnel dust, and a catalytic converter</i>) 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	$0.2 \mu\text{g L}^{-1}$	[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 (<i>wastewater, tap water, well water, river water, and bottled water</i>), honey and rice samples	DES-VAME	HG-AAS	DES: choline chloride–oxalic acid, 1:1; 2 mL sample solution; 600 μL dithizone ($3 \times 10^{-3} \text{ mol L}^{-1}$); 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 μL $1 \times 10^{-4} \text{ mol L}^{-1}$ 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) $\mu\text{g}\cdot\text{L}^{-1}$	
Cadmium and zinc	Oil samples (<i>fish oil capsules, butter and margarine</i>)	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 $\mu\text{g L}^{-1}$ for Cd(II) and Zn(II), respectively	[56]
Cadmium and zinc	Water (<i>surface water and tap water</i>) and fruit juice (<i>cherry and peach juice</i>) 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 $\mu\text{g L}^{-1}$ for Cd(II) and Zn(II), respectively	[57]
Cobalt and nickel	Water (<i>well water, urban water, river water</i>), and juices (<i>grape and peach</i>) 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 $\mu\text{g L}^{-1}$ for Ni(II) and Co(II), respectively	[58]
Copper and nickel	Water (<i>spring water, tap water, and seawater</i>) and biological (<i>human serum and urine</i>) samples	SPE (<i>DES modified cotton</i>)	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 $\mu\text{g L}^{-1}$ for Cu and Ni, respectively.	[59]
Nickel and cobalt	Food (<i>broccoli and spinach</i>) and water (<i>tap, mineral, sea, and river</i>) 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 $\mu\text{g L}^{-1}$	[60]



				bath; DES phase increased to 1 mL with ethanol		
Lead and cadmium	Cosmetic samples (<i>lipsticks and eye shadows</i>)	UA μ E-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 $\mu\text{g L}^{-1}$, 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 $\mu\text{g L}^{-1}$ (Pb) and 0.75 $\mu\text{g L}^{-1}$ (Cd)	[62]
Lead and cadmium	Vegetable samples (<i>leek, spinach, dill, parsley, mint, arugula, eggplant, dry tea</i>)	HI-DES-ME	FAAS	DES: citric acid–sucrose, 1:3; 2 mL vegetable solution; 600 μL 100 $\mu\text{mol L}^{-1}$ 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 (<i>tap water, well water, river water and Caspian Sea</i>), 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) $\mu\text{g L}^{-1}$	[64]
Lead and cadmium	Edible oils (<i>sesame oil, soybean oil, olive oil, sunflower oil, and corn oil</i>)	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 $\mu\text{g L}^{-1}$, As: 0.50 $\mu\text{g L}^{-1}$	[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 (<i>spinach, coriander, basil and radish</i>) 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 (<i>muscle, liver, and gills</i>)	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 (<i>radish, spinach, coriander and carrot</i>) 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 (<i>walnut, rice, tomato paste, spinach</i>) and non-alcoholic beverages (<i>orange juice, black tea, and river water</i>)	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 (<i>sunflower oil, baby oil, trout, waste frying oil and syrup-soaked pastry oil</i>)	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 $^\circ\text{C}$; vortexed 2 min; centrifuged, 5 min, 4000 rpm (<i>oil and DES rich phase obtained</i>); DES decanted and methanol added	Pb: 2.4, Co: 4.6, Ni: 7.5, Mn: 1.0 $\mu\text{g L}^{-1}$	[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 (<i>radish, spinach, coriander and carrot</i>) 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 $\mu\text{g kg}^{-1}$	[76]
Speciation of arsenic	Water (<i>lake water, mineral water, tap water and river water</i>), food (<i>edible mushrooms, fish, green tea,</i>	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; centrifuged 5 min, 3500 rpm; DES	10 ng L^{-1}	[77]

	<i>black tea, rice</i>), cigarette and soil samples			phase, acidic ethanol added up to 1 mL; injected 20 μL		
Speciation of chromium	Water (<i>river, tap, well, industrial wastewater</i>) 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 $\mu\text{g L}^{-1}$	[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 $\mu\text{g L}^{-1}$	[82]
Speciation of chromium	food (<i>mushrooms and soybean</i>) and water (<i>tap and river</i>) 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 (<i>rice and sausage</i>) and water (<i>tap water, river water, and mineral water</i>) 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 (<i>tap water, chromium plating factory wastewater and lake water</i>)	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 $\mu\text{g L}^{-1}$	[85]
Speciation of mercury	Water (<i>bottled mineral water, river water, tap water</i>) and biological (<i>freshwater fish</i>) 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 $\mu\text{g L}^{-1}$	[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 (<i>tap water and mineral water</i>) and food (<i>sheep milk, cow milk, yogurt, mixed fruit juice, egg, orange juice, grapefruit, honey, canned fish and edible mushrooms</i>) 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;
 [P₆₆₆₍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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